

Symposium T: Nanomaterials for Polymer Electrolyte Membrane Fuel Cells

Polymer electrolyte fuel cells are being developed worldwide for applications including portable power, stationary power, and transportation, and nanomaterials play a key role in present and emerging technologies. The symposium covered fuel oxidation catalysts, primarily on direct methanol oxidation; emerging electrolytes; the critical issue of durability and also how computational modeling can be used to predict and understand properties from catalyst performance to platinum stability; and oxygen reduction catalysts. The overall conclusions from the symposium were that nanomaterials are presenting solutions across the board in catalysis and membranes, however not without considerations of materials durability. Advanced modeling and characterization tools are able to determine novel mechanisms and reactions paths. Nanomaterials research is key to industrial as well as academic research.

Symposium U: Materials Challenging Facing Electrical Energy Storage

Presentations in Symposium U on Materials Challenges Facing Electrical Energy Storage were primarily dedicated to materials for electrochemical capacitors. P. Simon (Universite Paul Sabatier, France) described materials that store energy using ion adsorption (electrochemical double layer capacitors) while K. Naoi (Tokyo Univ. of Agriculture & Technology), B. Dunn (Univ. of California, Los Angeles), and E. Frackowiak (Poznan Univ. of Technology, Poland) reported on pseudocapacitors that use fast surface redox reactions. Supercapacitors can complement or replace batteries in electrical energy storage and harvesting applications when high power delivery or uptake is needed. Combination of pseudo-capacitive nanomaterials, including oxides, nitrides, and polymers, with the latest generation of nanostructured Li electrodes (hybrid capacitors) can bring the energy density of supercapacitors closer to that of batteries. A notable improvement in material performance has been achieved due to recent advances in understanding charge storage mechanisms and the development of advanced nanostructured materials, such as carbide-derived carbons and nanotube films.

MEETING SCENE

Day 1

About 300 attendees packed the room on Monday to hear the invited talk of Prof. Yet-Ming Chiang (MIT) on Electrical Energy Storage for Transportation and Renewable Energy in Symposium U. Few people doubt nowadays that renewable resources and nuclear power generation will largely replace fossil fuels within the next decade or two. However, the energy produced from renewable resources is primarily electrical energy. Therefore, solving the problem of electrical energy storage is the critical issue in the transition to renewable energy economy. It will be impossible to become independent on gasoline, coal and natural gas, if we don't develop much better and more efficient

solutions for storing electrical energy. Improved electrical energy storage systems, such as electrochemical capacitors (supercapacitors) and batteries, are needed to move from “chemical” (fossil fuel) to “physical” (electrical) energy. Therefore, research electrical energy storage materials helps to make this planet cleaner and healthier and our country less dependent on oil supplies. A similar interest was shown by the meeting attendees to the opportunities for nano-materials for lithium-ion batteries. Dozens of people were standing in the fully packed room to listen to Prof. M. Stanley Whittingham’s talk on this subject. The use of carbon nanotubes and active material nanoparticles may drastically improve the performance of secondary Li-ion batteries, even when using already known anode and cathode materials.

Day 2

Presentations at Symposium U were primarily dedicated to materials for electrochemical capacitors, also called supercapacitors. Patrice Simon from France described materials that store energy using ion adsorption (electrochemical double layer capacitors) while Katsuhiko Naoi from Japan, Bruce Dunn from UCLA, and Elzbieta Frackowiak from Poland reported on pseudo-capacitors that use fast surface redox reactions. Supercapacitors can complement or replace batteries in electrical energy storage and harvesting applications, when high power delivery or uptake is needed. Combination of pseudo-capacitive nanomaterials, including oxides, nitrides and polymers, with the latest generation of nano-structured Li electrodes (hybrid capacitors) can bring the energy density of supercapacitors closer to that of batteries. A notable improvement in material performance has been achieved due to recent advances in understanding charge storage mechanisms and the development of advanced nanostructured materials, such as carbide derived carbons and nanotube films. Ion desolvation that occurs in pores smaller than the size of solvated ions was reported by Katsumi Kaneko from Japan. Understanding of this fact opens the door to designing high-energy density capacitive storage devices using a variety of electrolytes. Mathematical modeling and simulation of capacitive storage, which will be the key to success in designing tomorrow’s high-energy and high-power devices, was described by Vincent Meunier from Oak Ridge National Laboratory. Chung-An Max Wu, a freshman at the Massachusetts Institute of Technology, showed that the energy and power of electrochemical capacitors and batteries can be limited by local and global depletion of ions in the electrolyte phase. He presented an experimentally verified model of limitations on charging rate caused by local depletion in nanoporous gold supercapacitor electrodes. He identified scaling of the effect with pore size and ion concentration, and proposed ways to alleviate the problem. Wu performed this work as a high school student under the direction of David B. Robinson at Sandia National Laboratories in Livermore, California.



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T: Nanomaterials for Polymer Electrolyte Membrane Fuel Cells

November 29 - December 2, 2009

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* Invited paper

TUTORIAL

Nanomaterials, e.g. catalysts, catalyst supports, etc., are critical to the successful implementation of proton exchange membrane (PEM) fuel cells; and characterization of these nanomaterials is necessary to elucidate their contribution(s) to the fuel-cell performance and subsequent degradation arising from use. However, the characterization of individual nanomaterial components within the fuel-cell membrane electrode assemblies (MEAs) can be extremely complicated. Analysis is especially difficult *in situ*, since PEM fuel cells operate under a potential in the presence of hydrogen, oxygen, and water with the metallic nanoparticles embedded in mixtures of carbon and polymers.

Recently, new analysis methods have been developed for the successful characterization of PEM fuel-cell nanomaterials. High-resolution transmission and scanning transmission electron microscopy (TEM/STEM) techniques are being used for *ex situ* (post-mortem) MEA analysis to correlate PEM fuel cell performance with material stability. For example, high-angle annular dark field (HAADF) STEM, equipped with energy dispersive spectroscopy (EDS), is now routinely used for sub-Å-scale imaging and microanalysis of catalyst nanoparticles. Specialized specimen holders are being developed for TEM/STEM that contain liquid-

filled cells to study liquid-solid interfaces, catalyst coalescence, etc., under relevant PEM fuel-cell operating conditions.

The *in situ* performance of PEM fuel-cell catalysts can be better understood now, thanks to a new x-ray absorption spectroscopy (XAS) analysis technique, the Δ XANES (Delta X-ray Absorption Near Edge Structure) method. The Δ XANES method is used to isolate the photoelectron scattering contribution arising from adsorbates such as O, OH, H, SO_x , CO, and C_2 on the catalysts that can exist under operating conditions in the fuel cell. This information allows binding site and coverage to be determined, and then, along with EXAFS (Extended X-ray Absorption Fine Structure) results, allows adsorbate coverage to be correlated with catalysts structure. While publications exist on each of these methods, the "art" of the methods is often not translated, making a tutorial in the analysis methods essential.

The tutorial will describe recent progress in these advanced analysis techniques. For TEM/STEM methods, Karren More has developed and implemented novel sample preparation methodologies and used high-resolution imaging and microanalysis to understand the complex composite structures of PEM electrodes from the bulk-(μm) to the atomic-(sub- \AA)-scale. For the Δ XANES method, David Ramaker will explain how to study adsorption phenomena on the PEM fuel-cell catalysts. If time permits during the Δ XANES segment, participants will be given data to analyze on their laptop computers. (Graduate student aides with expertise in the Δ XANES method will be present to help). These sessions will provide scientists with training in state-of-the-art methods for fuel-cell nanomaterials characterization.

Instructors:

Karren L. More, Oak Ridge National Laboratory

David Ramaker, George Washington University

SESSION T1: Fuel Oxidation Catalysts

Chair: David Ramaker

Monday Morning, November 30, 2009

Room 301 (Hynes)

8:30 AM *T1.1

Structure-catalytic Functionality of Pt Nanoparticles by Tuning their Shape and Composition. Shi-Gang Sun, Chemistry Department, Xiamen University, Xiamen, Fujian, China.

Nanoparticles of Pt and its alloys are most widely used electrocatalysts in methanol fuel cells and other applications. The catalytic property of nanoparticle catalysts (NCs), i.e. the activity, stability and selectivity, are strongly dependent on their surface structure and electronic structure. This study puts emphasis upon understanding the structure-catalytic functionality of Pt NCs by tuning both the surface structure through shape-control synthesis and the electronic structure via composition alteration. In a conventional shape-control synthesis of NCs, the necessity of minimizing energy limits the synthesized nanoparticles to those shapes enclosed with closest packed facets, e.g. for fcc metals, the conventional shapes of NCs are cubes, tetrahedra, octahedra, cuboctahedra bounded with respectively facets of $\{100\}$, $\{111\}$, and $\{100\}+\{111\}$. We have recently developed an electrochemical method to control the growth and the surface structure of metal nanoparticles, and synthesized successively tetrahedral Pt nanocrystals bounded by 24 high-index facets of $\{730\}$, $\{520\}$ and vicinal planes, which display much higher catalytic activity and stability than that of commercial Pt nanocatalysts. Furthermore Pt and Pd NCs of well-defined shapes were obtained, such as tetrahedral NCs with 24 $\{hk0\}$ facets, trapezohedral NCs with 24 $\{hkk\}$ facets, concave hexoctahedral NCs with 48 $\{hkl\}$ facets, as well as multiple twinned nanorods with $\{hk0\}$ and $\{hkk\}$ facets. In order to manipulating the electronic structure of NCs, Pt alloy nanoparticles were prepared by electrochemistry together with charge-displacement technique. The nanoparticles of PtCo, PtNi and PtPb of different composition and different shape (nanoplate, core-shell, chain, etc.) exhibit enhanced catalytic activity and stability towards electrocatalytic oxidation of methanol or other small fuel molecules. The electronic structure effects of the Pt alloy nanoparticles were investigated by using in-situ molecule-probe FTIR spectroscopy and ex-situ methods of XRD, TEM, XPS, etc., and correlated with electrocatalytic property of the synthesized Pt alloy nanoparticles. Acknowledgements. This study was supported by NSFC (20833005), the MOST (2007DFA40890), and Fujian key project (2008I0025) Related papers: 1. Na Tian, Zhi-You Zhou, Shi-Gang Sun, Yong Ding, Zhong Lin Wang, Science, 2007; 316: 732. 2. Na Tian, Zhi-You Zhou, Shi-Gang Sun, J.Phys.Chem.C (Feature Article), 2008, 112: 19801. 3. Zhi-You Zhou, Na Tian, Zhi-Zhong Huang, De-Jun Chen, Shi-Gang Sun, Faraday Discussions, 2008, 140: 81-92 4. Na Tian, Zhi-You Zhou, Shi-Gang Sun, Chem. Commun., 2009, 11: 1502-1504. 5. Qing-Song Chen, Shi-Gang Sun, Zhi-You Zhou, Yan-Xin Chen, Shi-Bin Deng, Phys. Chem. Chem. Phys., 2008, 10(25): 3645-3654 6. Xin-Wen Zhou, Qing-Song Chen, Zhi-You Zhou, Shi-Gang Sun, J. Nanoscience and Nanotechnology, 2009, 9(4): 2392-2397

9:00 AM *T1.2

Small Molecule Decomposition on Catalytic Electrodes by the use of Vibrational BB-SFG and Electrochemistry. Andrzej Wieckowski, Rachel L. Behrens, Robert Kutz, Daniela Marques dos Anjos and Mary Choules; Chemistry, University of Illinois, Urbana, Illinois.

Several overlapping themes will be entertained, all related to the methods of study: broadband sum frequency generation spectroscopy (BB-SFG) and electrochemistry [1]. The first part will be dedicated to kinetics of adsorption/decomposition of formic acid on platinum (single crystal and polycrystalline) in 0.1 M H_2SO_4 . We will discuss the electrode potential dependent properties of the products and we address the issue of formic acid reactivity and poisoning in electrocatalysis. We will next discuss our recent data on decomposition of ethanol on platinum. Here, we first explored spectroscopically and electrochemically the ethanol oxidation reaction in acidic media for polycrystalline platinum and for Pt(111) and investigated the distribution of ethanol oxidation products: CO, acetic acid, and acetaldehyde. We have screened several catalysts for the ethanol oxidation reaction in basic

media and concluded that the family of palladium catalysts gives the best performance. Data on the electrode potential dependent BB-SFG spectra from Pt(111)-CO in CO-saturated media will also be reported including potential-dependent (2×2) - 3CO to a $(\sqrt{19} \times \sqrt{19})\text{R}23.4^\circ$ - 13CO phase transition of Pt(111) in the 0.1 M H_2SO_4 electrolyte. On the Pt(111)-CO, the SFG CO atop intensity jumps and the SFG spectrum of threefold CO sites is transformed into a bridge site spectrum with an overall small decrease in the integrated SFG intensity. This occurs because the SFG signal is sensitive to both the coverage and changes in the local field that results from the changing adlayer structure. Finally, some essential details of the vibrational femtosecond broadband sum frequency generation spectroscopy will be provided [1]. In BB-SFG, the gap between the electrode and the optical window is relatively thick (25 μm) and the voltammetric characterization of the electrode is not affected by the electrolyte ohmic drop as long as the sweep rate does not exceed 5 mV/s. The spectroscopic advantages of the method are: a nonlinear coherent nature of the method and exclusive sensitivity to the species at the interface (SFG generates the signal only when the inversion symmetry is broken, which occurs at the electrode surface). Filling and emptying the gap is carried out without changing the electrode/optical window configuration, adding to the reliability of measurements. The SFG has a combined advantage of FTIR and SHG, the issue that will be explored in future studies of physics and physico-chemical principles of the solid liquid interface. Acknowledgements Financial support by the Army Research Office (W911NF-05-1-0345 and MURI DAAD19-03-1-0169) is greatly acknowledged. Reference 1. G. Q. Lu, A. Lagutchev, T. Takeshita, R. L. Behrens, Dana D. Klott and A. Wieckowski, in: "Fuel Cell Catalysis: A Surface Science Approach", M. Koper (Ed.), "Broad-Band Sum Frequency Generation Studies of Surface Intermediates Involved in Fuel Cell Electrocatalysis", John Wiley & Sons, Inc., 2009.

9:30 AM T1.3

Oleylamine-Mediated Synthesis of Monodisperse Pd-Composite Nanoparticles for Catalytic Formic Acid Oxidation.
Vismadeb Mazumder and Shouheng Sun; Chemistry, Brown University, Providence, Rhode Island.

The need to limit Pt usage in fuel cell catalysis, has promoted the search for non-Pt nanoparticle (NP) catalysts with analogous property. Among all noble metal based catalysts studied thus far, Pd is a promising alternative. We report a facile synthesis of monodisperse Pd NPs by the reduction of Palladium Acetylacetonate with oleylamine and borane tributylamine complex. Oleylamine's versatility is displayed in its role as a solvent, surfactant and reductant. The synthesis' flexibility allows the incorporation of 5nm Au seeds - leading to a size-controlled synthesis of Au/Pd core-shell NPs. The oleylamine coated Pd-composite NPs are readily "cleaned" by a 99% acetic acid wash and characterized by TEM, HR-TEM, XRD, EDAX and ICP-MS. The Pd-based NPs supported on the Ketjen carbon are catalytically active for formic acid oxidation in HClO_4 solution. Along with the activity, we have also attempted to address the stability issue in catalysts for fuel cell reactions, when comparing to commercially available catalysts. Our catalysts show no obvious activity degradation after 8000 cycles in an oxygen saturated electrolyte. These Pd-composite NPs hold promise as a highly active non-Pt catalyst for fuel cell applications.

9:45 AM T1.4

Electrochemical Synthesis of Pt and PtRu Nanoparticles at High Surface Area Carbon Support for Fuel Cell Applications.
Carlos R. Cabrera¹, Diana Santiago¹, Amit Palkar² and Luis Echegoyen²; ¹Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico; ²Department of Chemistry, Clemson University, Clemson, South Carolina.

The development of electrochemical techniques for the bulk preparation of Pt and PtRu nanoparticles for the use in direct methanol fuel cell (DMFC) is of importance. An effort to develop smaller and well disperses catalytic material at high surface area supports and to reduce the catalyst loading is an area of current research. In the present work Pt/C and PtRu/C nanoparticles have been prepared by electrodeposition at constant potential using a glassy carbon rotating disk slurry electrode technique. Simultaneous and sequential electro-deposition of bimetallic and metal-metaloxide systems have been done following published methods. Hydrodynamic methods, at constant potential, have been used to deposit Pt/CeO₂ electrocatalyst on glassy carbon electrodes. More recently, rotating hydrodynamic disk slurry electrode (RoDSE) methods have been used to deposit Pt nanoparticles and PtRu on carbon black powder (Vulcan). The electrodeposition was carried out in a solution containing carbon black (Vulcan XC-72R), K_2PtCl_6 and 0.1M H_2SO_4 . The hydrodynamic convection of the rotating disk electrode technique, and the applied potential, allows the deposition of Pt and Ru at Pt nanoparticles at different sides of the carbon powder particles. The use of different types of carbon support have been used in the electrodeposition method. The metal and alloy deposition was analysed by transmission electron microscopy (TEM), nano X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The TEM image showed Pt particles with sizes between 2 and 12 nm in diameter. The nano XRF, XPS, and XRD confirm the presence of platinum nanoparticles showing the characteristic peak of this element. XRD analysis demonstrate the polycrystalline structure of the platinum deposited with the (111), (220) and (200) peaks. The comparative analysis shows the improvement of the novel rotating disk-slurry electrode technique. The use of the rotating disk-slurry technique was an effective method for the platinum electrodeposition at carbon powder material because we can obtain well-dispersed Pt and PtRu nanoparticles for fuel cell applications.

10:30 AM *T1.5

Analysis of DMFC Catalysts. Christina Roth¹, Frank Ettingshausen¹, Ditty Dixon¹, Alexander Schoekel¹, Anna Korovina², Frieder Scheiba¹ and David E. Ramaker²; ¹TU Darmstadt, Darmstadt, Germany; ²Chemistry, George Washington University, Washington DC, District of Columbia.

In direct methanol fuel cells (DMFC), ruthenium is added to the standard carbon-supported Pt anode catalyst in order to increase its carbon monoxide tolerance. According to the so-called bifunctional mechanism, Ru is able to provide oxygen-containing adsorbates at lower potentials than Pt, which in turn can reduce CO adsorbates at Pt sites. Regardless of the mechanism, CO poisoning is an important issue, which leads to a significant performance loss in fuel cells operated with either reformat gas or methanol. Unfortunately, the harsh conditions at the DMFC anode lead to major degradation of PtRu catalysts over time, basically

due to the dissolution of the less-noble Ru from the alloy. Another degradation phenomenon is the corrosion of the carbon support at the high potentials of the fuel cell cathode. This carbon corrosion can facilitate sintering and dissolution of the metallic nanoparticles. And finally, in automotive applications under pure hydrogen, the noble platinum can still become oxidized. Pt ions can then move into the polymer membrane and re-deposit as crystals with sizes of 100 nm and more inside the membrane. To follow these phenomena, new electron microscopy techniques have been developed in our group, which make a detailed study of membrane-electrode assemblies (MEA) feasible. The polymer electrolyte distribution as well as the porosity of the electrodes can be studied using transmission electron microscopy (TEM). We will present a new TEM acquisition routine that prevents extensive beam damage of the sample. The polymer electrolyte distribution is imaged via the fluorine signal in an energy-filtered TEM. Ex situ studies of fresh and degraded DMFC catalysts, using a combination of several spectroscopic, microscopic, and diffraction techniques, will be presented. The investigated samples were taken from stack MEAs after testing. We will focus on site-dependent information and Ru dissolution (at methanol inlet, methanol outlet and center). A special in situ fuel cell set-up has also been developed recently, which allows for spatially- and time-resolved X-ray absorption spectroscopy (XAS) studies. First results in different fuel cell operation modes will be presented.

11:00 AM T1.6

PtRu Nanoparticle - Graphene Hybrid Material: Synthesis, Characterization and Electrocatalytic Oxidation of Methanol.

Surbhi Sharma¹, Laurence Farrington¹, Imran N. Quereshi¹, Jeremy Hamilton¹, [Pagona Papakonstantinou](#)¹, Xiaopei Miao² and Meixian Li²; ¹School of Engineering, Nanotechnology and Integrated BioEngineering Centre, University of Ulster, Newtownabbey, United Kingdom; ²College of Chemistry and Molecular Engineering, Peking University, Beijing, China.

The controlled assembly of different nanoscale materials, having distinct chemical or physical properties into novel types of hybrid nanostructures with unique functionality, constitutes a key challenge in nanoscience. Hybrid nanostructures if appropriately designed are expected to combine the merits of the individual building nanomaterials. Graphene, a single atom thick sheet of hexagonally arrayed sp² bonded carbon atoms in a two dimensional lattice is a particularly promising vehicle to create hybrids. In this study we report a new approach to deposit platinum and platinum ruthenium, nanoparticles onto graphene sheets. This was achieved by means of a microwave-assisted process, employing K₂PtCl₆ and RuCl₃ precursors in a graphene oxide (GO) suspension. The graphene/ Pt or PtRu hybrids were deposited as films onto glassy carbon. The Pt and PtRu nanoparticles, which are uniformly dispersed on graphene, have diameters of 2-4 nm. All the Pt and PtRu/graphene hybrids display the characteristic diffraction peaks of a face centred cubic Pt structure, and exhibit a shift in the 2θ values to slightly higher values. The electrocatalyst performance was evaluated through their ability to achieve facile electro- catalytic oxidation of methanol. Cyclic voltamograms, CV show approximately 2.5 times higher current response for PtRu compared to their Pt graphene counterparts. The PtRu/graphene hybrid shows better performance in the direct electrooxidation of methanol than the Pt/graphene. Our results demonstrate the role of graphene as an effective catalyst support material in fuel cells.

11:15 AM T1.7

X-ray Absorption Spectroscopy Studies on the Effects of Long-Term Electrochemical Cycling on Carbon Supported PtRu Nanocatalyst.

[Kee-Chul Chang](#)¹, Junji Inukai², Masahiro Watanabe², Daniel Hennessy¹ and Hoydoo You¹; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Clean Energy Research Center, University of Yamanashi, Kofu, Japan.

The direct methanol fuel cell (DMFC) is a promising power source for personal electronics because of its efficiency and compactness. But a significant issue for DMFC performance is the CO produced during methanol oxidation at the anode, which can easily poison the Pt catalyst. Alloying Pt anodes with another metal is known to increase its CO tolerance and Pt-Ru bimetallic alloy was found to be the most CO-tolerant catalyst for fuel cells. Unfortunately, state-of-art PtRu catalyst suffers from durability problems such as agglomeration and Ru leaching during practical fuel cell operating conditions. We investigate the relationship between the atomic structure of PtRu nanocatalysts and its degradation due to long-term potential cycling. PtRu catalysts of different Pt:Ru ratios were prepared with the nanocapsule method and treated with long-term potential cycling between 0.06 and 0.40 V vs RHE in 0.1 M HClO₄ at 50 °C to simulate operating DMFC conditions. For comparison, commercial PtRu (from Tanaka) were treated with the same method. Pt L₃ and Ru K edge X-ray absorption spectroscopy results show more uniform mixing for the PtRu samples prepared with the nanocapsule method, which was also found to be more electrochemically stable under potential cycling.

11:30 AM T1.8

High Throughput Methanol Oxidation and Structural Characterization of Composition Spread Thin Film Catalysts.

[John M. Gregoire](#)¹, Michele E. Tague², Hector D. Abruna², Francis J. DiSalvo² and R Bruce van Dover³; ¹Physics, Cornell University, Ithaca, New York; ²Chemistry and Chemical Biology, Cornell University, Ithaca, New York; ³Material Science and Engineering, Cornell University, Ithaca, New York.

Sputter co-deposition from elemental targets is used to create thin film catalyst libraries. Extensive characterization of the composition spread thin films by a new high energy x-ray diffraction technique provides a map of the phase fields and crystallographic orientation (fiber texture). Additionally, a fluorescence assay serves as a parallel screening of the activity of the catalysts toward the oxidation of methanol. Further electrochemical characterization provides surface area measurements at two characteristic length scales and the ensemble of measurements provides detailed insights into the nature of the catalytically active surface. In the Pt-Ta chemical system, this approach reveals aspects of the role of Ta toward improved catalytic activity previously identified in the literature.

11:45 AM T1.9

Air Independent Fuel Cells Utilizing Borohydride and Hydrogen Peroxide. Richard C. Urian, Naval Undersea Warfare Center, Newport, Rhode Island.

The US Navy continues to pursue electrochemical power sources with high energy density for low rate, long endurance air independent, undersea applications. The use of borohydride and hydrogen peroxide as fuel and oxidant sources offer several different fuel cell configurations; each with their own advantages and technical challenges. The direct electro-oxidation and electro-reduction of sodium borohydride and hydrogen peroxide is conceptually a simple system. In the fuel cell configuration where Nafion 115 is used and both electrolyte solutions are allowed to have a pH >8, high efficiencies (>70%) can be maintained with careful control of the concentration of reactants in the flowing electrolyte, choice of catalyst and electrode architecture. The onset of borate precipitation is offset by diffusion of water created by the osmotic pressure between anode and cathode. The direct liquid/liquid system has the potential to be a "2V" system if the pH of the hydrogen peroxide catholyte is maintained at a pH <1. In order to make this a viable system for Naval applications, the amount of acid used in the catholyte to establish the desired pH needs to be minimized. The key enabling technology is the development of a suitable anion exchange membrane. The characteristics of the anion membrane are: 1) conduct hydroxides generated at the cathode to the anode in order to minimize its concentration buildup in the catholyte solution and to maintain the desired pH <1, 2) minimize hydrogen peroxide cross-over and 3) afford high ionic conductivity. Efforts are currently underway to improve the understanding of the reaction mechanism of borohydride at the catalyst surface and to identify membranes with higher ionic conductivity. These efforts have been identified as critical paths for the successful development of a liquid/liquid borohydride/hydrogen peroxide fuel cell.

SESSION T2: Electrolyte Membranes
Chair: Karen Swider Lyons
Monday Afternoon, November 30, 2009
Room 301 (Hynes)

1:30 PM *T2.1

Thin Film Oxide Ion and Proton Conducting Membranes. Fritz B. Prinz, ME, MSE, Stanford, Stanford, California.

This talk will discuss ion incorporation and transport phenomena in ultra thin oxide films of both oxide ion and proton conducting materials. Opportunities and limitations for fuel cell applications employing thin films will be discussed. Recent simulations, micro structural characterization, and I-V performance measurements will be at the center of this presentation.

2:00 PM T2.2

Nanostructural Control in Midblock-Sulfonated Triblock Copolymers. Tomonori Saito, Hunter D. Moore and Michael A. Hickner; Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Sulfonated polymers possess interesting properties for a wide variety of applications such as fuel cells, water treatment membranes, and chemical protection barriers. In many studies, the importance of hydrophilic/hydrophobic phase separation at the nanoscale to form ion-rich transport domains has been noted, but creating well-defined ionic nanostructures and tuning their geometry and arrangement has proven difficult. Investigation of the structure-property relationships of well-defined ion-containing block copolymers will be critical in fostering further development of these materials as the molecular properties of the block copolymers can be tuned precisely. Molecular control, in turn, provides a route to tuning the solid-state morphology and thus developing robust geometries in which to study the morphology effects on the water uptake and conduction properties. We have designed midblock-sulfonated triblock copolymers. Placing sulfonated blocks in the center of the ABA triblock, where the outer blocks B blocks are hydrophobic, is expected to provide more mechanical integrity to the membrane as opposed to placing sulfonated blocks at the end of the chains. Poly(hexyl methacrylate)-b-polystyrene-b-poly(hexyl methacrylate) and poly(perfluorooctyl methacrylate)-b-polystyrene-b-poly(perfluorooctyl methacrylate) were first synthesized using atom-transfer radical polymerization. The triblock copolymer precursors were subsequently sulfonated. The hydrophilic portion of the molecule can be controlled by the extent of functionalization of the center block, while the hydrophobic phase can be tuned by the type of outer blocks used. We observe distinct differences in the solid-state morphology of the midblock sulfonated triblock copolymers as their ion content is increased. Attaching more ionic groups to the center block induces disorder in the block copolymer structure due to strong aggregation of the ionic domains. Additionally, the swelling of the triblock copolymers for a given ion content is decreased by using more rigid perfluorooctyl methacrylate end blocks versus more flexible hexyl methacrylate endblocks. Finally, the proton conductivity increases dramatically once a threshold value of the ion content is achieved in the sulfonated phase indicating the formation of transport domains within the hydrophilic phase. This talk will discuss our results on formulating chemistry-morphology-property relationships for sulfonated polymers. We will also use these insights gained on proton exchange materials to design new block copolymer anion exchange membranes with high conductivity and water stability.

2:15 PM T2.3

Ultrathin Layered Proton Conductive Membrane Based on Polymer Langmuir-Blodgett Film. Jun Matsui^{1,2}, Hiromu Miyata¹, Yu Hanaoka¹, Rinko Kudo¹ and Tokuji Miyashita¹; ¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; ²PRESTO, JST, Kawaguchi, Japan.

Recently, synthesis of polymer proton conductive membrane has attracted much attention for polymer fuel cell devices application. Usually, fluoropolymer, such as Nafion was used as a proton exchange membrane (PEM) because of its high proton

conductivity. However, other polymer based PEMs are required because of high production cost of fluoropolymer and limitation of conductivity in temperature higher than 80 degree C. Moreover, several groups report an enhancement of proton conductivity at an area confined in a nanometer scale. Therefore, an ultrathin proton conductive membrane will be interesting for new concept PEM. In this paper, we prepare a ultrathin proton conductive film based on polymer Langmuir-Blodgett film. poly(N-dodecylacrylamide-co-2-acrylamide-2-methyl propane sulfonic acid) (pDDA/AMPS) was synthesized by radical copolymerization of each monomers. The monolayer property of pDDA/AMPS was studied by surface pressure-area isotherm measurement. The isotherm of pDDA/AMPS shows a steep rise in surface pressure with decreasing surface area, which indicates a stable monolayer formed at the air-water interface. The monolayer was transferred onto a solid substrate using the Langmuir-Blodgett technique to prepare a multilayer film of pDDA/AMPS. X-ray diffraction pattern of the multilayer film shows a strong peak at $2\theta=2.47$ which indicates that the film shows a layered structure with 1.8 nm periodicity. The proton conductivity of the multilayer film of 10-5 (S/cm) at 24 C, 100% RH, whereas it increase to 10-2S/cm at 70 C, 100% RH

2:30 PM T2.4

Viscoelasticity and Ionic Conductivity of Nanocomposite - Electrolyte Membranes. [Angel Romo-Urbe](#)¹ and Judith Cardoso²; ¹Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, Cuernavaca, Morelos, Mexico; ²Física, Universidad Autónoma Metropolitana-Iztapalapa, Mexico D. F., Mexico.

The polymer polydimethylaminoethylmethacrylate (herein named PDMAEM) was used to prepare a protonated polymer (PDMAEMH), as well as nanocomposites based on PDMAEMH / montmorillonite (P/clay). Montmorillonite was functionalized with two different surfactants (sulfobetaine and ammonia) and added to PDMAEMH at different concentrations (1%, 3%, 5% w/w). Investigation of the nanostructure via transmission electron microscopy (TEM) showed evidence of nanoclay intercalation and exfoliation. The thermal and dynamic mechanical properties showed that PDMAEM exhibited a glass transition temperature (T_g) of 51C. Strikingly, the protonated polymer, PDMAEMH, showed a $T_g=184C$, that is, over 120C increase relative to the untreated polymer precursor. Small-strain oscillatory shear showed that the polymer precursor, the protonated polymer as well as the nanocomposites obeyed the time-temperature superposition principle. Master curves covering at least 10 decades in frequency were constructed. The viscoelastic properties showed that PDMAEM behaves predominantly viscous ($G''>G'$). On the other hand, the protonated polymer exhibited a predominantly elastic behavior ($G''<G'$), resembling an entangled polymer melt. As the polymer precursor is not entangled, it is suggested that ionic interactions give rise to this viscoelastic behavior, resembling "sticky" reptation. Addition of nanoclay slightly increased T_g and modified the rheological properties. The electric conductivity was increased by five orders of magnitude, but it was found that the conductivity is strongly influenced by the type of surfactant added to the nanoclay.

2:45 PM T2.5

Nafion® /Ex-situ Silica Nanocomposite Membranes with Different Size Particles for Application in PEM Fuel Cells. [Beatrice Muriithi](#) and Douglas A. Loy; Material science and engineering, University of Arizona, Tucson, Arizona.

Polymer electrolyte membrane fuel cells are highly efficient, emit low levels of pollutants and have attracted a lot of scientific interests as portable or stationary power sources. Currently and commercial membranes materials are the perfluorinated materials that suffer from temperature and dehydration limitations. However, for most of this application the PEMF cell must be operated at temperature above 1000C. Incorporation of inorganic fillers into the polymer electrolyte membranes (PEM) has been shown to increase the working temperature range, low dehydration and improve mechanical properties of the PEM. In this work, nanocomposite membranes were prepared using well defined, spherical and monodispersed silica particles (15-200nm in diameter). The morphological properties were characterized using AFM and SEM. The results indicate that the morphological distribution of the particles in the membranes is dependent on the size of the particles. Experimental results indicate that the size of silica nanoparticles in Nafion® silica nanocomposite has an impact on the improvement of the nanocomposite properties such as water uptake, proton conductivity and strength. The smaller particles (20nm) are easily mixed homogenously in the polymer matrix which leads to higher improvement compared to the large particles (200nm). However, the properties of the nanocomposite were always better than recast Nafion® especially at high temperatures. The results of our morphological studies and the influence of the size of the well-defined silica particles on the properties of the nanocomposite membranes, such as water uptake and proton conductivity, mechanical properties at high temperatures, will be presented.

3:30 PM *T2.6

The Opportunity of Using Hybrid Organic-Inorganic Membranes in PEMFC. [Christel Laberty](#), UPMC-CNRS UMR7574, Paris, France; UPMC/College de France, Paris, France.

Hybrid organic-inorganic materials exhibit unique physical properties because it combines the properties of the inorganic and organic materials, respectively. The arrangement of the materials in space is usually critical to achieve the desired performance. Controlling the inorganic and organic networks at the nanoscale level is essential. Using this concept, we design and develop low-cost and durable hybrid electrolyte membranes for fuel cell membranes for system operating at high temperature (up to 120°C) and low humidity (RH) (25-50% RH). A careful control of both the chemistry of the organic-inorganic solution and the processing, the phase-separated hydrophobic and hydrophilic domain in the final membrane can be tuned, giving rise to membranes with different properties including proton conductivity, mechanical strength, and water uptake. This conference will present some of the routes and innovative strategies that we develop to tailor proton conductivity in hybrid organic-inorganic materials. For example, "sol-gel" in-situ growth of acid functionalized inorganic network in a non porogenic organic matrix was proposed to fabricate novel hybrid organic-inorganic membranes exhibiting satisfactory proton conduction (25 mS/cm at 25°C, 100%). The main advantage of this "in-situ" growth is the design of a continuous mesostructured, functionalized silica network in a chemically and thermally inert organic matrix. Other combinations between functionalized (-SO₃H and -PO₂H₃ groups) silica network and polymer (sPEEK and

PVDF-HFP) will be presented. Proton conductivity will be discussed as function of the functionalized inorganic network, the hybrid organic/inorganic interface, the pores network and the positioning of -OH and SO₃H or/and -PO₃H₂ groups in the inorganic network. * Valle K., Belleville P., Rereira F., Sanchez C., Nature Materials, 2006, 5, 107. * Sel. O, Laberty-Robert C., Azais T., Sanchez C., Phys. Chem. Chem. Phys., 2009, 11, 3733.

4:00 PM T2.7

Silica Phospho-Siloxane Nanocomposite Membranes Exhibiting High Proton Conductivity in Dry Atmosphere. Martin Mika, Jakub Michal, Bretislav Klapste and Petr Hron; Department of Glass and Ceramics, Institute of Chemical Technology Prague, Prague, Czech Republic.

Currently, the low operating temperatures of available proton conducting polymer membranes and their humidity requirements for achieving sufficient conductivity add high complexity to fuel cell systems that impacts their cost and durability. Therefore, our research was focused on the development of new polymer nanocomposite membranes with better medium temperature performance at lower cost. The membranes are able to operate in H₂/O₂ fuel cells at temperatures around 130°C in dry atmosphere. They are formed from hybrid inorganic-organic phospho-siloxane polymers. Their backbone is the polydimethylsiloxane polymer with phosphorous heteroatoms. The synthesis is based on the reaction of dimethyldichlorosilane and tetraethoxysilane in liquid or molten orthophosphoric acid. This preparation procedure ensures a high concentration of relatively stable hydroxyl groups in the structure of the polymer. These groups are close to each other forming diffusion pathways suitable for fast proton migration in dry conditions. The membrane's proton conductivity was precisely measured by using electrochemical impedance spectroscopy in the interval from 25 to 180°C. The impedance data were recorded by the potentiostat Autolab PGSTAT30 in the frequency range from 10 mHz to 1 MHz. The resulting impedance spectra were analyzed in the Bode and the complex Nyquist plane diagrams by using the equivalent circuit approach. From circuit's parameters we calculated the proton conductivity. To promote proton conductivity at medium temperatures in dry atmosphere, we filled the polymers with spherical SiO₂ nanoparticles with size from 5 to 20 nm and specific surface 200 m²/g. Their surface was covered with -OH functional groups. We achieved the conductivity about 0.05 S/cm at 130°C in dry atmosphere. We also tested the performance of the membranes in a laboratory H₂/O₂ fuel cell in the range from 20 to 180°C using dry H₂ and O₂ input gases. The fuel cell was equipped with standard electrodes made of carbon paper with Pt/C catalyst. The surface area of the electrodes was 5 cm². The performance of the fuel cell significantly improved as the temperature increased. Power density maxims increased and moved to higher current densities and current/voltage characteristics became less steep. The prepared membranes were also characterized using other analytical tools, including optical and electron microscopy (SEM-EDS), differential thermal analysis-thermal gravimetric analysis, infrared and Raman spectroscopy, and nuclear magnetic resonance. We discuss the effects of composition and preparation procedure on the properties of the membranes as well as their performance in the H₂/O₂ fuel cell at elevated temperatures using dry reactant streams.

4:15 PM T2.8

Characterization of Drying and Degradation of Perfluorinated Fuel Cell Membranes by Solid State NMR Spectroscopy. Lida Ghassemzadeh^{1,2}, Klaus-Dieter Kreuer¹, Klaus Mueller² and Joachim Maier¹; ¹Max Planck Institute for Solid State Research, Stuttgart, Germany; ²Institute of Physical Chemistry, University of Stuttgart, Stuttgart, Germany.

A new ex-situ method has been developed to mimic the degradation of polymer electrolyte membranes in PE fuel cells (caused by the cross-leakage of H₂ and O₂ in PEFCs) and the results are compared to these of corresponding in-situ fuel cell tests.¹ In the ex-situ setup it is possible to expose membranes to flows of different gases with a controlled temperature and humidity. H⁺-form Nafion films with and without electrode layer (catalyst) have been treated in the presence of different gases in order to simulate the anode and cathode side of a PEFC. The polymer structure after these tests was analyzed by variable temperature solid-state ¹⁹F and ¹³C NMR spectroscopy, and the segmental mobility of the ionomer was investigated by ¹⁹F T₁ and T_{1ρ} relaxation time measurements. The ¹⁹F NMR and ¹³C{¹⁹F} CP/MAS spectra before and after degradation demonstrate that degradation is particularly affecting the side chain of the ionomer (decrease of the signals due to the SO₃H, CF₃, OCF₂ and CF groups). The same results have been observed after in-situ degradation in a fuel cell, however with a lower degradation rate. The analyses have been carried out in the dry and wet state in order to make sure that the results are not affected by different water contents. Degradation only occurs when both H₂ and O₂ are present. The decomposition rate was higher for the membranes with the electrode layer which proves the effect of Pt as a catalyst in the degradation reactions. The degradation rate caused by the cross-leakage of H₂ and O₂ in PEFCs is higher at the anode side than at the cathode. Reproducing the degradation results by the ex-situ setup, without applying any potential, shows that the degradation phenomena is a chemical reaction more than an electrochemical process. The ¹⁹F NMR relaxation data showed that upon degradation, chain motions become slower. Reference: 1. Ghassemzadeh, L.; Marrony, M.; Barrera, R.; Kreuer, K. D.; Maier, J.; Müller, K., Chemical Degradation of Proton Conducting Perfluorosulfonic Acid Ionomer Membranes studied by Solid-State NMR Spectroscopy. Journal of Power Sources 2009, 186, 334-338.

4:30 PM T2.9

SFM Study of Phase Segregation in Fuel Cell Membranes as a Function of Solvent and Relative Humidity. Marilyn E. Hawley¹ and Yu Seung Kim²; ¹Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico; ²Materials Physics and Applications, Los Alamos National Laboratory, Los Alamos, New Mexico.

Scanning force microscopy (SFM) phase imaging provides a powerful method for directly studying and comparing phase segregation in fuel cell membrane materials due to different preparation and under a variety of potential temperature and humidity exposure. In this work, we explored two parameters that can influence phase segregation: the polarity of solvents using in casting membrane films and how these solvent affect phase segregation with exposure to boiling water as a function of time. SFM was used under ambient conditions to image phase segregation in Nafion samples prepared using five different solvents. Samples were then subjected to water vapor maintained at 100°C for periods ranging from 30 minutes to three hours and re-imaged using the same phase imaging conditions. Data will be presented showing what appears to be an increase in phase segregation as a function of solvent polarity. In addition, phase images revealing the changes in the phase segregation as a function of time will be presented. Time allowing, I will include an introduction to the use of SFM phase imaging and electrical studies to electrode composites.

4:45 PM T2.10

Measurements of the Glass Transition Temperature with 50 nm Resolution in PMMA:SAN Phase Separated Thin Films.

Maxim P. Nikiforov¹, S. Gah², Stephen Jesse¹, R. J. Composto² and Sergei V. Kalinin¹; ¹CNMS, ORNL, Oak Ridge, Tennessee; ²University of Pennsylvania, Philadelphia, Pennsylvania.

Polymer membranes are the important components of PEM fuel cells. There are main 16 types of polymer formulations for fuel cell membrane applications; however, a lot of effort is put into developing new polymer formulations with improved properties such as better temperature stability etc. Quality control of the casted polymer film is a vital part in fuel cell research. The measurements of the phase transition temperature (glass transition, softening etc.) in polymer films with high spatial resolution provide knowledge about local phase composition of the film. We developed a quantitative method for the local measurements of mechanical properties of the polymers as a function of temperature. Since phase transitions in polymers are usually associated with large change in mechanical properties this method allows us to detect the temperature of the phase transition. Our method is based on the scanning thermal expansion microscopy, where heating of the atomic force microscopy probe results in the local thermal expansion of the sample. We developed and validated an experimental protocol that provides reproducible measurement of a polymer's thermomechanical properties. To date, local thermal analysis utilizes either the displacement of the tip due to penetration into the sample or the change in thermal impedance as detection mechanisms for the onset of melting transition. Due to the large noise inherent in static cantilever deflection detection systems, a measurable signal cannot be determined before a large-scale (>100nm) cavity is formed, thus limiting the spatial resolution. Our approach allows to measure glass transition temperature with 50 nm resolution, which was demonstrated by studying the kinetic of phase separation in PMMA:SAN system. The dependencies of glass transition temperature distributions as a function of annealing time of PMMA:SAN system is discussed. This research at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

SESSION T3: Fuel Cell Overview I
Chair: Ting He
Tuesday Morning, December 1, 2009
Room 301 (Hynes)

8:30 AM *T3.1

Nano Materials and Structures for the 4th Innovation of PEFC. Hyuk Chang, Energy Lab, SAIT, Samsung Electronics Co., Ltd., Suwon, Korea, South.

Material development of sulfonated polymer based proton conducting membrane (1960's) initiated worldwide research efforts on Polymer Electrolyte Fuel Cell (PEFC), which is regarded as the 1st innovation in this promising technology of energy conversion device having potential of high efficiency, environmentally benign and mobility. Since then, technology kept evolution and followed by the 2nd and 3rd innovations of highly efficient catalyst electrode structure (ionomer in the catalyst layer, early 1990's) and low resistance membrane structure (ionomer in microporous membrane substrate, late 1990's), respectively. These three subsequent innovations, which were based on bulk properties of materials and structures, led PEFC technology to near commercialization. However, it is still not enough to replace competing technologies in the view of efficiency, cost and life time, which are critical to energy conversion device. It is anticipated that the technical challenges heading for the next inflection point will be based on the nano technologies. Among them, nano scaled catalyst, nanocomposite membrane and nano structured membrane electrode assembly (MEA) are the major approaches. More specifically, SAIT conducts following activities : i) nano structured catalyst having platinum nanoparticles of 3nm can enhance the catalyst activity. Also, the nanoporous carbon can be utilized as support material for controlling the catalyst particle size and distribution. Especially when oxygen reduction co-catalyst such as Ru-N complex and highly metal-interactive element such as S are embedded in the nanoporous carbon, the catalyst is functionalized for enhancing activity and stability. ii) nanocomposite hydrocarbon membrane with exfoliated clays, especially in direct methanol fuel cell, provides high ionic conductivity and low methanol permeability because of its high enough sulfonation degree and low resistance in 50um thin but mechanically durable membrane. iii) in addition, nanostructured MEA with high surface density can reduce both ohmic and activation losses during polarization and enhance fuel efficiency, so that overall efficiency of fuel cell can be increased by more than 40%. In this presentation, the author would like to introduce the above three nano-based approaches and discuss that nano technologies in materials and structures will bring along the 4th innovation, so that the PEFC technology will be fulfilled for entering the commercial stationary, mobile and massive vehicle markets in the near future.

SESSION T4: Catalyst Degradation
Chairs: Ting He and Yu-min Tsou

Tuesday Morning, December 1, 2009
Room 301 (Hynes)

9:00 AM *T4.1

Platinum-Cobalt Cathode Catalyst Degradation in Proton Exchange Membrane Fuel Cells: Nano-Scale Transformations Observed by High-Resolution Microscopy. Shuo Chen^{2,3}, Hubert A. Gasteiger^{2,3}, Katsuichiro Hayakawa⁴, Tomoyuki Tada⁴ and Yang Shao-Horn^{1,2,3}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Electrochemical Energy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁴Tanaka Kikinzo Kogyo K. K., Hiratsuka, Kanagawa, Japan.

Compared to platinum, platinum-cobalt alloy catalysts show enhanced activity for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) and are commonly considered to be more stable toward platinum dissolution under automotive load-cycling (i.e., voltage cycling) conditions. For pure platinum catalysts, the platinum surface area loss produced by voltage-cycling is well understood, consisting both of Ostwald ripening of platinum nanoparticles on the carbon support in the cathode electrode and of the loss of platinum into the membrane/ionomer phase where large and electrically isolated platinum crystallites are formed. On the other hand, the microscopic degradation mechanisms of PtCo cathode catalysts are still unclear and more insight is required in order to develop strategies for cathode catalysts with improved durability. Using (scanning) transmission electron microscopy, (S)TEM, and spot-resolved X-ray energy dispersive spectroscopy, EDS, we have examined the microscopic processes leading to the aging of PtCo catalysts during voltage-cycling. While the formation of pure platinum crystallites in the membrane/ionomer phase is the same as what had been observed with conventional platinum catalysts, the morphological changes of nanoparticles in the cathode electrode are very different. We found that the majority of Pt-Co nanoparticles transformed into Pt-shell/PtCo-core nanoparticles. At the same time, we observed the formation of highly percolated nanoparticles, which consisted of nearly pure platinum and exhibited a bi-continuous porous structure which resembles that of dealloyed AuAg films. To our knowledge, this is the first time that this phenomenon was reported for the degradation of Pt-based alloy nanoparticles in PEMFC cathode, and we propose that these percolated, nearly pure platinum nanoparticles were derived from PtCo alloy nanoparticles with cobalt compositions beyond the dealloying threshold of ca. 55 atomic% Co. The mechanisms of surface area and activity loss will be discussed.

9:30 AM T4.2

Size and Composition Dynamics of Nanoparticle Electrocatalysts Probed by in situ X-ray Scattering. Michael F. Toney¹, Chengfei Yu², Shirlaine Koh² and Peter Strasser²; ¹Stanford Synchrotron Radiation Lightsource, Menlo Park, California; ²Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas.

The durability of the electrocatalysts in polymer electrolyte membrane fuel cells (PEMFCs) is one of the factors limiting use of this technology. To improve durability, the macroscopic durability (e.g., loss of catalyst surface area) must be understood in microscopic terms: we need to better understand the nanoparticle electrocatalyst structural dynamics at an atomic scale and in real time during electrochemical stressing. Such experiments require an in-situ approach. We are using in-situ synchrotron X-ray scattering, both small angle X-ray scattering (SAXS) and X-ray diffraction (XRD), to probe the structural dynamics of electrocatalyst nanoparticles. We use a three electrode arrangement in spectroelectrochemical flow cell to follow the SAXS and XRD patterns as function of time, voltage, and potential protocol. This enables us to monitor, in real time, the atomic scale structure of the electrocatalysts such as particle size, lattice constant and extent of crystallinity (diffracted intensity). In this talk, I describe in-situ scattering experiments of Pt and CuPt alloy nanoparticle electrocatalysts under conditions that mimic the degradation environment in operating fuel cells (electrode potential cycles and holds). For pure Pt, the goal is to explain the observed change in catalyst surface area. We observe nanoparticle growth with potential cycling with smaller particles growing faster than larger ones. This is related to change in catalyst surface area and a comparison with this suggests that cycling can improve Pt utilization. Our results further suggest that below a critical diameter (that is anodic turning potential dependent) the Pt particles are unstable and hence not useful in PEMFCs. These experiments will be compared with models of corrosion and particle size growth. For CuPt alloy nanoparticle electrocatalysts, the situation is more complex as both size and composition can change. We observe an initial shrinkage of particle size (due to loss of the active Cu) followed by coarsening, which are both more severe at higher turning potential. For a larger initial particle size, there is only the initial decrease in size. XRD data show a fast, enormous loss of diffracted intensity which we interpret as due to the formation of a poorly ordered Pt-rich region at the nanoparticle shell. This region slowly recrystallizes with time.

9:45 AM T4.3

Transmission Electron Microscopy Observation of the Corrosion Behaviors of Platinized Carbon Blacks under Thermal and Electrochemical Conditions. Vic Liu¹, Junliang Zhang¹, Paul T. Yu¹, Jingxin Zhang¹, Rohit Makharia¹, Karren L. More² and Eric A. Stach³; ¹Fuel Cell Research Lab, General Motors, Honeoye Falls, New York; ²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Department of Materials Engineering, Purdue University, West Lafayette, Indiana.

Carbon blacks such as Vulcan® XC-72 (Cabot Corp., USA) are widely used to support platinum (Pt) or Pt-alloy catalysts in proton-exchange membrane (PEM) fuel cells. Despite their widespread use, carbon blacks are susceptible to corrosion during fuel cell operations. In this work, the corrosion behaviors of Pt nanoparticles/Vulcan under thermal and electrochemical conditions were monitored by transmission electron microscopy (TEM) via in-situ (gas phase) and ex-situ electrochemical methods. The in-situ experiment was carried out in a 2% oxygen/helium environment at 500°C in an FEI Titan 80-300 environmental TEM which

allows a direct observation of the thermal oxidation behavior of the Pt/Vulcan nanoparticles. The ex-situ electrochemical experiment was done by first loading the Pt/Vulcan nanoparticles bound by trace Nafion® DE2020 (DuPont, USA) on a TEM gold grid, and then electrochemically corroding the nanoparticles at 25°C and 1.5 V vs. reversible hydrogen electrode step by step for 10, 100, 1000 and 4000 minutes followed by taking TEM images from exactly the same nanoparticles after each step. This work revealed that the corrosion of the Pt/Vulcan nanoparticles proceeds via at least three modes: 1) total removal of structurally weak carbon nanoparticles; 2) breakdown of high-aspect-ratio carbon nanoparticles; and 3) inside-out corrosion of carbon nanoparticles with a well-defined amorphous core and graphitic shell. The above corrosion modes lead to a non-uniform corrosion of the carbon catalyst support and may cause a premature collapse of the fuel cell electrode structure. The results obtained from this work will provide new insight on carbon corrosion and its effects on fuel cell long-term performance and durability.

10:30 AM *T4.4

New Modeling Approaches for Investigating Long-Term Platinum Nanoparticle Stability in PEM Fuel Cells. Dane Morgan¹, Edward Holby¹, Wenchao Sheng² and Yang Shao-Horn³; ¹Materials Science and Engineering, University of Wisconsin - Madison, Madison, Wisconsin; ²Mechanical Engineering and Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

One of the major barriers to implementation of practical PEMFCs is the degradation of the cathode catalyst under operating conditions. Present cathode catalysts are usually made from carbon supported Pt or Pt alloy nanoparticles, which have large surface area and high catalytic activity. However, fuel cell efficiency is reduced as electrochemically active surface area is lost over time, limiting the lifetime of the fuel cell. In this talk I will focus on understanding the mechanisms of surface area loss in Pt nanoparticle cathodes. In particular, I will discuss how we have constructed an electrochemical rate model for Pt degradation and what it can tell us about mitigation strategies. I will focus on the effects of particle size distribution, and demonstrate that surface energy driven instability changes dramatically in the commercially relevant region of 2-5nm diameter particles. I will also show a surprising role for hydrogen crossing over from the anode, demonstrating that it can dramatically alter the mechanisms and extent of surface area loss.

11:00 AM *T4.5

In-Situ Microscopy of Fuel Cell Nanoparticle Catalyst and Catalyst-Support Degradation. Karren L. More, Lawrence Allard and K. Shawn Reeves; Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Atomic-scale imaging of the structural changes to individual Pt-based catalyst nanoparticles supported on carbon black (such as Vulcan XC-72 or Ketjen Black) using in-situ Z-contrast Scanning Transmission Electron Microscopy (STEM) is being used to directly understand the mechanism(s) of catalyst particle growth/coalescence under simulated fuel cell operating conditions. Specialized in-situ holders for the STEM are being developed to image catalyst particles and their support structures during exposure at temperatures <120°C, with and without ionomer films. These in-situ microscopy studies include heating the catalyst and support materials in air and in water vapor environments. Near-live-time observations of the changes to the catalyst nanoparticles and supports in-situ will help elucidate the primary corrosion mechanisms contributing to catalyst and catalyst-support degradation during the operation of PEM fuel cells. Results will be presented that focus primarily on (1) nanoparticle microstructural features related to the stability of several Pt-based alloy cathode catalysts and (2) observed catalyst-support interactions and their effect on nanoparticle stability. Mechanisms of nanoparticle coalescence in air and water-vapor, as well as in the presence of Nafion ionomer films, will be compared. _____ Research sponsored by (1) the Office of Hydrogen, Fuel Cells, and Infrastructure Technologies, Office of Energy Efficiency and Renewable Energy, the U.S. Department of Energy and (2) ORNL's SHaRE User Facility, Scientific User Facilities Division, Office of Basic Energy Sciences, the U.S. Department of Energy.

11:30 AM T4.6

Mechanisms of Pt Degradation in PEM Fuel Cells. Qingmin Xu, Eric Kreidler and Ting He; Honda Research Institute USA, Columbus, Ohio.

The direct conversion of chemical energy to electricity via fuel cells has attracted significant attention for many decades. However, due to the sluggish kinetics of oxygen electroreduction and particularly the poor durability of fuel cell system in service, the mass utilization of fuel cells has been inhibited. To overcome the technical barriers associated with fuel cell durability, it is necessary to understand the degradation mechanisms of oxygen reduction electrode and propose countermeasures. In this presentation, we will report our new findings on the mechanisms of coarsening and dissolution of Pt catalysts at fuel cell cathodes. It has been found that the coarsening is a result of double-layer-potential-induced Ostwald ripening whereas the dissolution results from direct-oxidation of Pt nanoparticles. Details of these new findings will be discussed and countermeasures will be proposed.

11:45 AM T4.7

Degradation of Pt Catalysts in Polymer Electrolyte Fuel Cells. Eric Kreidler and Ting He; Honda Research Institute, Inc., Columbus, Ohio.

The mass commercialization of polymer electrolyte fuel cells for transportation applications is significantly inhibited by high materials costs and poor service life which can be largely attributed to the Pt catalysts used at the cathodes. Previously, we reported in-situ electrochemical scanning tunneling microscopy studies on the coarsening behavior of Pt nano crystals under potentiostatic holding and potential cycling as well as the direct dissolution of Pt nanoparticles as a function of electrochemical potential [1,2]. It was found that Pt nano crystal coarsening is a result of double-layer-potential-induced Ostwald ripening and Pt

particle dissolution results from direct electro-oxidation of Pt nanoparticles. To verify these findings, fuel cell tests utilizing Pt black and carbon-supported Pt cathode electrocatalysts were conducted. Individual fuel cells were operated under high potential (850 mV), double-layer potential (600 mV), and potential cycling (open circuit to 300 mV and back) conditions for extended periods of time. Electrochemical active surface area (ECSA) was measured as a function of time and the catalyst layers were analyzed after operation using x-ray diffraction (XRD), electron microprobe analysis (EPMA), and transmission electron microscopy (TEM). Details of the experiments and results will be presented and discussed. [1] Q. Xu, E. Kreidler, D.O. Wipf, and T. He, J. Electrochem. Soc. 2008, 155, B228. [2] L. Tang et al., to be published.

SESSION T5: Fuel Cell Overview - II
Chair: Ting He
Tuesday Afternoon, December 1, 2009
Room 301 (Hynes)

1:30 PM *T5.1

PEM Fuel Cells. Yu-Min Tsou, BASF Fuel Cells, Somerset, New Jersey.

This presentation will address two important topics in PEM fuel cells. The first one is approaches to eliminate/reduce the most commonly observed durability problems: carbon corrosion. The second one is the fundamental understanding of nano-sized Pt particles in the context of characterization with electrochemical and spectroscopic methods. Carbon support corrosion problem is one of the most important barriers in hampering the commercialization of fuel cells. Support corrosion results in the loss of electrochemical activity through agglomeration of catalyst particles and loss of conductivity of catalyst layer. Even a loss of 10-15% of carbon support can lead to severe performance drop due to electrode conductivity loss from the support contact loss. Most severe support loss occurs during shutdown/re-start-up periods when gas mixing occurs. Feeding H₂ into air filled anode chamber can easily set up local battery effect that drives carbon support to corrosion potentials. While mitigation processes have been proposed to reduce corrosion but they are hard to practice and also very costly. Therefore, development of materials solution to overcome carbon corrosion becomes the focus of BFC's work. The first approach is using corrosion resistant carbon. Electrochemical carbon screening methodology will be presented and successful examples are demonstrated. Unsupported catalyst is another attractive approach. BFC has extended the high performance supported Pt catalysts technology to synthesize high surface area unsupported Pt catalysts. 3-5 nm is the typical size, affording high surface area. Cell stack testing indicates the much better durability of gas diffusion electrode (GDEs) with unsupported catalysts (USC) in 3000-4000 hour experiments. GDEs with UNC also showed advantage in low humidity operation and fast break-in. Technology in optimizing the performance durability, related to water management, of GDEs with UNC will be illustrated. Ion beam deposition (IBD) is demonstrated to afford anode GDEs with similar performance to conventional one with complete dry process and without incorporating ionomer for proton conductivity. Cathode IBAD GDEs exhibit mass transport problem. Roll-to-roll IBAD manufacture is demonstrated. BFC is capable of manufacturing Pt particles with very small crystallite sizes even at very high loadings on supports. With a series of Pt catalysts we are able to use cyclic voltammograms as useful characterization tools. The main findings include (i) intensity of weak hydrogen adsorption peak is associated to low coordination defect sites in addition to edge/corner sites, thus indicative of "extent of disorder" of a Pt particle; (ii) size effect for oxygen reduction reaction is proposed to be composed of primary effect associated with large activity difference between Pt atoms on crystalline planes and those on defect sites, and secondary effect associated with size of crystalline plane. Primary particle size effect becomes important only when the percentage of corner/edge/ becomes so high that they dominate the activity, i.e., as particle size falls below 18-20 Å. Experimental results are supplied to support the two-effect hypothesis; (iii) voltammetric peaks for reduction of OH on corner/edge/defects are identified at 180-280 mV more negative of that on crystalline planes. The corresponding OH formation peak is at very positive potential and can be attributed to be responsible for CO stripping from all sites. The origin of multiple CO voltammetric peaks will be discussed in detail.

SESSION T6: Computational Modeling
Chair: Ting He
Tuesday Afternoon, December 1, 2009
Room 301 (Hynes)

2:00 PM *T6.1

Effects of Core Composition on the Activity and Stability of Pt-skin Surfaces in Fuel Cell Cathodes. Perla B. Balbuena, Chemical Engineering, Texas A&M University, College Station, Texas.

Pt-skin surfaces have been shown to offer good activity and stability properties for the reduction of molecular oxygen in acid medium. Such behavior is attributed to favorable interactions with subsurface atoms that play a significant role in modifying the electronic structure and geometric properties of the surface. Here we report systematic density functional theory studies of the effect of changes in the electronic structure of the core on the performance of Pt-skin (111) surfaces towards oxygen reduction reaction activity and stability of the Pt surface atoms against dissolution in acid medium. We first investigate trends of pure cores to segregate to the surface and show how this trend is related to the core electronic structure and what the influence of such electronic distribution on the stability of the Pt surface atoms is. By examination of the oxygen reduction reaction activity of the group of stable pure metal cores it is concluded that a rational alloy core design may be obtained by combining elements of the stable (M) and stable or unstable cores (Y) of M_xY_{1-x} composition. The results will be illustrated for Pt/Pd₃Y alloys. Interesting trends are found for the stability and activity of the surface Pt atoms as a function of the differences in electronic structure between the surface and the subsurface. We also discuss the effect of the increase of the shell thickness on the stability and activity properties, and we demonstrate that the beneficial effect of the surface/subsurface interaction is lost when the shell thickness grows beyond one monolayer.

2:30 PM T6.2

A First-Principles Study of the Electropotential Dependent Shape Stability of Metal Nanoparticles. Nicephore Bonnet¹, Ismaila Dabo² and Nicola Marzari¹; ¹MIT, Cambridge, Massachusetts; ²CERMICS-ENPC, Marne la Vallée, France.

Understanding the catalytic activity of transition metal nanoparticles is a central issue in the development of novel fuel cell materials. Observed trends are often interpreted in terms of the size dependent morphology of nanoparticles, in particular the relative density of low coordination sites. However, no consensus exists regarding the direction or the mechanism of such an effect. In this context, ab-initio methods can be useful to extract relevant parameters. Here, we calculate surface energies under realistic electrochemical conditions and use the Wulff construction to infer stable nanoparticle contours. The electropotential is adjusted through its conjugate variable, the charge, and density countercharge periodic-image corrections are applied [1]. The surrounding solvent is treated as a combination of a continuum dielectric and a classical ionic distribution at equilibrium. Two quantities are studied. One is the metal surface capacitance with no specific adsorption. It is shown that unspecific electrostatics have no effect on the nanoparticle shape. The other one is the Pourbaix diagram of interfacial water including O and OH as oxidized species. An effect on the nanoparticle shape is predicted from the surface orientation and potential dependent coverages of those species. References [1] I. Dabo, B. Kozinsky, N.E. Singh-Miller, N. Marzari, Electrostatics in periodic boundary conditions and real-space corrections, PRB 77, 115139 (2008)

2:45 PM T6.3

Computational Design of Nanosegregated Catalysts for Polymer Electrolyte Membrane Fuel Cells. Guofeng Wang, Department of Mechanical Engineering, Indiana University Purdue University Indianapolis, Indianapolis, Indiana; Richard G. Lugar Center for Renewable Energy, Indiana University Purdue University Indianapolis, Indianapolis, Indiana.

Knowledge on the arrangement of different elements in surface region is critical in the design and synthesis processes of Pt alloy electro-catalysts for their applications in PEM fuel cells. Particularly, there is a useful material process which we can take advantage of during catalyst design. It is called surface segregation, which refers to the phenomenon that chemical composition at the surface of multi-component materials differs from the corresponding value in the bulk. In this work, I employed an atomistic Monte Carlo simulation method to predict the equilibrium structure and surface composition of nanosegregated Pt alloy nanoparticles considering surface segregation process. The approach consists of two integrated parts: (1) developing interatomic potentials for Pt alloys within the modified embedded atom method based on first-principles computation data, and (2) applying these potentials to determine the chemical composition of extended and nanoparticle surfaces of Pt alloys using the Monte Carlo method. I have examined the reliability of the developed computational approach for three Pt bimetallic alloys that represent different fashions of Pt segregation to surfaces: Pt-Ni (strong and oscillatory surface segregation), Pt-Re (strong and monotonic surface segregation), and Pt-Mo (weak and monotonic surface segregation). Moreover, I have extended this multi-scale computational approach to study the equilibrium structure of Au/PtFe core-shell ternary alloy nanoparticles.

3:00 PM T6.4

Multiscale Modeling of Electrocatalysis in PEM Fuel Cell. Liang Qi¹, Joshua Fujiwara^{1,2} and Ju Li¹; ¹Dept. of Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Honda Research Institute, Columbus, Ohio.

In proton-exchange membrane (PEM) fuel cells, oxygen reduction reaction (ORR) on cathode is a complex multi-electron transfer process and its reaction mechanism is still unclear, partially because of the difficulties in direct investigation of its reaction intermediates, such as O₂^{*}, OOH^{*}, O^{*} and OH^{*} (* means adsorbed state), and corresponding electron transfer dynamics. We analyzed the charge states of all ORR intermediates adsorbed on catalyst surfaces based on first-principles calculations and found that all of them are in near-neutral states, which indicate that the electron transfer in ORR should occur through proton-coupled mechanism (PCET). Then first-principle methods were used to study PCET near different metallic surfaces, which show that there are negligible activation barriers for PCET near the surfaces except the energy differences between the initial and final states. However, there are still potential-dependent activation barriers for proton transfer from bulk electrolyte to catalyst surface. Based on these reaction mechanisms illustrated by first-principles analysis, a kinetic model of total ORR rate is built by considering coverage-dependent reaction rate and energies for each elementary step, which can semi-quantitatively explain the activity differences between different catalyst surfaces.

3:15 PM T6.5

Theoretical Study of Au-modified Pt as ORR Catalysts. Joshua Fujiwara^{1,2}, Liang Qi¹ and Ju Li¹; ¹Dept. of Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Honda Research Institute, Columbus, Ohio.

Pt and its alloys are used as catalysts for oxygen reduction reaction (ORR) in proton-exchange membrane (PEM) fuel cells. However, these catalysts would lose electrochemical active surface area (ECSA) during long-time operation due to the dissolution of Pt atoms and coarsening of Pt nanocrystals on electrodes. Recently Pt-Au alloys are reported to have considerable catalytic activity and better stability than pure Pt. To confirm and explain this result, we study different types of Au clusters on Pt (111) surface. The results show that although stable Au clusters have too weak adsorption ability for ORR intermediates, such as O^{*} and OH^{*}, for good catalytic activity, the adsorption properties of Pt surface close to Au clusters are modified, so that it may have better ORR activity to compensate the loss of active surface area covered by Au clusters. For the stability issue, Pt surface oxide formation during cathodic polarization is one of the key steps to induce the dissolution of Pt atoms in the anodic polarization. Au clusters would change the oxidation process on Pt surfaces, which results the increase of anti-corrosion stability.

3:30 PM T6.6

Ab-initio Analysis of CO Adsorption in Pd₇₀Co₂₀X₁₀ (X=Au, Mo, Ni) Compounds for PEM Fuel Cell Catalysts. Mauricio A. Garza-Castanon¹, Marco A. Jimenez¹, Jorge L. Acevedo-Davila¹, Luis E. Garza⁴, Oxana V. Kharissova² and Velumani Subramaniam³; ¹Postgraduate Studies and Research, COMIMSA, Saltillo, Mexico; ²Facultad de Ciencias Fisico-Matematicas, Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza, Mexico; ³Fisica, Instituto Tecnologico y de Estudios Superiores de Monterrey, Monterrey, Mexico; ⁴Mecatronica, ITESM - Monterrey, Monterrey, Mexico.

Application of trimetallic nanoparticles is becoming more important, the local atomistic structure of such alloyed particles, which is critical for tailoring their properties, is not yet very clearly understood. In this work we present detailed theoretical analysis on the atomistic structure and CO adsorption in Pd₇₀Co₂₀X₁₀ (X=Mo,Au,Ni) trimetallic composite alloys for their application in the proton exchange membrane (PEM) fuel cells as oxygen reduction reaction (ORR) catalysts. The basic structure and their most stable configuration for all the three composites are determined. Quantum mechanical approaches and classic molecular dynamics methods are applied to model the structure and to determine the lowest energy configurations. Our theoretical results almost coincide with the experimental results of XRD. Taking those structures as base, simulations were performed to determine the magnitude of CO poisoning. The results obtained by ab-initio techniques allow us to estimate the CO-tolerance that these catalysts might have and compare with Pt (1 1 0) used as a commercial catalyst. From these results, a comparison has been made to show different CO adsorption strengths. This is the first step to make an efficient engineering that allows us to obtain highperformance, low-cost nanostructured catalysts.

3:45 PM T6.7

The Influence of Morphology on the Mechanical Properties of Proton Exchange Membranes. Yue Qi¹ and Yeh-Hung Lai²; ¹Materials and Processes Lab, GM R&D Center, Warren, Michigan; ²Fuel Cell Research Lab, GM R&D Center, Honeoye Falls, New York.

The nano-scale morphology of proton exchange membrane (PEM) determines the network connectivity of hydrophilic domains and strongly influences its proton conductivity and mechanical performance. In this study a multi-scale modeling approach has been developed to first obtain the morphologies of hydrated Perfluorosulfonic Acid (PFSA) membranes and then to predict their mechanical properties based on the simulated morphology. Two representative morphologies were compared, namely spherical and cylindrical ionic domains to represent cast and extruded membranes. The overall elastic moduli are very close for both morphologies and agree well with experiments. The nano-scale phase segregation in hydrated PFSA induces non-uniform distribution of local stress. The cylindrical morphology develops much lower peak stress than the isotropic spherical morphology under the same level of strain. The peak stress is localized at the smeared water/PFSA interface. These results may be able to explain the difference of recast and extruded PEM samples, which show similar modulus but the extruded membrane shows 10 times longer life time.

SESSION T7: Electrodes and MEAs
Chair: Guofeng Wang
Tuesday Afternoon, December 1, 2009
Room 301 (Hynes)

4:00 PM T7.1

Integrated Pt/CNT Based Electrodes for High Efficiency Proton Exchange Membrane Fuel Cells. Zhe Tang¹, Daniel H. Chua¹ and How Y. Ng²; ¹Department of Materials Science & Engineering, National University of Singapore, Singapore, Singapore; ²Division of Environmental Science and Engineering, National University of Singapore, Singapore, Singapore.

Carbon nanotubes (CNT) have shown promising characteristics as alternative catalyst support material for proton exchange membrane (PEM) fuel cells. Previous studies on CNT based electrode have suggested that CNT support with high surface area and chemical stability could enhance the electrocatalyst's activity and stability of platinum (Pt) particles by their active interaction. However, typically the coating of Pt catalyst on CNT requires a series of complicated wet-chemical processes such as surface oxidation and purification of CNT, as well as reduction of Pt precursor solution. In addition, an additional carbon black based gas diffusion layer is still necessary for CNT supported catalyst thus limiting its overall effectiveness. In this work, an integrated Pt/CNT based electrode has been fabricated by an efficient two-step process, including in-situ growth of a dense CNT layer on plain carbon paper using chemical vapor deposition (CVD) technique followed by direct sputter-deposition of Pt nanoparticles onto the CNT layer. The in-situ grown CNT layer on carbon paper showed tunable diameter and density under different growth processes. Brunauer-Emmett-Teller (BET) and scanning electron microscopy (SEM) characterization demonstrated that with optimum morphology and coverage the CNT layer is able to provide extremely high surface area and porosity which can serve as both gas diffusion layer and catalyst layer simultaneously. Microstructure of the sputter-deposited Pt catalyst on carbon nanotubes was characterized by transmission electron microscopy (TEM), which illustrated well-dispersed Pt nanodots with nanoscaled grain size and small size distribution. In polarization test, the Pt/CNT based electrode showed notable improvement compared to conventional ink-process prepared electrodes with different commercial carbon black supported Pt catalysts. A higher maximum power density of 650 mW cm⁻² has been obtained with 0.04 mg cm⁻² Pt loading on both anode and cathode. In-situ characterization techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and accelerated degradation test (ADT) have been carried out to fully evaluate the Pt/CNT based electrode. Results confirmed that the Pt/CNT catalyst can yield higher Pt utilization as well as superior electrochemical stability compared with commercial catalysts. Moreover, the reduced charge transfer and mass transport resistance of the Pt/CNT electrode suggested that the integrated CNT gas diffusion layer and catalyst layer sputtered with highly localized Pt catalysts has an intrinsic structural merit for high Pt utilization.

Therefore, this combined fabrication method shows a great potential for the ease of scale-up and mass production of PEMFC electrodes.

4:15 PM T7.2

Improvement of the Pt/Graphene Interface Adhesion by Metallic Adatoms for Fuel Cell Applications. Fatih G. Sen¹, Yue Qi² and Ahmet T. Alpas¹; ¹Department of Mechanical, Automotive and Materials Engineering, University of Windsor, Windsor, Ontario, Canada; ²Materials and Processes Laboratory, General Motors R&D Center, Warren, Michigan.

The degradation of carbon supported Pt catalyst limits the lifetime of polymer electrolyte membrane (PEM) fuel cells. In order to understand and prevent Pt particle loss, first principles calculations were carried out for searching metallic adatoms that can enhance the Pt and carbon interface adhesion. Graphene was used to represent carbon surface, since it has negative bonding energy with Pt, and thus mimics the weak bond formed between Pt and carbon support in fuel cells. Various metallic adatoms were systematically adsorbed on the graphene surface and the favourable adsorption sites were determined. The interface was modeled by a slab by six layers of Pt(111) planes and a graphene plane with one metal atom adsorbed on its favourable site. In this way the adhesion strength between the Pt atoms and the modified graphene surface was evaluated. Accordingly, Pt/graphene interface strength increased with modification of the graphene surface by metal adatoms. The work of adhesion values decreased with increasing the atomic number within the elements at the same row of the periodic table. Early transition metals belonging to the IIIB-VB group, such as Ti, V, Zr and Nb, were found to be the most promising candidates for bridging the Pt to graphene. Especially, Zr and Nb were found to enhance the adhesion of Pt to carbon at most, correlated with an increase in the rumpling of the Pt surface. These atoms formed strong bonds with both carbon and Pt due to their particular electronic structure with unfilled d orbitals, which enhance their bonding affinity to both carbon and Pt. Electronic structure investigations revealed that considerable amount of charge transfer occurred at the interface from the adatoms to Pt and graphene surface and the work of adhesion values were shown to be proportional to the amount of charge transfer.

4:30 PM T7.3

Integration and Performance of Supportless Nanoporous Metal Membrane Electrodes into PEM Fuel Cells. Joshua D. Snyder^{2,1} and Jonah Erlebacher^{1,2}; ¹Materials Science, Johns Hopkins University, Baltimore, Maryland; ²Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland.

Similar surface area/volume, specific surface area, and precious metal loading as nanoparticle-based PEM fuel cell catalysts can instead be made by using ultrathin (~100 nm) nanoporous metal membranes. We discuss here how ultrathin porous membranes can be made using electrochemical dealloying, and how to integrate such membranes into functional fuel cells. Dealloying is the selective dissolution of one or more components from a non-porous precursor alloy. Under the right electrochemical conditions, the remaining alloy component(s) are driven to diffuse along the alloy/electrolyte interface to form a porous metal with pores even smaller than 5 nm. Nanoporous metals can be intrinsically catalytic toward oxygen reduction, or can be coated with thin catalyst layers to form low Pt core-shell catalysts. Using nanoporous metal electrodes for fuel cell catalysis may remove stability issues associated with carbon supports, and opens new avenues for catalyst design.

4:45 PM T7.4

AFM Imaging of PFSA Polymer Adsorption on Model Graphite, Mica and Platinum Surfaces. Roland Koestner¹, Sergiy Minko² and Yuri Roiter²; ¹Fuel Cell Research Laboratory, General Motors, Honeoye Falls, New York; ²School of Arts & Sciences, Clarkson University, Potsdam, New York.

The interaction of perfluorosulfonic acid polymer (PFSA, EW ~ 900 g/mol) with atomically flat graphite, mica and Pt surfaces is visualized at the single molecule level using in situ liquid atomic force microscopy (AFM) experiments. The adsorbed PFSA chains are characterized quantitatively within a controlled liquid environment that includes substrate surface charge, solvent composition, pH(e) and polymer aggregation in the liquid phase. The polymer structure in the liquid phase is imaged by rapid deposition on mica via spin coating (aggregation level) and by weak adsorption on highly oriented pyrolytic (HOPG) graphite (globular vs micellar conformation). This adsorption is driven by electrostatic interaction of the pendant sulfonate groups which is then correlated with the HOPG surface charge by zeta potential (net) and AFM force-distance curves (local) at varying solvent composition and pH(e). In contrast, the polar mica surface shows much stronger adsorption, while the bare Pt surface is much weaker than graphite. In summary, molecular-level mapping of the PFSA polymer interaction with these model surfaces should provide a quantitative basis to improve its distribution and morphology in Proton Exchange Membrane Fuel Cell (PEMFC) electrode layers.

SESSION T8: Poster Session: Fuel Cell
Chairs: Ting He, Byungwoo Park and Karen Swider Lyons
Tuesday Evening, December 1, 2009
8:00 PM
Exhibit Hall D (Hynes)

T8.1

A New Membrane Electrode Assembly for Low-Temperature PEM Fuel Cells having a Nanocomposite Catalyst Layer. David Dvorak¹ and Mohsen Shahinpoor²; ¹School of Engineering Technology, University of Maine, Orono, Maine; ²Mechanical Engineering, University of Maine, Orono, Maine.

Studies are currently underway to manufacture a novel membrane electrode assembly (MEA) for polymer electrolyte fuel cells. Specifically, innovative processes are being developed for applying a nanocomposite form of catalysts to the ion exchange polymer membrane. This MEA will be designed to incorporate a nanocomposite catalyst layer comprising a functionally graded distribution of Platinum nano particles chemically embedded near boundaries and surfaces of the polyelectrolytic membrane. The nanochemistry involved is called REDOX operation in which first the ionic polymer PSM is oxidized with a catalyst metal salt and then reduced in a reduction solution. This manufacturing technique incorporates two distinct processes. Initial process of oxidizing the PSN ionic polymer with an organometallic salt of a catalyzing metal salt such as $\text{Pt}(\text{NH}_3)_4\text{HCl}$ in the context of chemical reduction processes. After oxidation, the ionic polymer is reduced to create functionally-graded conductor composite and near boundary porous electrodes. This membrane-catalyst layer nanocomposite is then sandwiched between two porous carbon gas diffusion layers. The catalyst layers of the membrane also function as electrodes, eliminating the need for a separate porous layer applied to the GDL. The whole assembly is then sandwiched between two flow-field or bi-polar plates in a standard fashion, thus giving rise to a 5-layer fuel cell rather than the currently standard 7-layer fuel cells. Note that precious metal catalysts can be combined with not-precious metal species to improve conductivity and lower cost. The penetration of the catalyst layer into the membrane can be controlled, as can the composition of the metallic species. Thus, deeper layers of metallic nanocomposites can be constituted of low-cost non-precious metals to allow electronic conduction (reducing the effective ionic conduction thickness of the membrane) while concentrating catalytic precious metals closer to the surface of the membrane. Initial performance tests of fuel cells incorporating these membranes show promising results which will serve as a baseline for further process optimization.

T8.2

Synthesis and Characterization of Polythiophene-composited Pd Catalysts for Hydrogen Electrooxidation. EunJa Lim, Min Ho Seo, Sung Mook Choi, Hyung Ju Kim and Won Bae Kim; Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea, South.

Although there have been many attempts to develop a new platinum-free catalyst for proton exchange membrane fuel cell (PEMFC), Pt is still the only metal showing the high and stable performance on hydrogen oxidation in the acid-based PEMFCs. Development of Pt-free catalysts is necessary for reducing fuel cell stack cost, but unfortunately pure and composited catalysts based on common transition metals is not stable in acid condition because of its thermodynamically and electrochemically unstable property at low pH and high potential region. In our previous work[1], composited Pd with a conducting polymer of polypyrrole (Pd-PPy) demonstrated high activity levels with practical implications for the hydrogen fuel oxidation electrodes of PEMFCs. As further work, here, we also propose that polythiophene(PTh) as other conjugated polymer could stabilize the Pd metal. The Pd-PTh composite shows an improved stability and activity for hydrogen oxidation compared to electrodeposited bare Pd. Such catalytic stability and activity of Pd-PTh are demonstrated by half-cell test and cyclic voltammetry test together with physico-chemical characterization. While the bare Pd shows a poor stability on the hydrogen oxidation performance, the Pd-PTh composite catalyst maintains the activity up to 500 cycles. It seems that the conducting polymer of the polythiophene layer effectively prevents the active Pd catalyst from undergoing oxidative dissolution, allowing the high electrocatalytic activity of Pd to be maintained under acidic conditions. This should enable a new strategy for electrocatalyst development through the stabilization of highly reactive but otherwise unstable non-noble metal catalysts. [1] M. H. Seo. et.al, submitted for the publication.

T8.3

Synthesis of Carbon Nanofiber-Supported Pt by Polyol Processing Technique for Use as Electrodes in DMFCs. Zhan Lin, Mariah D. Woodroof, Liwen Ji, Yingfang Yao and Xiangwu Zhang; Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina.

Direct methanol fuel cells (DMFCs) have been considered as one of the promising energy systems since they produce electric power by the direct conversion of the methanol fuel at the anode of fuel cells. In this study, Pt/carbon nanofiber composites (Pt/CNFs) were prepared by depositing Pt nanoparticles onto electrospun carbon nanofibers (CNFs) using polyol processing technique, and their electrocatalytic properties were characterized towards the oxidation of methanol. Transmission electron microscopy images show that CNFs exhibit smooth and straight fibrous morphology with diameters ranging from 200 to 300 nm, and Pt nanoparticles are observed on the surface of CNFs after chemical deposition. However, there are just a few relatively large Pt nanoparticles and their diameters are around 20.0 nm on CNFs without any surface treatment. After treatment, Pt nanoparticles are evenly distributed on the surface of CNFs, and their diameters are much smaller, which are between 3.0 - 5.0 nm. Cyclic voltammetry was used to study the electrocatalytic activity of Pt/CNF composite electrodes toward the oxidation of methanol. A small methanol oxidation peak of Pt/CNFs without any surface treatment is found around 0.80 V (vs. $\text{Ag}/\text{AgCl}/4.0\text{ M KCl}$), however, there is no peak found when scanning back. In comparison, Pt/CNF electrodes present the electro-oxidation of methanol, which starts at + 0.42 V and then the current density increases to a maximum at + 0.63 V. Moreover, another current peak is found at +0.55 V when scanning back, which signifies the desorption of CO generated through the methanol oxidation. It is also seen that the current density peaks of Pt/CNFs with 1-aminopyrene functionalization are much larger than that of Pt/CNFs with $\text{HNO}_3 + \text{H}_2\text{SO}_4$ acid oxidation, which means that the 1-aminopyrene functionalization leads to better catalytic activity toward the oxidation of methanol. In summary, Pt nanoparticles deposited on CNFs by the polyol processing technique exhibit good electrocatalytic activity toward the methanol oxidation, and can be potentially used as electrodes in DMFCs.

T8.4

Synthesis of Cobalt/Polypyrrole/Carbon Nanotube and Catalytic Activity for Oxygen-reduction Reaction. Hye-mi Bok¹, Hyun-Jong Kim¹, Kyoungjun An¹, Mk Han¹ and Hansung Kim²; ¹Nano surface technology team, Korea Institute of Industrial Technology, Incheon, Korea, South; ²Department of Chemical Engineering, Yonsei university, Seoul, Korea, South.

Fuel cells have been recognized as clean energy-converting devices due to their high efficiency and low/zero emissions. Especially, study of non-platinum catalysts is important and attractive issue in the energy conversion efficiency of polymer electrolyte membrane fuel cells (PEMFC) because it is a new class of low cost nano-composite catalysts compared to platinum catalysts. Herein, we described a cobalt/polypyrrole/carbon nanotube (Co/PPy/CNT) as non-platinum catalysts for PEMFC. PPy-CNT composite was first prepared by using chemical oxidation polymerization of pyrrole in the presence of ferric chloride (FeCl_3) and the obtained material was mixed with a solution containing cobalt(Co) ion. The PPy/CNT was characterized by Fourier transform-infrared (FT-IR) spectroscopy and X-ray diffraction (XRD). FT-IR spectra indicated that each individual CNT could be well coated by PPy. XRD patterns showed the presence of characteristic broad peak of PPy and the strong peaks of CNT. The tubular morphology of Co/PPy/CNT was observed with scanning electron microscopy (SEM). Also, Extended X-ray absorption fine structure (EXAFS) spectroscopy revealed that the Co ion is successfully coordinated by nitrogens(N) atoms. Electrochemical oxygen-reduction reaction was measured by using the rotating disk electrode. An onset potential of catalyst was approximately 0.69 V (NHE) and the PEMFC performance was 50 mA cm^{-2} at 0.6 V in both H_2 - O_2 condition. The electrocatalytic activity was dependant on Co/N ratio and thermal treatment conditions. Therefore, the interaction between Co ion and N atom should play as active site. Also, the heat treatment is a necessary step to enhance activity and stability of this catalyst.

T8.5

Electrochemical Characterization of Air-breathing Direct Methanol Fuel Cells Cathodes Under Flooding Conditions. Ana Tavares and Francesca Capitanio; Energie, Matériaux et Télécommunications, Institut National de la Recherche Scientifique, Varennes, Quebec, Canada.

Small fuel cells that run on methanol have intrinsically higher energy density than batteries, improved autonomy and instant re-charge. However, in air breathing DMFC the cathode performance is strongly limited by the flooding due to water and methanol accumulation. To quantify the factors governing the cathode deactivation under flooding, a series of DMFCs electrodes with catalyst layers of different structure and hydrophilic degree were electrochemically characterized in 0.5 mol dm^{-3} H_2SO_4 . This condition was chosen to simulate severe flooding. Nafion and Teflon were used as binders in the fabrication of the catalyst layers, and their content was varied between 15/0 and 0/15 wt% Nafion/Teflon with respect to Pt. The Pt loading was 3 mg cm^{-2} and the electrodes were prepared by spray deposition on non teflonized carbon cloth. Cyclic voltammetry in N_2 saturated solution revealed that the Pt electrochemical surface area is 19 m^2g^{-1} for the Nafion bonded electrodes and 15 m^2g^{-1} for all other compositions. Since the Pt utilization is almost the same, differences in the cathodes' performance can be ascribed to variations into their hydrophilic character and/or in their morphology. AC electrochemical impedance spectroscopy was carried out in N_2 saturated solution and a DC voltage in the double layer charging region was applied as bias potential. The Nyquist plot of the 15 wt% Nafion electrode include a 45° region at high frequencies due to the ion diffusion through the electrode porous structure. The extent of this region decreases when Nafion is partially replaced by Teflon and the capacitance feature dominates the EIS spectra of Teflon bonded electrodes. The cathodes were also investigated for oxygen reduction in the O_2 saturated solution. Steady state polarization curves reveal the strong influence of the binder nature: the overpotential for the ORR is lower for the more hydrophilic electrode, but the Tafel slope is lower for the Teflon bonded electrode (81 mV) and the limiting current increases by one order of magnitude by replacing Nafion with the Teflon. The higher limiting current for the ORR reaction on the Teflon bonded electrodes was expected, but this study clearly shows that a hydrophobic polymer has to be used as the main binder in the catalyst layer of an air-breathing DMFC cathode in order to keep it operating under flooding. A hydrophilic component is necessary for the ORR reaction but its content in the catalyst layer has to be minimized, or other alternatives Nafion have to be used. The morphology of the electrodes will be analysed by SEM, and water absorption capacity of the cathodes will be quantified by Dynamic Vapor Sorption. The cathodes performance in DMFC operation will be also investigated.

T8.6

Abstract Withdrawn

T8.7

Synthesis and Characterization of Gold-Platinum Nanoparticles as Electrocatalysts for Fuel Cells. Bridgid N. Wanjala, Derrick Mott, Rameshwori Loukrakpam, Jin Luo, Peter N. Njoki, Bin Fang and Chuan-Jian Zhong; Department of Chemistry, State University of New York at Binghamton, Binghamton, New York.

Bimetallic nanoparticles exhibit interesting electronic, optical, and chemical or biological properties due to bifunctional or synergistic effects. Several types of gold-based bimetallic nanoparticles for catalytic reactions have recently been studied. One example involves use of AuPt nanoparticles as electrocatalysts for fuel cell reactions. The ability to synthesizing and processing the bimetallic nanoparticles with controllable composition in a wide range is an important focus of the exploration. This presentation discusses recent results of our investigation of the synthesis and processing of AuPt bimetallic nanoparticles in organic solvents. By controlling the feed ratios of Au and Pt precursors, the relative concentrations, the reducing and capping agents, AuPt nanoparticles with bimetallic compositions ranging from 0-100 Au% and particle sizes ranging from 2 to 4 nm were synthesized. The composition was determined by direct current plasma - atomic emission spectroscopy. A 1:1 linear correlation between the precursor feed ratio and the nanoparticle compositions was established. The size and morphological properties were characterized using transmission electron microscopy and X-ray diffraction. A focus of the discussion will be the correlation between the bimetallic composition and the electrocatalytic activity of the catalysts for oxygen reduction reaction (including fuel cell performance). Selected examples of the bimetallic nanoparticles for the design of fuel cell catalysts will also be discussed with emphasis on electrocatalytic characterization.

T8.8

Rotating Disk Electrode Study of the Electrocatalytic Activity and Stability of Bimetallic/Trimetallic Nanoparticle Catalysts for Oxygen Reduction Reaction.

Peter N. Njoki, Bridgid N. Wanjala, Rameshwori Loukrakpam, Bin Fang, Jin Luo and Chuan-Jian Zhong; Department of Chemistry, State University of New York at Binghamton, Binghamton, New York.

Fuel cells represent a promising front of research and development in exploring alternative future energies, which are highly efficient and environmentally clean. A key challenge for the commercialization of fuel cells is availability of active, robust, and low-cost catalyst. The development of effective strategies for the synthesis of alloy nanoparticles with controllable size and composition is an important approach to the catalyst preparation. This poster will discuss recent results of an investigation of the electrocatalytic activity and stability of bimetallic/trimetallic nanoparticle catalysts for oxygen reduction reaction. A focus of the discussion is the correlation of the nanoscale size and composition with the electrocatalytic activity and stability. In addition to synthesis of multimetallic alloy nanoparticles with controlled size and composition, the electrocatalytic activity and stability of the catalysts for oxygen reduction reaction are investigated using cyclic voltammetry and rotating disk electrode techniques. The electrocatalytic activity and stability of selected catalysts will be discussed, along with their correlation with preliminary performance evaluation in fuel cells.

T8.9

High Surface Area Catalyst Support Structures for Oxygen Reduction. Ryan T. Tucker^{1,3}, Michael D. Fleischauer¹, Arman Bonakdarpour², Hillary P. Cheng², David P. Wilkinson² and Michael J. Brett^{1,3}; ¹NRC-National Institute for Nanotechnology, Edmonton, Alberta, Canada; ²Chemical & Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada; ³Electrical & Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

Nanostructured thin film oxygen reduction catalysts consisting of Pt nanocrystals on crystalline organic whisker supports offer considerable stability and performance enhancements over standard carbon-supported dispersed Pt.¹ Whisker-like support structures consist of aligned crystals of a perylene derivative on the order of 50 nm in width and upwards of one micron in length numbering ~50 per square micron.² Magnetron sputtered Pt nanocrystals nucleate uniformly every 6-8 nm over this high surface area support,³ leading to large electrochemical surface areas. The electrochemical surface area is stable with potential cycling, indicating a high stability of Pt catalysts against corrosion.⁴ The nanostructured thin film (NSTF) supports used with a Pt-based catalyst have demonstrated significant enhancements in both specific activity and durability.³ However, non-noble metal catalysts such as Fe-C-N are not compatible with the organic whisker supports since a high temperature "activation" step is required.⁵ Metal oxides such as Ti₄O₇ and Ti_{0.9}Nb_{0.1}O₂ have demonstrated better temperature stability and are thus being considered as alternate catalyst support materials.⁶ We have recently demonstrated that the Glancing Angle Deposition (GLAD)^{7,8} thin film fabrication technique can be used to produce columnar Ti supports for Pt oxygen reduction catalysts.⁹ Here we report on expanding this work to the Ti-O system - chosen for stability, variable conductivity, and ease of fabrication - as a model for high surface area metal oxide supports. The GLAD technique offers a high degree of control over the architecture of porous nanostructured thin films. Arrays of micron-long vertically aligned posts ~30 nm to ~200 nm in diameter can be produced with this method. Control of the deposition angle alters film porosity between 20% and 100% of bulk material. We will report on the oxygen reduction performance (determined by rotating disk electrode measurements and cyclic voltammetry) of Pt on Ti-O supports as a function of Pt loading, support porosity, and support conductivity, and outline the potential of columnar high surface area metal oxide supports. References: ¹ M.K. Debe et al., ECS Trans., **1**, 51 (2006). ² M.K. Debe and R.J. Poirier, J. Vac. Sci. & Tech. A, **12**, 2017 (1994). ³ L. Gancs et al., Chem. Mater., **20**, 2444 (2008). ⁴ M.K. Debe et al., J. Power Sources, **161**, 1002 (2006). ⁵ E.B. Easton et al., Electrochem. Solid-State Lett., **9**, A463 (2006). ⁶ G. Chen et al., J. Electrochem. Soc., **149**, A1092 (2002). ⁷ U.S. Patents 5,866,204, 6,206,065, 6,248,422, 6,549,253. ⁸ K. Robbie and M.J. Brett, J Vac. Sci. & Tech. A, **3**, 1460 (1997). ⁹ A. Bonakdarpour et al., Appl. Catal. A, **349**, 110 (2008).

T8.10

High Methanol-tolerant DMFC Cathode Catalyst based on Palladium. Man-Yin Lo, Ying-Chieh Chen and Yen-Ze Chen; ITRI, Hsin-Chu, Taiwan.

Platinum is by far the best catalyst for the cathodic oxygen reduction reaction (ORR) in DMFC without the presence of methanol. However, the performance of Pt catalyst has not reached a status set forth for the commercialization of DMFC. The most serious problem to the cathode catalyst is mainly caused by the methanol crossover from the anode through the membrane. Methanol undergoes oxidation reaction at the cathode because Pt is one of the most active methanol oxidation catalysts. Mixed-potential due to cathodic methanol oxidation is detrimental to the performance of the cathode catalyst. Furthermore, incomplete oxidation of methanol also resulted in the accumulation of CO on the Pt surface. This CO poisoning effect greatly reduces the availability of Pt active site needed for the cathodic ORR. In order to alleviate the poisoning effect of methanol at the cathode, palladium based catalyst with both high ORR activity and methanol tolerance was explored as a replacement of Pt catalyst. Details concerning the preparation of Pd and PdM (M=Fe, Cu, Co and, etc.) catalysts and their ORR performance in the presence of methanol will be reported in this paper.

T8.11

Amorphous Carbon Film Coating on Stainless Steel Bipolar Plate for Fuel Cell. K. Kohara, K. Takahashi, Y. Nishimura, Y. Fukami, H. Murata and Yoshiyuki Show; Dept. of Electrical and Electronic Engineering, Tokai University, Hiratsuka, Japan.

Stainless steel bipolar plate for the polymer electrolyte membrane and the direct methanol fuel cells(FCs) has advantages of high

manufacturability and mechanical strength. Passive film (Chrome oxidized) exists on its surface and plays role of anticorrosion layer. However, this oxidized layer increases contact resistance between bipolar plate and membrane electrode assembly (MEA) in fuel cell (FC) and decreases output power of the FC. In this study, amorphous carbon (a-C) film was coated on bipolar plate made of the stainless steel to prevent the formation of the oxidized layer. Stainless steel electrode was used as metal bipolar plate. The a-C film was grown on the bipolar plates by using plasma CVD equipment. Acetylene gas was used as source gas. Growth temperature was varied from room temperature to 600°C. Growth time was fixed at 30 min. The polymer electrolyte membrane and direct methanol fuels cell assembled with the a-C film coated bipolar plates. Fuel cell assembled with bare (no a-C coated) stainless steel showed maximum output power of 2.5W. The a-C film coating on the bipolar plate increased the maximum output power of the FC to 3W which was 1.2 times higher than that of the bare bipolar plate. The contact resistance measurement revealed the electrical resistance between the bipolar plate and the MEA surface was reduced from 17 to 12 mOhm by the a-C coating. These results indicate that the coating of the a-C film on the bipolar plate increases output power of the fuel cell resulting in the decrease in the contact resistance.

T8.12

Block Terpolymer Derived Nanocomposites Towards Designer Electrode Materials. Morgan Stefik, Francis J. DiSalvo and Ulrich B. Wiesner; Cornell University, Ithaca, New York.

Fuel cell electrode operation requires three interconnecting and continuous pathways for the transport of electrons, ions, and fuel/oxidant. Toward this end, we report on the synthesis of three-component nanocomposites derived from the microphase separation of pentablock terpolymers. These polymers were designed to have three chemically distinct polymer blocks in order to facilitate the transport of the three chemical species of interest. The block terpolymer contained a block with a high yield of carbon upon pyrolysis, a block which was swellable with oxide sol, and a block that was thermally removable to result in porosity. The resulting nanocomposites contained electrically conductive carbon, surface proton conductive oxide, and fuel/oxidant pathways. The average mesopore size, wall thickness, and weight fraction of carbon in these materials were all controlled by the block terpolymer chemistry.

T8.13

Nanoparticle Enhancement of Polymer Electrolyte Membrane Fuel Cell Power Output. Cheng Pan¹, Kenny Kao², Sijia Zhao¹ and Miriam Rafailovich¹; ¹Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York; ²George School, Newtown, Pennsylvania.

PEM fuel cell technology is one of the most promising future alternative energy sources because it has relatively low operating temperature, high power density, quick response, pollution-free operation. However, its relatively low power output compared to that of its price has prevented it from many practical applications. Nanoparticles have been widely known to possess catalytic capabilities. Marvrikakis et al have predicted that gold nanoparticles that are platelet shaped and have direct contact to the substrate to be the "perfect" catalysts. We have shown that such particles can be synthesized by first starting with the standard two phase method, which produces spherical gold (Au) and palladium (Pd) nanoparticles. When a solution containing these particles is spread at the air water interface, X-ray reflectivity and EXAFS spectroscopy indicate that some of the Au or Pd atoms are removed, as the water displaces the hydrophobic thiol chains from the particle surface, resulting in platelet shaped particles with a 2:1 aspect ratio. Furthermore, if the particles are spread on a Langmuir trough where surface pressure can be applied to compress them, they form films consisting of one or more monolayers. These particle films can then be lifted onto a solid surface, such as the PEM membrane where the particle surface can make direct electronic contact with the fuel cell membrane, greatly increasing the efficiency of the catalysis process and increasing the ion current through the membrane. A series of parallel experiments were done to explore the various factors that may affect the performance of PEM fuel cell, such as hydrogen flow rate, metal-thiol ratio of nanoparticles, type of nanoparticles, surface pressure of the LB trough etc. We found that under the optimal hydrogen flow rate of 20 CCM (cubic centimeter per minute), the addition of 1:1 metal-thiol gold nanoparticles resulted in more than 80% increase in the power output of the fuel cell.

T8.14

Micro Polymer Electrolyte Membrane Fuel Cell Based on Fully Conventional Semiconductor Processing. Jin Tae Kim¹, Chan Hyeok Yeo¹, Won Suk Chang¹, Kyu Hyung Cho¹ and Yeon Ho Im^{1,2}; ¹School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju, Korea, South; ²Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, Jeonju, Korea, South.

Currently, there has been increasing research interest in micro power sources for portable and autonomous micro systems drives research on micro fuel cell systems as a key component of micro power generation system. The goal of this work is to develop novel monolithic type microfuel cell based on conventional semiconductor processing. In order to form monolithic type fuel cell, thin film type proton exchange membrane which consists of micro-structure arrays and sulfonated fluorocarbon films, was developed in this work. The Si based micro-structures were used to increase the surface area of the effective proton exchange membrane. The proton conductivities of the synthesized polymer electrolyte membrane were evaluated as functions of temperature and humidity. Finally, Pt catalytic could be formed by thermal evaporator system, and fuels were supplied through micro-channels formed by polydimethylsiloxane (PDMS). Therefore, the developed micro fuel cell is fully compatible with the conventional semiconductor technology. The performance of novel micro fuel cell was evaluated under CH₃OH and KMnO₄ flow using Potentiostat.

T8.15

Variable Pressure and Temperature Study of Water Self-Diffusion in Composite Polymer Fuel Cell Membranes. Jaime Farrington¹, Bruno Pinto¹, Alessandra D'Epifanio², Nicola Boaretto³, Phillip Stallworth¹ and Steve Greenbaum¹; ¹Physics and Astronomy Dept., Hunter College of CUNY, New York, New York; ²Chemistry Dept., University of Rome Tor Vergata, Rome, Italy; ³Chemistry Dept., University of Padova, Padova, Italy.

Proton exchange membrane fuel cells (PEMFCs) operating in the normal 60-80°C temperature range, face problems including poor carbon monoxide tolerance and heat rejection. These drawbacks can be overcome by increasing the operation temperature range up to 110-150°C. However, this causes rapid water loss from Nafion electrolyte membranes. Since the proton conductivity of Nafion is critically dependent on water content, PEM fuel cell performance degrades severely. On the other hand, composite membranes prepared by the addition of metal oxide particles to Nafion demonstrate enhanced fuel cell performance at elevated temperatures under reduced humidity conditions. Interactions between the polymer and the particle surface can have a significant effect on the membrane microstructure. There are powerful Nuclear Magnetic Resonance (NMR) techniques that can be applied to these materials that yield important dynamic and structural information. In particular, activation parameters for ionic and molecular transport can be obtained by self diffusion NMR measurements. Activation energies are obtained from variable temperature studies while activation volumes are collected from variable pressure data. By independently controlling two thermodynamic variables, a broader characterization of the transport properties of ionic conduction membranes can be achieved. An experimental setup has been engineered to perform water self diffusion NMR measurements while independently controlling pressure and temperature. Measurements were performed on Nafion doped with mixed oxides such as ZrO₂/SiO₂ and ZrO₂/HfO₂, Nafion doped with SnO₂·nH₂O and pure Nafion, which was used as a reference. Preliminary results suggest a decrease in activation volume for water diffusion in fully hydrated Nafion. Results for the composite membranes with variable water content will be presented.

T8.16

Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. Byungkwon Lim¹, Majiong Jiang², Pedro Camargo¹, Eun Chul Cho¹, Jing Tao³, Yimei Zhu³ and Younan Xia¹; ¹Department of Biomedical Engineering, Washington University, St Louis, Missouri; ²Department of Chemistry, Washington University, St Louis, Missouri; ³Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York.

Platinum (Pt) is the most effective catalyst to facilitate both hydrogen oxidation and oxygen reduction in a proton-exchange membrane fuel cell, but several critical issues still need to be addressed before such cells can be commercialized for automotive applications: For example, the oxygen reduction reaction (ORR) is kinetically limited at the cathode, and the scale of the Pt crystallites leads to high costs for Pt-based electrocatalysts with sufficient surface area and activity. In order to overcome these barriers, it is necessary to maximize the activity of a Pt-based catalyst by engineering its morphology and/or composition. Here we present a facile, aqueous-phase route to synthesize bimetallic nanodendrites consisting of a dense array of Pt branches on a core of palladium (Pd) nanocrystal. In this approach, truncated octahedral nanocrystals of Pd with an average size of 9 nm were used as seeds so as to direct the dendritic growth of Pt upon the reduction of K₂PtCl₄ by L-ascorbic acid in an aqueous solution. Using this simple approach, we routinely produced Pd-Pt bimetallic nanodendrites with high surface areas and the particularly active facets for the ORR in high yields. These Pd-Pt nanodendrites were two and a half times more active on the basis of equivalent Pt mass for the ORR than the state-of-the-art Pt/C catalyst and five times more active than the first-generation supportless Pt-black catalyst. This synthesis also provides a convenient and environmentally benign route to large-scale production because it does not require high temperature, organic solvent, or electrochemical deposition.

T8.17

Synthesis and Characterization of Different Carbon Nanotube Supported Catalysts and Their Effects on Methanol and Ethanol Electro-oxidation. Raghavendar Reddy Sanganna Gari¹, Zhou Li² and Lifeng Dong¹; ¹Department of Physics, Astronomy, and Materials Science, Missouri State University, Springfield, Missouri; ²Greenwood Laboratory School, Missouri State University, Springfield, Missouri.

Both direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs) are extensively studied as potential power sources for portable electronic devices and automobiles. However, their performances are limited by low electrochemical activity of methanol and ethanol electro-oxidation. Recently, carbon nanotubes (CNTs) were demonstrated as a desirable catalyst support for improving catalytic activity. A primary goal of this work is to systematically study the electrochemistry of both methanol and ethanol oxidation on different carbon nanotube supported catalysts. In this work, both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) supported Pt and Pt-Ru catalysts were synthesized by an ethylene glycol (EG) reduction method. The morphology and catalyst distributions of both Pt/CNTs and Pt-Ru/CNTs were characterized by field emission scanning electron microscope (FESEM) equipped with X-ray energy dispersive spectrometer (EDS). Comparative electrochemical measurements of Pt/SWCNTs, Pt-Ru/SWCNTs, Pt/MWCNTs, and Pt-Ru/MWCNTs catalysts were conducted using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry techniques. Experimental results show that, SWCNTs supported Pt and Pt-Ru catalysts have higher catalytic activity and lower charge transfer resistance towards methanol and ethanol oxidation in comparison to MWCNTs supported catalysts. Acknowledgement: This work was partially supported by a Faculty Research Grant from Missouri State University, the American Chemical Society Petroleum Research Fund (47532-GB10), and the National Science Foundation (DMR-0821159).

T8.18

Characterization of Polymer Blends for Proton Exchange Membranes. B. Seyhan Gunduz¹, Jingjing Pan³, Christopher

Sloan², Ashley Speranza⁴, Joshua Wilson⁴, Thomas Smith³ and Peggy Cebe¹; ¹Physics and Astronomy, Tufts University, Medford, Massachusetts; ²Chemistry and Physics, Gallaudet University, Washington, District of Columbia; ³Chemistry, Rochester Institute of Technology, Rochester, New York; ⁴Rochester Institute of Technology, Rochester, New York.

We report the phase structure, morphology, and properties of a binary polymer blend for use as a proton exchange membrane. The blend comprises a semicrystalline polymer, poly(vinylidene fluoride), PVF₂, with an amorphous polymer, poly[4(5)-vinylimidazole], PVIm, doped with trifluoro-methylsufonylimide, TFSI. Blends of PVF₂/PVIm/Im⁺TFSI⁻ were prepared in dimethylformamide with 15, 25, 35, and 50 mol% of TFSI. Real-time simultaneous wide and small angle X-ray diffraction showed that films cast from solution contained polar beta phase PVF₂ crystals. Heat treatment, by cooling from the melt, resulted in formation of the non-polar alpha crystallographic phase and altered both the thermal properties and the crystal morphology of the blends. Impact of TFSI content on conductivity using dielectric relaxation spectroscopy will be reported. Research supported by the National Science Foundation, Division of Materials Research, Polymers Program, through DMR-0906455.

SESSION T9: ORR Catalysts I

Chair: Hyuk Chang

Wednesday Morning, December 2, 2009

Room 301 (Hynes)

8:30 AM *T9.1

Pd Alloy-supported Pt Monolayer O₂ Reduction Electrocatalysts: From Single Crystal to Nanoparticle Scale-up

Synthesis Studies. Weiping Zhou¹, D. Su², J. Wang¹, K. Sasaki¹, M. B. Vukmirovic¹, W. F. Chen¹, Y. M. Zhu² and R. R. Adzic²; ¹Chemistry Department, Brookhaven National Laboratory, Upton, New York; ²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

The polymer electrolyte membrane fuel cell (PEMFC) is considered a potential power source for automotive and residential applications. However, high content of Pt as the cathode catalysts and the slow kinetics of oxygen reduction reaction (ORR) on conventional Pt catalysts is still one major obstacle for its wide-spread commercialization. The PtML acting as the ORR catalyst when deposited on suitable metal [1] or oxide surfaces [2] is a very attractive approach for solving these problems encountered in conventional Pt electrocatalysts. This study of ORR on a PtML covered Pd alloy surfaces, Pd₃Fe(111) and Pd₂Co/C nanoparticles, is a continuation of efforts to achieve a fundamental understanding of the substrate effect on chemical and electrocatalytic properties of Pt monolayers and to manipulate this effect on nano-scale materials. We studied the ORR on a well-ordered Pd₃Fe(111) with and without Pt monolayer in 0.1 M HClO₄ at room temperature. By comparing the specific activity at 0.9 V, we observed that a Pt monolayer supported on Pd₃Fe(111) shows higher ORR kinetics compared with Pt(111), increased by a factor of at least 2, and also demonstrates significantly increased ORR activity in comparison with PtML/Pd(111), while the bare Pd₃Fe(111) surface has comparable ORR activity to a Pt(111). We synthesized a small quantity of well-defined Pd₃Fe (core) - and Pd₂Co (core) - Pt(shell) nanoparticles (on a R.D.E) and also a several hundred milligram-batch using the Cu upd and Pt replacement method. High Pt mass activities are achieved for those core shell materials under RDE test conditions. EELS and HAADF-TEM techniques provided insights on the structure property of these core-shell catalysts. This will be discussed in detail at the meeting. This work is supported by U.S. Department of Energy, Divisions of Chemical and Material Sciences, under the Contract No. DE-AC02-98CH10886. 1. J. Zhang, M. B. Vukmirovic, Y. Xu, M. Mavrikakis, and R. R. Adzic, *Angew. Chem. Int. Ed* 44 (2005) 2132. 2. K. Sasaki, L. Zhang, and R. R. Adzic, *Phys. Chem. Chem. Phys.* 10 (2008) 159.

9:00 AM T9.2

Organically Capped Platinum Nanoparticles as Electrocatalyst for Oxygen Reduction. Henri Perez¹, Bertrand Baret¹, Laurent Akrou¹, Christelle Cremona¹, Arnaud Morin² and Arnaud Etcheberry³; ¹DSM/IRAMIS/SPAM-LFP, cea, Gif sur Yvette, France; ²DRT/Liten/DTH/LCPem, CEA, Grenoble, France; ³Institut Lavoisier UMR 8180, CNRS/Université de Versailles Saint Quentin, Versailles, France.

Platinum is still the reference material as electrocatalyst for oxygen reduction and hydrogen oxidation in Proton Exchange Membrane Polymer Fuel Cells (PEMFC). The efficiency and optimization of the electrocatalyst incorporated in the electrodes of fuel cells depend on the features of the catalyst itself (size and/or shape of the nanoparticles) and those of the active layer in which it is incorporated. With these respects the bottom-up approach which consists in pre-synthesizing nanoparticles followed by their controlled organisation in an active layer is of particular interest. Indeed, using organic capping which strongly interacts with the nanoparticle surface, wet chemistry routes allows the nanoparticles to be isolated as powder, which can be further re-dissolved and handled in adapted solvents. However, regarding electrocatalysts related to PEMFC, they are still quite few reports dealing with the use or study of such capped electrocatalyst [1-3]. In this paper we present our results recorded in this field, which are based on the synthesis of crown derivatized platinum nanoparticles [4]. These nanoparticles can be organized in mixte Langmuir-Blodgett thin films and their electrochemical behaviour studied as a function of platinum amount deposited or as a function of the features of the organic crown [5]. The interesting results recorded recently led us to contemplate the controlled combination of the capped electrocatalysts with carbon nanotubes and the formation of porous active layers on carbon felts. These electrodes were studied over a wide range of platinum loading, down to few µg/cm² [6]. Electrochemical characterizations were performed by cyclic voltametry in such conditions that the integrity of the capped electrocatalyst was preserved. We believe that this research is both, of fundamental and practical interest. Indeed, our latest results show that these electrodes formed with capped platinum electrocatalyst exhibit high performances with quite low platinum loading when used in real fuel cell devices.

9:15 AM T9.3

Platinum Nanorod Arrays for PEM Fuel Cell Electrodes. Wisam J. Khudhayer¹, Ali U. Shaikh² and Tansel Karabacak¹;
¹Applied Science, UALR, Little Rock, Arkansas; ²chemistry department, university of arkansas t little rock, little rock, Arkansas.

Vertically aligned platinum (Pt) nanorod arrays produced by glancing angle deposition technique (GLAD) have been investigated for their electrochemical properties as a cathode in polymer electrolyte membrane (PEM) fuel cells. These single-layer catalyst nanorods without any carbon support have been produced at lengths varying between 50-600 nm, which correspond to Pt loadings as low as 0.04-0.50 mg/cm². Pt nanorods were deposited on flat Pt film coated silicon substrates at a glancing angle of $\theta = 85^\circ$ with respect to substrate normal. Substrates were also rotated azimuthally along their substrate normal axis at a speed of 1 rpm. Prior to Pt film deposition, a thin layer of chromium was deposited as an adhesion layer to the silicon substrate in order to avoid delamination during electrochemical tests. Conventional polycrystalline Pt thin film were also produced at a normal incidence ($\theta = 0^\circ$) flux to be compared to Pt nanorods for their material and electrochemical properties. Cyclic voltammetry (CV) and rotating ring disk electrode (RRDE) voltammetry were performed to characterize the electrochemical activity and kinetics of the Pt nanorods. The well-defined peaks in the CV profile of the nanorods represent various crystal plane orientations and indicate that Pt nanorods are electrochemically more active than Pt thin films. In addition, RRDE results show that the oxygen reduction occurs through direct four-electron process. Morphology and crystallographic structure of Pt nanorods have been studied using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. SEM results reveal that Pt nanorods are well-isolated, vertically aligned, and single-crystal with atomically sharp tips. The single-crystal property allows enhanced electrochemical activity and reduced surface oxidation, while the isolated nature of the rods in lateral directions can provide a channeled porosity for effective transportation of gases in a PEM fuel cell. In addition, the XRD results illustrate that Pt nanorods are mainly oriented in the (220) direction unlike the typical (111) texture of the polycrystalline Pt film. Pt (111) is the energetically favorable growth plane of Pt films and has a poorer electrochemical activity than that of Pt (110) and Pt (100) planes due to the relatively strong adsorption of bi-sulfate ions as confirmed in the previous studies. It has been observed that as the length/loading of Pt nanorods increases, Pt (110) planes become more dominant and this enhancement is less pronounced for Pt (100). Our results demonstrate that GLAD technique is a promising approach to control the crystal orientation by promoting the crystal orientation of Pt (110) growth which is the most active surface for oxygen reduction reaction in PEM fuel cells.

9:30 AM T9.4

Nanoscale Control of Pt-Based Electrodes. Changwoo Nahm, Chunjoong Kim, Yejun Park and Byungwoo Park; Materials Science and Engineering, Seoul National University, Seoul, Korea, South.

Proton exchange membrane fuel cell (PEMFC) and direct-methanol fuel cell (DMFC) are promising power sources for the environmental-friendly low/zero emission devices. However, prohibitive issues remain, such as the inefficient utilization of Pt, low efficiency of cathode for oxygen-reduction reaction (ORR), the loss of Pt activity by a long-term operation, etc. To resolve these, highly efficient Pt-based electrodes have been synthesized by optimizing the nanostructures, and the physical/chemical origins of the improved properties are examined. Iron-phosphate/Pt/C nanocomposites showed the enhanced stabilities during long-term operation of PEMFCs. The well-dispersed FePO₄ nanoparticles prevented both the dissolution and agglomeration of Pt nanoparticles, and thereby preserving the Pt surface activities during long-term cycles. Also, for porous Pt, Pt_xAl_{1-x} alloyed thin films were examined by repeated electrochemical cycles. Nanoporous Pt thin films were straightforwardly synthesized by complete dissolution of Al. Higher methanol-oxidation activities were also observed in the nanoporous thin films. [1] C. Kim, B. Lee, Y. Park, B. Park, J. Lee, and H. Kim, *Appl. Phys. Lett.* **91**, 113101 (2007). [2] Y. Park, B. Lee, C. Kim, Y. Oh, S. Nam, and B. Park, *J. Mater. Res.* (in press). Corresponding Author: Byungwoo Park: byungwoo@snu.ac.kr

9:45 AM T9.5

Synthesis of Monodispersed Platinum Nanoparticles Supported on Functionalized Multi-walled Carbon Nanotubes and their Electrochemical Activity. Wenchao Sheng¹, Shuo Chen², Ethan Crumlin², Seung Woo Lee³ and Yang Shao Horn^{2,4};

¹Department of Chemistry, MIT, Cambridge, Massachusetts; ²Department of Mechanical Engineering, MIT, Cambridge, Massachusetts; ³Department of Chemical Engineering, MIT, Cambridge, Massachusetts; ⁴Department of Material Science and Engineering, MIT, Cambridge, Massachusetts.

Hybrid nanomaterials such as carbon nanotube supported metal nanoparticles (NPs) have seen wide potential application in heterogeneous catalysis. Ultra fine, surfactant-free and highly monodispersed platinum NPs supported on functionalized multi-walled carbon nanotubes (MWCNTs) were synthesized through 1) immobilization of anionic platinum precursor onto positively charged MWCNTs by electrostatic interaction; and 2) pyrolysis of platinum precursor/MWCNTs composite at elevated temperatures. The loading of platinum species on MWCNTs was found to be related to the pH level of the suspension of anionic platinum precursor and MWCNTs, as well as the concentration of the platinum precursor. Pyrolysis of platinum precursor/MWCNTs composite at high temperature generated platinum nanoparticles smaller than 2 nm with a narrow size distribution. Electrochemical characterization in acidic environment exhibited a two-fold enhancement towards oxygen reduction reaction (ORR) and comparable methanol oxidation reaction activity on Pt NPs/MWCNTs over commercial Pt NPs supported on high surface area carbon. The mechanisms for enhanced ORR activity will be presented. The catalytic stability is under investigation. This method can be potentially extended to produce other metal NP/MWNTs hybrid systems.

10:30 AM *T9.6

Design and Nano-Engineering of Multimetallic Catalysts for PEM Fuel Cells. Chuan-Jian Zhong¹, Jin Luo¹, Bin Fang¹, Peter Njoki¹, Bridgid Wanjala¹, Rameshwori Loukrakpam¹, Jun Yin¹, Derrick Mott¹ and Ting He²; ¹Department of Chemistry, State

University of New York at Binghamton, Binghamton, New York; ²Honda Research Institute USA, Inc., Columbus, Ohio.

Proton exchange membrane fuel cells (PEMFCs) are attractive because of the high conversion efficiency, low pollution, lightweight, and high power density. A major area of challenge is the design and engineering of active, robust, and low-cost electrocatalysts. We have been exploring nano-engineered multimetallic nanoparticles as active, robust, and low-cost electrocatalysts to address some of the challenges. This presentation discusses recent findings of our investigations of the design and nano-engineering of platinum- and gold-based multimetallic nanoparticles and catalysts in terms of nanoscale size, shape and composition parameters. Examples of transition metals in our Pt- and Au-based multimetallic nanoparticles include Fe, V, Ni, Cu, Co, W, Pd, Cr, Zr, Ti, Ag, Ir, Rh, etc. The nano-engineering work focuses on developing novel synthetic methods to produce the desired multimetallic nanoparticles, probing the synergistic electrocatalytic properties for oxygen reduction reaction, and establishing the correlation among size, shape, phase, and composition of the multimetallic nanostructures. PEMFC performance evaluation and theoretical modeling of the nanostructured catalysts are also part of our overall efforts. Current challenges and opportunities in the development of advanced fuel cell catalysts will also be discussed.

11:00 AM T9.7

Electrodeposition of Pt-(Ni,Co,Cu,Pb) Alloys and Intermetallics for Fuel Cell Applications. Thomas Moffat¹, Liang-Yeuh Ou Yang¹, Jon Mallett¹, Sun-Mi Hwang^{1,2}, Ugo Bertocci¹, John Bonevich¹ and Jae Jeong Kim²; ¹NIST, Gaithersburg, Maryland; ²Seoul National University, Seoul, Korea, South.

Recently the ability to electrochemically co-deposit Pt_{100-x}TM_x alloys (where TM=Fe, Co, Ni, Cu) at potentials above that required to deposit the pure TM has been demonstrated. The growth process is sustained by the strong bonding enthalpy between Pt and TM that in the first approximation can be envisioned as underpotential TM deposition coupled with on going overpotential deposition of Pt. In order to gain better insight into the co-deposition process a study of underpotential deposition of Co and Ni on Pt single crystal surfaces has been initiated. At the same time the study has been expanded to examine the formation of Pt alloys and intermetallics using alloying elements whose up behavior is reasonably well known, such as Cu and Pb. All of the above alloy systems are known to have interesting catalytic activity towards either oxygen reduction or organic fuel oxidation reactions. Experiments detailing the relationship between the co-deposition process and the relevant electrocatalytic activity will be described.

11:15 AM T9.8

Preparation and Property of Platinum-on-Metal Heterogeneous Electrocatalysts. Zhenmeng Peng, Jianbo Wu and Hong Yang; Department of Chemical Engineering, University of Rochester, Rochester, New York.

Heterogeneous nanostructures that contain discrete domains of platinum and other metals are attractive candidates as advanced fuel cell catalysts. In this talk we present the preparation of various platinum-on-metal (Pt-on-M) bimetallic nanostructures in non-hydrolytic systems. We show fine controls over the heterogeneous nucleation and growth of secondary nanoparticles are possible.[1] Platinum can be deposited on different metal nanoparticles through the reduction of platinum salt precursors at elevated temperatures. Using these Pt-on-M nanoparticles as starting material, platinum nanostructures can be obtained via post-synthesis treatments. The electrochemical properties of both Pt-on-M and their derived nanostructures have been characterized in detail. The Pt-on-Pd electrocatalyst exhibits a high area-specific current density of 307 mA/cm² metal at 0.9 V, a value almost doubles that for a commercial Pt catalyst (166 mA/cm² Pt) towards the oxygen reduction reaction (ORR). [2] This catalyst also has an impressive stability, with 12% loss of its electrochemical active surface area (ECSA) and a degradation of 9 mV in the half-wave potential over 30,000 cycles in the accelerated stability test. On the contrary, 39% in ECSA and 35 mV in half-wave potential are observed for a size-comparable pure Pt electrocatalyst.[2] The Pt-Au bimetallic heterogenous electrocatalysts made from the Pt-on-Au nanoparticles are much more active than pure Pt in formic acid oxidation reaction (FAOR) and show large negative shifts in on-set potentials and over eight times of enhancement in its peak current density.[3] References: (1) Peng, Z. M.; Yang, H. Designer platinum nanoparticles:Control of shape, composition in alloy, nanostructure and electrocatalytic property. Nano Today 2009, 4, 143-164. (2) Peng, Z. M.; Yang, H. Synthesis and oxygen reduction electrocatalytic property of Pt-on-Pd bimetallic heteronanostructures. J. Am. Chem. Soc. 2009, 131, 7542-7543. (3) Peng, Z. M.; Yang, H. Structures and electrocatalytic properties of PtAu bimetallic heteronanostructures made from Pt-on-Au nanoparticles. Nano Res. 2009, 2, 406-415.

11:30 AM T9.9

Platinum Nanoparticles Supported on Tantalum and Niobium Oxyphosphates and Oxides for High Activity Oxygen Reduction Electrocatalysts. Yannick Garsany, Albert Epshteyn, Andrew Purdy and Karen Swider-Lyons; Chemistry Division, Naval Research Laboratory, Washington, District of Columbia.

Lower-cost, more durable oxygen-reduction electrocatalysts are needed for oxygen reduction at the cathodes of proton exchange membrane fuel cells (PEMFCs). We are researching platinum on tantalum oxy-phosphate, niobium oxy-phosphate, tantalum oxide and niobium oxide, all which are impregnated on Vulcan carbon [1]. The key to high activity catalysts is synthetic routes which facilitate high contact between the Pt nanoparticles and oxide or oxy-phosphate support. We use both reverse micelle and solution deposition techniques directly onto the carbon support to make high surface area active nanoparticles. The catalysts are characterized using both rotating disk electrode methodology and in 10 cm² fuel cells. The mass activity of the platinum-tantalum oxyphosphate/carbon catalyst is 2x that of a 50% Pt/C standard from TKK. The platinum/niobium oxyphosphate/carbon catalysts also show high mass activity. The oxyphosphates appear to be better supports than the oxides. We conclude that the tantalum and niobium-based supports impart metal-support interactions on platinum that improve its activity for oxygen reduction. [1] K.

Swider-Lyons, et al., in "Catalysts for Oxygen Electroreduction - Recent Developments and New Directions," 2009: 169-193 ISBN: 978-81-7895-313-7 Editor: Ting He.

11:45 AM T9.10

Mechanism for Increased ORR Reactivity with Pt Nanoparticles on Niobium Oxide and Oxyphosphate Supports as

Revealed by *in situ* XAS Analysis. [Anna Korovina](#)^{1,2}, Yannick Garsany¹, Albert Epshteyn¹, Karen Swider-Lyons¹ and David E. Ramaker^{2,1}; ¹Chemistry, Naval Research Laboratory, Washington, District of Columbia; ²Chemistry, George Washington Univ, Washington, District of Columbia.

Promotion effects for the oxygen reduction reaction (ORR) and other fuel cell reactions [1,2,3] have been reported recently for Pt/Nb₂O₅. However, the exact nature of this promotion effect has not been clarified. We have found that the electrochemical activity for 2-3 nm Pt particles is also enhanced when supported on Nb₂O₅ or niobium oxyphosphate (NbOPO₄) with Vulcan carbon (VC), the Vulcan carbon providing good electrical conductivity in an electrochemical cell. We correlate the ORR activity of these materials, either Pt-Nb₂O₅/VC or Pt-NbOPO₄/VC (about 20% Pt, 5% oxide, and 75% VC) to their physical and chemical properties as determined by *in situ* X-ray absorption spectroscopy (XAS) at the Pt L₃ and Nb K edges. The ORR activity of the electrocatalysts follows the order: Pt-NbOPO₄/VC > Pt-Nb₂O₅/VC > the Pt/VC standard. The XAS data, taken *in situ* with the electrocatalysts as cathode in 1M HClO₄, are analyzed utilizing the Δμ XANES adsorbate isolation technique [4]. The Pt L₃ Δμ reflects the OH and O adsorbate coverage on Pt with potential, the Nb K edge Δμ reflects the oxidation state of the oxide, and the EXAFS analysis provides the particle morphology and cluster size. The Pt L₃ edge Δμ shows the OH adsorption onset is shifted up and the H adsorption onset shifted down in potential compared to Pt/VC indicating that both the Pt-OH and Pt-H bond strength is increased relative to that for Pt/VC. This indicates that the NbX supports are more ionic and exert a ligand effect on the Pt. However the onset for O adsorption on Pt shows a delayed onset, with adsorption on the support occurring concurrently. This strongly suggests O spill-over from the Pt to the support occurs, a common occurrence with oxide supports. The delayed onset for O on the Pt leaves more sites free for the ORR, leading to higher activity. Similar studies on Pt-Ta₂O₅/VC and Pt-TaOPO₄/VC, show these supports to be more covalent (delaying the OH onset potential), with only a very small spillover effect. Since the Pt-TaOPO₄ shows the highest reactivity, this suggests that the electronic ligand mechanism and its strong effect on the coverage of OH/Pt is the most critical to determining the ORR reactivity. [1] K. Sasaki et al, Phys. Chem. Chem. Phys., **10**, 159 (2008) [2] J.-S. Huang et al, J. Solid State Electrochem. **12**, 113 (2008) [3] S. Guerrero et al, J. Cat. **262**, 102 (2009) [4] M. Teliska; W. E. O'Grady; D. E. Ramaker, J.Phys. Chem. B, **109**, 8076, (2005).

SESSION T10: ORR Catalysts II

Chair: Byungwoo Park

Wednesday Afternoon, December 2, 2009

Room 301 (Hynes)

1:30 PM T10.1

Nanostructural Formation of Pd-Co Nanoparticles on HOPG Surfaces and High Surface Area Carbon Support. [Carlos R. Cabrera](#), Lisandra Arroyo and Raphael Raptis; Department of Chemistry, University of Puerto Rico, San Juna, Puerto Rico.

A new single source approach was developed to synthesize Pd-Co nanoparticles using a bimetallic compound, [Et₃NH]₂[CoPd₂(μ-4-I-3,5-Me₂pz)₄Cl₄] (CoPd₂), as a precursor to obtain dispersed catalyst on highly ordered pyrolytic graphite (HOPG) surfaces and high surface area carbon support, in view of preparing oxygen reduction catalysts for direct methanol fuel cells. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques were employed to characterize the nanostructure formations and to determine the composition and morphology of the complex on the HOPG. Results of high resolution XPS analysis (HR-XPS) revealed the binding energies corresponding to the atomic constituents of the precursor. When the precursor solution was placed on the surface of the HOPG, the bimetallic complex assumes a tubular structure and it appears that the surface of the HOPG offers a ground for the self-organization of nanostructural formations. Nanoparticles were also formed on high surface area carbon support (e.g. Vulcan) and tested for the oxygen reduction reaction with and without methanol.

1:45 PM T10.2

A Facile Tuning of Bimetallic AuPd Nanoparticle Core Size onto Thiol Functionalized Carbon Nanotubes: Electrocatalytic Property. [Junhyung Kim](#)¹, Seung Woo Lee², Shuo Chen¹ and Yang Shao-Horn¹; ¹Department of Mechanical Engineering and Material Science and Engineering, MIT, Cambridge, Massachusetts; ²Department of Chemical Engineering, MIT, Cambridge, Massachusetts.

The deposition of metal nanoparticles onto carbon nanotubes is one of the methods to obtain new hybrid materials with useful properties for materials science, catalysis, sensors, and energy conversion applications. Monometallic Au, Pd nanoparticles and bimetallic AuPd nanoparticles with a few atoms in the cores without ligands were prepared from Au(III), Pd(II) precursor ions on thiol functionalized multiwalled carbon nanotubes (MWNTs) by NaBH₄ reduction at room temperature. XPS and XRD techniques evidenced the presence of Au, Pd, and bimetallic AuPd nanoparticles on the supported MWNTs. A stable few tens and hundred atoms of metal nanoparticle core sizes were tuned on the MWNT with high monodispersity, achieved by controlled temperatures from room temperature to 400 °C leading to core sizes in the range from 0.5 to 5.0 nm in diameter as indicated by transmission electron microscopy. The electrocatalytic activity of Au/MWNT and bimetallic AuPd/MWNT towards oxygen reduction was

examined in alkaline solution. The synthesis and characterization of Au based bimetallic AuPd nanoparticles on the thiol functionalized multiwalled carbon nanotubes for electrocatalytic oxygen reduction in alkaline media will be presented.

2:00 PM T10.3

Modification of Gold Catalysis with Aluminum Phosphate for Oxygen-Reduction Reaction. Yejun Park, Byungjoo Lee, Chunjoong Kim, Jongmin Kim, Seunghoon Nam, Yuhong Oh and Byungwoo Park; Material Science and Engineering, Seoul National University, Seoul, Korea, South.

Gold is an unusual catalyst in terms of its inertness in the bulk state and its catalytic activity with specific nanostructures. The catalytic nature of gold has been found to be tunable through the control of nanoparticle size, the selection of matrix materials, and the nanostructures of metal-matrix composites. There are number of concerns associated with the oxygen-reduction reaction under various conditions including acid or alkaline solutions. To resolve these, catalytic activities of the prepared Au/AIPO₄ nanocomposites were examined for oxygen-reduction reaction in the acidic or alkaline media. In the acidic media, the Au/AIPO₄ nanocomposites presented higher onset potential and the steeper reduction slope than that of the Au catalyst. In the alkaline media, more feasible reaction paths existed within the region of approximately 0.8 - 1.0 V (vs. reversible hydrogen electrode). It is believed that the transfer of electron density between Au and AIPO₄ plays an important role in controlling the Au catalytic activities with the modification of electronic structure. [1] C. Kim, B. Lee, Y. Park, B. Park, J. Lee, and H. Kim, *Appl. Phys. Lett.* **91**, 113101 (2007). [2] Y. Park, B. Lee, C. Kim, J. Kim, and B. Park, *J. Mater. Res.* **24**, 140 (2009). Corresponding Author: Byungwoo Park: byungwoo@snu.ac.kr

2:15 PM T10.4

Metallo-Macrocycle Functionalized Multiwall Carbon Nanotubes for Catalytic Oxygen Reduction. Robert McGuire^{1,2}, Seung-Woo Lee², Daniel G. Nocera¹ and Yang Shao-Horn^{2,3,4}; ¹Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Electrochemical Energy Lab, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁴Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The electrochemical reduction of oxygen imparts the largest current density losses in polymer electrolyte membrane fuel cells (PEMFCs). Consequently, lowering the operational overpotential requires the use of high surface area catalysts. Currently carbon supported platinum and platinum alloys are the most stable and efficient catalyst materials in use. However, platinum presents a large economic challenge to commercialization of PEMFCs. Replacement by less expensive and earth abundant materials is critical to the development of cost effective PEMFCs. One promising approach is the combination of macrocyclic cobalt and iron complexes with high surface area carbon supports. It has been well established through molecular models that a cofacial arrangement of electro-active metal centers with a spacing of ~ 4 Å offers an ideal geometry for O-O bond breaking and the direct 4e- reduction of oxygen. In this study, we use multiwall carbon nanotubes (MWCNTs) to support these molecular catalysts, and undertake a study of MWCNTs functionalized with a series of mono- and dimeric molecular catalysts for oxygen reduction. MWCNTs covalently modified with carboxylic acid groups were further functionalized noncovalently with monomeric iron and cobalt phthalocyanine (pc), 5,10,15,20-tetraphenyl porphyrin (tpp), and tetramethyl-dibenzotetraaza[14]annulene (taa) catalysts. These materials allow the effect of different macrocycle properties including cavity size and redox potential to be tuned in conjunction with MWCNTs for the first time. Metallo-macrocycle functionalized MWCNTs were characterized by a range of techniques such as XPS, FTIR, and UV-vis spectroscopy. The electrocatalytic activity and mechanism of the series toward oxygen reduction determined by rotating ring disk electrode measurements will be discussed in the context of the various macrocycle properties.

2:30 PM T10.5

Study of Carbon Nanofiber as Support Materials for RuSe Based Oxygen Reduction Reaction Catalyst for Polymer Electrolyte Fuel Cells. Sauradip Malkhandi¹, Petra Bele¹, Odysseas Paschos¹, Siegfried Schreier¹ and Ulrich Stimming^{1,2,3}; ¹Department of Physics E19, Technische Universität München TUM, Garching, Germany; ²NANOTUM, Center for Nanotechnology and Nanomaterials, Technische Universität München, Garching, Germany; ³ZAE Bayern, Garching, Germany.

The advances of various novel carbon based nano-structures open up further possibilities of a new 'class' of catalyst support materials aiming at an improved performance for polymer electrolyte fuel cells. This presentation covers the study of carbon nanofiber platelets (CNF-PL) supported RuSe catalyst for oxygen reduction reaction (ORR) for polymer electrolyte methanol fuel cell system. One main obstacle is the proper synthesis of RuSe nano-particle catalysts on CNF-PL support. Further, the influences of the CNF-PL support on the ORR by RuSe catalysts are still partly unknown and therefore, requires more detailed investigations. In this work, for the first time CNF-PL supported RuSe nano-particle catalysts are synthesized. The properties of this synthesized new catalysts are investigated by electrochemical methods and Transmission Electron Microscopy (TEM). In initial measurements, it is found that the synthesized catalysts have 10 ~ 5 nm particle size and the mass specific ORR current is about 10.8 mA/mg at 0.7 V (RHE) on 177 µg/cm² loading. Electrochemical results indicate that the synthesized CNF-PL supported RuSe catalysts have similar performance to carbon black supported RuSe catalysts.

2:45 PM T10.6

Electronic Structure Versus Electrocatalytic Activity of Perovskite-class Oxides as Studied by X-ray Absorption Spectroscopy (XAS) and Rotating Disk Electrode. Jin Suntivich, Naoaki Yabuuchi, Hubert Gasteiger and Yang Shao-horn;

Materials Science and Engineering, and Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Efficient, inexpensive electrocatalysts for the Oxygen Reduction Reaction (ORR) in hydrogen fuel cells is indispensable for enabling hydrogen-based energy storage. The lack of better ORR electrocatalysts is attributed to the lack of fundamental understanding of the electronic structure parameters that govern the ORR activity. To develop an understanding of the governing electronic structure needed to design a better electrocatalyst, we have synthesized a series of perovskite oxide (ABO_3 formula, where A is La, and B is a 3d transition metal) model compounds to study the relationship between electronic structure and the ORR activity. We examined the correlation between the perovskites with different B-site metals (B = Cr, Mn, Fe, Co, Ni) and found that the ORR activity increases with decreasing O K-edge XAS energy position, which we believe reflects the positive effect of decreasing O adsorption strength on ORR activity. Furthermore, we will discuss the effect of partial substitution of B-site metals on ORR activity and catalyst stability.

3:30 PM T10.7

Combinatorial Investigation of Pb-Ru Pyrochlores for Oxygen Reduction. Jonathan R. Petrie¹, John M. Gregoire², Michele E. Tague², Hector D. Abruna², Frank J. DiSalvo² and R. B. van Dover¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

With a relatively high oxygen reduction (ORR) activity in acidic mediums, Pb-Ru pyrochlores present an intriguing alternative to Pt cathodes in PEM fuel cells. This study employed a combinatorial co-sputtering process to explore nanometer-scale thin films exhibiting a spread of Pb:Ru composition ratios. We have developed a high-throughput fluorescence technique that allowed identification of binary regions with high catalytic activity towards oxygen reduction. These regions were tested by voltammetry in a miniaturized electrochemical cell. In addition, data on the effects of adding a third cation to the Pb-Ru pyrochlore phase to further increase the ORR activity will be presented.

3:45 PM T10.8

Underpotential Deposition of Ni, Co, Cu and Pb on Flame Annealed 1x2 and 1x1 Pt(110). Liang Yueh Ou Yang and Tomas P. Moffat; Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

In the last decade significant attention has been given to exploring the effect of alloying on electrocatalysis. Pt alloys with Ni, Co, Cu and Pb are known to exhibit enhanced performance towards oxygen reduction as well as organic fuel oxidation reactions, respectively. These alloys and intermetallics may be produced by a variety of means as well as different morphologies. Co-deposition by means of underpotential processes is a particularly easy and inexpensive means to generate such bimetallic materials. However, much remains to be understood about the role of crystalline anisotropy in the deposition and performance of these systems. In this talk, Ni, Co, Cu and Pb underpotential deposition on single crystal Pt surfaces will be discussed. Particular attention will be given to the Pt(110) surface. Careful control of the flame annealing process allows one to generate either the 1x1 and 1x2 surface. Voltammetric and STM experiments of underpotential deposition reactions on these surfaces will be detailed.

4:00 PM T10.9

Fuel Cell Performance of Platinum-Based Multimetallic Nanoparticle Catalysts in PEMFC. Bin Fang, Jin Luo, Peter N. Njoki, Rameshwori Loukrakpam, Derrick Mott, Bridgid Wanjala, Xiang Hu and Chuan-Jian Zhong; Department of Chemistry, State University of New York at Binghamton, Binghamton, New York.

Proton exchange membrane fuel cells are becoming increasingly attractive power sources because of the high conversion efficiencies and low pollution. The high cost and poor activity of many existing Pt-based cathode catalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC) has been a long-standing problem. The ability to engineer multimetallic nanoparticles in terms of size and composition represents an important approach to the ultimate development of active, robust and low-cost fuel cell catalysts. This presentation reports our recent findings of the electrocatalytic performance of the nanostructured bimetallic and trimetallic nanoparticle catalysts in PEMFCs. One example involves membrane electrode assembly (MEA) using nano-engineered Pt_mVnFe_{100-m-n} nanoparticles (~3 nm) supported on carbon as the cathode electrocatalysts. The fuel cell performance and stability data for the PtVFe/C catalysts were compared with those obtained using MEAs prepared with commercial Pt/C catalysts. The results reveal that the PtVFe/C catalysts exhibited much better fuel cell performance and better durability than that using the commercial Pt/C catalyst. The results have demonstrated potential applications of the nano-engineered multimetallic catalysts in PEMFCs.

4:15 PM T10.10

Metal Nanoparticle/Block Copolymer Self-assembly as a Potential Synthetic Method for Fuel Cell Electrodes. Zihui Li^{1,2}, Hiroaki Sai², Scott C. Warren^{1,2}, Marleen Kamperman², Sol M. Gruner³ and Ulrich Wiesner²; ¹Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York; ²Department of Material Science and Engineering, Cornell University, Ithaca, New York; ³Department of Physics, Cornell University, Ithaca, New York.

Nanostructured metal materials are of potential interest for fuel cell electrode applications as they combine the catalytic activities of metals as well as the high specific surface area of nanostructured materials. By utilizing ligand-stabilized platinum nanoparticles (Pt NPs) in the self-assembly with poly (isoprene-block-dimethylaminoethyl methacrylate) (PI-b-PDMAEMA) or poly

(styrene-block-dimethylaminoethyl methacrylate) (PS-b-PDMAEMA) block copolymers, organic-inorganic hybrid materials with high metal loadings were synthesized and four different morphologies were generated. Further processing such as disassembly or heat treatment can convert the hybrids into isolated nano-objects or mesoporous Pt materials, respectively. Results of Pt NP ligand head group density estimation based on HAADF-STEM images and thermo gravimetric analysis (TGA) data will be compared to results for alkanethiol self-assembled monolayers (SAMs) on Pt {111} surface.

4:30 PM T10.11

In situ Real-time X-ray Diffraction Study of Phase Transformations in Au-Pt Nanocatalysts. Oana Malis¹, M. Radu², D. Mott³, B. Wanjala³, J. Luo³ and Chuan-Jian Zhong³; ¹Physics Dept., Purdue University, West Lafayette, Indiana; ²Physics Dept., Binghamton University, Binghamton, New York; ³Chemistry Dept., Binghamton University, Binghamton, New York.

Platinum has long been established as the catalyst of choice in a series of important chemical reactions. In particular the catalytic role of Pt in the oxygen reduction reaction (ORR) is of considerable importance for applications in fuel cells. However, Pt is expensive and in short supply world-wide. Moreover, it has limited catalytic efficiency and is dissolved in the ORR reaction [1]. Therefore, efforts to identify materials with reduced Pt content and improved activity and stability have been stepped up in recent years. Most interestingly, Au clusters have been shown to improve the stability of Pt electrocatalysts without loss of activity [2]. Furthermore, Au nanoparticles have been proven to exhibit unprecedented catalytic activity of their own for CO and methanol oxidation [3], two other reactions of considerable importance for fuel cells. It is therefore believed that Au-Pt nanoparticles could exhibit synergistic catalytic properties that make them ideal for fuel cell applications [4]. In spite of the active research in the field, the exact structure of Au-Pt nanoparticles is not completely understood. The bulk Au-Pt phase diagram exhibits a miscibility gap, and therefore Au-Pt nanoparticles are expected to phase segregate into Pt-rich and Au-rich phases. However, alloyed Au-Pt nanoparticles have been synthesized over almost the entire composition range [4]. The effect of phase segregation on the catalytic properties of nanoparticles is of considerable practical interest, but not completely understood at this time. We have performed a detailed in-situ time-resolved x-ray diffraction study of phase segregation and coarsening of 2-15 nm Au-Pt nanoparticles synthesized from solution on various substrates (Si, silica, carbon-black, and alumina membranes) during annealing at high temperatures. Contrary to the expectations from the bulk phase diagram, silica-supported Au-Pt nanoparticles have an alloyed structure that is preserved even after extensive annealing at temperatures as high as 700 C. In stark contrast, alumina-supported Au-Pt nanoparticles exhibit a rich phase behaviour that is sensitive to alloy composition and the details of the synthesis process. In particular, low-density as-prepared Au₄₁Pt₅₉ nanoparticles exhibit the signature of incipient phase-segregation that develops into full phase separation during annealing at high temperature. We will also discuss the results of an ongoing study of the early stage of catalyst synthesis, i.e. while the nanoparticles are annealed at low temperatures (at or below 300 C). [1] Ferreira P J, la O' G J, Shao-Horn Y, Morgan D, Makharia R, Kocha S and Gasteiger H A 2005 J. Electrochem. Soc. 152 A2256-71. [2] Zhang J, Sasaki K, Sutter E and Adzic R R 2007 Science 315 220-222. [3] Haruta M 2004 J. New Mat. Electrochem. Sys. 7 163-172. [4] Mott D, Luo J, Njoki P N, Lin Y, Wang L and Zhong C-J 2007 Catalysis Today 122 378-385.

4:45 PM T10.12

Green Synthesis of Platinum-encapsulated Nickel Nanocatalyst and Its Microstructure Evaluation. Jingbo Liu¹, Iliana Medina-Ramirez² and Sajid Bashir³; ¹Chemistry, Texas A&M University-Kingsville, Kingsville, Texas; ²Chemistry, Universidad Autonoma de Aguascalientes, Aguascalientes, Mexico; ³Chemistry, Texas A&M University-Kingsville, Kingsville, Texas.

Fuel cells are green energy resources in that they can spontaneously convert chemical energy into electricity, releasing heat and water when electrochemical reaction occurs. Proton exchange membrane fuel cells (PEMFCs) are devices, which consist of a solid Nafion polymer as the electrolyte, are drawing significant attention. It is commonly agreed that platinum (Pt) is the most efficient electrocatalyst. However, due to its high cost, it is unfeasible to use a stand-alone Pt catalyst for PEMFC commercialization. To remedy this problem, a platinum-encapsulated nickel (PEN) nanocatalyst was fabricated using the cost-effective green colloidal chemistry to obtain higher catalytic activity. The green colloidal method allows for precise formulations at low temperature with controlled monodispersity and the elemental composition to be tailored at the molecular level. The state-of-the-art instruments have been employed to characterize the crystalline and atomic structure, elemental composition, and stability of the colloids. The morphology and crystallinity was determined using a Tecnai F20-G2 transmission electron microscopy (TEM). In this study, the high resolution TEM equipped with post-column Gatan Image Filter was applied. It can be seen that PEN-nanocatalysts were mono-dispersed and highly crystalline. In order to identify the elemental composition, X-ray energy dispersive (equipped with the TEM) and X-ray photoelectron spectroscopy were used as complementary techniques to ensure the quality of the quantitative analysis. The elemental composition is determined to be aligned well with the experimental design. The monodispersity and electrophoretic mobility was evaluated using ZetaPALS facility, which is significantly sensitive to the analyte compared with other techniques. The application of low fields to eliminate thermal problems allows for the excellent results. The measured value (-39.44 to -40.27 mV) under various fabrication parameters of the PEN indicates that the colloid is highly stable and agglomeration is successfully prevented using a surfactant. The ultrafine particles provide large specific surface area, which favors the redox reaction on the catalyst to improve the PEMFCs performance. Cyclic voltammetry (CV) experiments were carried out using a Vanostat HA-301 potentiostat equipped with PowerLab Chart V4.0 for data acquisition. Aqueous solutions of 0.1 M NaOH were used as electrolyte and were deaerated by purging with nitrogen gas for 15 min before recording the CVs to remove the oxygen from the solution and prevent masking of the catalyst. The catalyst performance was determined using exchange current density with an average value of 310 mA/cm². It was noticed that the current density was independent on the sweep rates in the region of 2 mV/min and 100 mV/min, which indicates that the limiting reaction rate was resulting from the electron transfer instead of mass diffusion.



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U: Materials Challenges Facing Electrical Energy Storage

November 30 - December 3, 2009

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SESSION U1: Battery Materials
Chairs: Yang Shao-Horn and Stanley Whittingham
Monday Morning, November 30, 2009
Room 200 (Hynes)

8:30 AM *U1.1

Designing Advanced Anode and Cathode Materials for Lithium-Ion Batteries. [Michael Thackeray](#)¹, Christopher Johnson¹, Sun-Ho Kang¹, Harold Kung², Vilas Pol¹, Lynn Trahey^{1,2} and John Vaughey¹; ¹Electrochemical Energy Storage Department,

Argonne National Laboratory, Argonne, Illinois; ²Department of Chemical and Biochemical Engineering, Northwestern University, Evanston, Illinois.

State-of-the-art lithium-ion batteries do not yet meet the stringent energy and safety requirements for heavy-duty batteries being targeted for 'plug-in' hybrid electric vehicles (PHEVs) and all-electric vehicles (EVs). The energy limitation results predominantly from the inability of the anode and cathode materials to react with a sufficient amount of lithium during charge and discharge at acceptable potentials, whereas the safety limitation results largely from the instability and highly reactive nature of the fully charged electrodes and side reactions with the electrolyte that can ensue therefrom. In this presentation, various approaches to design high capacity and safe electrode materials will be discussed. Focus will be placed, in particular, on recent advances that have made in enhancing the electrochemical properties of lithium-mixed-metal-oxide cathodes, and intermetallic- and TiO₂ anodes by improved compositional and materials design.

9:00 AM U1.2

A 3D Ordered Carbon Nanotube Architecture as Active Cathode Material for Li-Ion Batteries. Joerg J. Schneider and Jayaprakash Khanderi; Department of Chemistry, TU Darmstadt, Darmstadt, Germany.

Inorganic oxides are currently intensively studied as cathode materials in Li-ion batteries. However, there inherently bad electrical conductivity is a serious drawback into the future development and optimization of these materials for applications. Currently, composite materials like carbon./LiFePO₄ conductive mixtures are used to enhance the electrical conductivity for the cathode side in battery applications. We will present our studies towards the development of a unique 3D carbon nanotube (CNT) grid which offers a highly ordered arrangement of CNTs over several mm² and allows the deposition of electroactive oxides like LiFePO₄ as well as other oxides in an ordered fashion on the outside of the tubes thus giving rise to a well ordered CNT grid cathode architecture. This new cathode grid structure has the potential to be integrated into a battery device structure. First studies will be presented into this.

9:15 AM U1.3

Understanding the Improvement in the Electrochemical Properties of Surface Modified 5 V Spinel Cathodes. Arumugam Manthiram and Jun Liu; Materials Science and Engineering, University of Texas at Austin, Austin, Texas.

With an aim to increase the energy and power densities, there is growing interest in 5 V spinel cathodes, particularly for automotive applications, as the three-dimensional lithium ion diffusion in the spinel lattice offers high intrinsic rate capability. Among the various 5 V spinel cathodes investigated, LiMn_{1.5}Ni_{0.5}O₄ has drawn much attention due to its high capacity arising from the operation of Ni^{2+/3+} and Ni^{3+/4+} redox couples. However, LiMn_{1.5}Ni_{0.5}O₄ is often accompanied by the formation of Li_xNi_{1-x}O impurity phase and is hampered by capacity fade due to the corrosion reaction between the cathode surface and the electrolyte at the high operating voltage of ~ 5 V. Partial substitution of Mn and Ni in LiMn_{1.5}Ni_{0.5}O₄ by other cations has been found to eliminate the impurity phase. However, only a few groups have focused on improving the cyclability by suppressing the corrosion reaction via surface modification. We present here a systematic investigation of various cation substituted LiMn_{1.5}Ni_{0.5}O₄ and their surface modification with Al₂O₃, ZnO, Bi₂O₃, and AlPO₄ by an electrostatic self-assembly method. The bare and surface modified samples are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), high resolution transmission electron microscopy (TEM), charge-discharge measurements in lithium cells, electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS). The surface modified samples exhibit better cycling performance, better rate capability, and better rate capability retention during cycling compared to the bare sample. EIS and XPS studies show that the inferior electrochemical performances of the bare spinel cathode are closely related to the formation of thick solid-electrolyte interfacial (SEI) layer at the high operating voltages of ~ 5 V. Surface modifications with nano-size Al₂O₃, ZnO, Bi₂O₃, and AlPO₄ suppress the formation of thick SEI layers on the spinel oxide and thereby improve the electrochemical performances significantly. Moreover, the differences in the surface compositions formed during the annealing or electrochemical cycling processes also influence the electrochemical properties.

9:30 AM U1.4

Understanding Phase Transformations and Conversion Reactions in Li₂Cu_xNi_{1-x}O₂ and Li₂CuO₂ Karen Swider-Lyons¹,

Wojtek Dmowski², Corey T. Love¹ and Michelle D. Johannes¹; ¹Naval Research Laboratory, Washington, District of Columbia;

²University of Tennessee, Knoxville, Tennessee.

We are pursuing high capacity cathodes for lithium-ion batteries. One high capacity material is Li₂Cu_xNi_{1-x}O₂, which has a high theoretical charge capacity (e.g., 320 mAh/g) due to the opportunity to intercalate more than one electron per metal atom [1,2,3]. The material has an orthorhombic *Immm* structure, which is unfortunately not stable upon lithium insertion. It undergoes a phase transformation upon discharge, plus much of the capacity is below 2.5 V, and appears to be due to an irreversible conversion reaction: M(Cu,Ni)O + 2Li → Li₂O + M(Cu,Ni). We probe the structural details of the phases that form during a charge-discharge cycle using pair density function (PDF) analysis, which can resolve the short range atomic structure of disordered materials. The resulting structures are modeled with density functional theory, to provide a better understanding of the phase diagram of Li₂Cu_xNi_{1-x}O₂. Li₂CuO₂ is studied as a model system. [1] C.T. Love, M.D. Johannes, A.M. Stux, and K.E. Swider-Lyons, ECS Transactions, 16 (29) 27-35 (2009). [2] N. Imanishi, K. Shizuka, T. Ikenishi, T. Matsumura, A. Hirano and Y. Takeda, Solid State Ion., 177, 1341 (2006). [3] K. Kang, C. H. Chen, B. J. Hwang and G. Ceder, Chem. Mat., 16, 2685 (2004).

10:15 AM *U1.5

Electrical Energy Storage for Transportation and Renewable Energy. Yet-Ming Chiang, W. Craig Carter, Bryan Y. Ho and Mihai Duduta; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Due to recent advances in Li-ion battery technology, the mass adoption of hybrid electric vehicles (HEVs) now seems assured, and the introduction of plug-in hybrids (PHEVs) is well underway. All-electric or "battery electric vehicles" (BEVs) can ultimately have the largest impact on oil use and greenhouse gas emission, but current development is restricted to vehicles of relatively small size and/or limited driving range. The reasons for this become apparent upon considering the specific energy (Wh/kg), energy density (Wh/L), and cost (\$/Wh) of current technology. Similarly, the growth of most forms of renewable energy will be constrained by the need to store energy efficiently and economically over relatively long durations (hours). Thus, the breakthroughs now needed lie more in the area of higher energy than higher power. Along with efforts to develop higher energy density storage materials, methods to improve the mass and volume efficiency of electric energy storage devices can have great impact. To illustrate, taking the active materials alone, existing lithium ion battery couples have the energy density to permit a 200 mile range for a 3000 lb electric car using ~150 kg of active materials. However, due to the inefficient design of present batteries, this mass is roughly tripled at the device level. In this talk, various use scenarios in transportation and electric grid storage that illustrate the important metrics, as well as the shortcomings of present technology, will first be presented. New device concepts that have the potential to increase stored energy density by factors of two or more, using existing and emerging storage materials, will be discussed. Results from prototype devices and the materials challenges within will be described.

10:45 AM U1.6

Advanced Lithium-Ion Batteries for High-Temperature Energy Storage. Sebastian Osswald, Yan Zhu, Qichao Hu, Steven A. Wesel, Robert C. Daniel, Luis Ortiz and Donald R. Sadoway; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The high temperature service of lithium-ion batteries is currently limited by the thermal stability of the electrodes in contact with carbonate electrolyte. Most carbonate-based electrolytes are considered volatile organic compounds (VOCs), thus their reactivity with cell components and volatility rise with temperature. There exist numerous applications that employ batteries at high temperature, but are forced to use primary systems. Recent advances in polymer synthesis lead to the development of novel materials that exhibit solid-like behavior while providing the ionic conductivity of liquid electrolytes. Graft copolymer electrolytes (GCEs) of poly[(oxyethylene)methacrylate]-g-poly(dimethyl siloxane) (POEM-g-PDMS) synthesized by free radical polymerization show high thermal stability over a wide temperature range (25-300 °C). Solid-state batteries comprised of a metallic lithium anode, a 0.1 μm thick LiFePO₄ cathode, and a 0.2 μm thick layer of lithium triflate-doped POEM-g-PDMS were tested at different temperatures. Our results demonstrate the opportunity for the GCEs to enable rechargeable high temperature energy storage systems.

11:00 AM U1.7

Co-synthesis of LiMn₂O₄ and Carbon Electrodes for High Power Batteries. Robert Buechel¹, Timothy J. Patey², See How Ng², Frank Krumeich¹, Petr Novak² and Sotiris E. Pratsinis¹; ¹D-MAVT, ETH Zurich, Zurich, Switzerland; ²Electrochemistry Laboratory, PSI, Zurich, Switzerland.

A flame spray and a diffusion flame are combined to continuously produce LiMn₂O₄ nanoparticles [1] and carbon black in a rapid, one-step and industrially scalable process [2]. The powder carbon content was varied by adjusting the diffusion flame conditions. The powders are characterized by X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and transmission electron microscopy (TEM), cyclic voltammetry (CV) and galvanostatic cycling for a range of current densities. These LiMn₂O₄/carbon nanocomposites retain over 80% of their initial galvanostatic discharge capacity for current densities ranging from 5 to 50C-rates and showed significantly better performance compared to pure LiMn₂O₄ nanoparticles mixed conventionally with commercial carbon blacks. The improved performance of the LiMn₂O₄/carbon nanocomposites was attributed to the carbon particle contact and/or film coating of the freshly-made LiMn₂O₄ nanoparticles. This additional well-distributed carbon provides an electrically conductive network that induces a more homogeneous charge transfer throughout the electrode. [1] F.O. Ernst, H.K. Kammler, A. Roessler, S.E. Pratsinis, W.J. Stark, J. Ufheil, P. Novak, Mater. Chem. Phys. 101 (2007) 372-378. [2] T.J. Patey, R. Buchel, S.H. Ng, F. Krumeich, S.E. Pratsinis, P. Novak, 189 (2009) 149-154.

11:15 AM U1.8

What's the Optimum Composition of LiNiyMnyCo_{1-2y}O₂? Zheng Li, Natasha A. Chernova, Megan Roppolo, Shailesh Upreti and Michael S. Whittingham; Institute for materials research, Binghamton University, Binghamton, New York.

An unresolved question for the layered oxides is: what is the optimum value of y in the formula LiNiyMnyCo_{1-2y}O₂? This work attempts to answer this question with a study of the specific capacity and rate capability of a series of layered compounds (y=0.5, further called 550; y=0.45, 992; y=0.4, 442; y=0.33, 333). Factors such as transition metal oxidation sequence, Li/Ni exchange rate, electronic conductivity and particle size that influence the capacity and rate capability were investigated. A higher nickel content in LiNiyMnyCo_{1-2y}O₂ leads to higher capacity when charging the cells to 4.3V. When focusing on 333, we find out that the Co³⁺/Co⁴⁺ redox reaction begin to get involved when more than 50% of the lithium ions were extracted. This leads to slightly smaller capacity than LiNiyMnyCo_{1-2y}O₂ with reduced cobalt. Using the same synthesis condition (mixed hydroxide method, 800 °C annealing followed by quenching the sample), the Li/Ni exchange rate decreases and particle size increases with increasing cobalt content. All these factors lead to rather complicated comparison results. On one hand, higher nickel content and smaller particle size result in better rate performance. On the other hand, less cobalt content means possibly lower lithium ion mobility and electronic conductivity. We found the best rate performance at moderate current density falls in the 992 or 442. In order to further improve the rate capability of LiNiyMnyCo_{1-2y}O₂ with reduced cobalt at high current density, we also investigate influence of the

morphology on rate performance through different synthesis procedures. Besides traditional co-precipitation method, spray dry or hard-template method is used to synthesize the large particles with mesoporous structure, which improves the contact between electrolyte and active material. This work is supported by the US Department of Energy Office of Freedom Car and Fuel Partnership through the BATT program at LBNL.

11:30 AM *U1.9

Binary Nickel Compounds as Negative Electrode Materials for Lithium Batteries: Syntheses and Performance. Frederic Gillot, Anne-Claire Louer and M. Rosa Palacin; Solid State Chemistry, Institut de Ciencia de Materials de Barcelona, Bellaterra, Catalonia, Spain.

Compounds allowing the so termed "conversion reaction" have been intensively studied in recent years as possible electrode materials to be implemented in lithium ion batteries. These are binary phases of general formula $MaXb$, ($X=O, S, N, P, H, F...$), that react with lithium to yield metallic nanoparticles embedded in a matrix of Li_yX . Many transition metal compounds that do not have any vacant sites in the structure had been disregarded as intercalation electrode materials but turned out to yield extremely high capacities associated to these conversion processes that entail full reduction of the transition metal. Though the initial reports dealt with oxides which are still and by far the most investigated class of compounds, conversion reactions have been shown to exist for other materials such as sulphides, nitrides, phosphides, fluorides and also hydrides. The potential of the reaction increases with the ionicity of the M-X bond and, with the exception of fluorides, is usually between 0.5 and 1 V vs. lithium metal. We will describe the synthesis of nickel oxide and nickel nitride through different routes involving mostly thermal decomposition of precipitated precursors (hydroxides and amides respectively). While hydroxides are easily obtained in aqueous alkaline medium, amides have been precipitated in liquid ammonia from a nickel salt and an alkaline amide using a specially designed experimental setup. Alternatively, nickel nitride was also prepared by ammonolysis of diverse precursors at different temperatures with comparative purposes. The effect of the synthesis conditions and further thermal treatments for the decomposition of precursors on the phase composition and microstructure of the obtained samples will be discussed. Though the reaction mechanism in the case of nickel nitride is still under study, preliminary electrochemical characterisation indicates that conversion reaction effectively takes place in all cases. Nonetheless, the reversibility of the process is severely dependent on the synthesis and processing conditions. Precipitation in the presence of carbon additive does have a beneficial impact in terms of cyclability, especially in the case of nickel oxide, certainly due to a more intimate mixture that results in enhanced electronic conductivity.

SESSION U2: *In-situ* Studies of Electrode Materials and Processes

Chair: Clare Grey

Monday Afternoon, November 30, 2009

Room 200 (Hynes)

1:30 PM *U2.1

In-situ Study on Morphological Evolution of Alloying Anodes of Li-Ion Batteries by Transmission X-ray Microscopy. Nae-Lih Wu, Chemical Engineering, National Taiwan University, Taipei, Taiwan.

Li-alloying anode materials suffer from cyclic volumetric expansion and contraction during the charging and discharging processes. Therefore, information regarding the morphological properties of working alloy anode particles during the cyclic processes will be valuable to the research in establishing viable Li-ion battery technology based on these materials. We demonstrate in this presentation the use of transmission X-ray microscopy to in-situ monitoring morphological variations of individual working Sn and SnO anode particles dispersed on graphite during the course of cyclic lithiation/delithiation. Micrographs of Sn particles subjected to different charge/discharge depth will be presented, along with real-time moving pictures of Sn particles during the courses of lithiation and delithiation. These results are also supplemented with in-situ XRD data.

2:00 PM U2.2

In-situ TEM Observations of LiNiO₂-based Batteries During Thermal Decomposition. Lijun Wu, Yongning Zhou, Xiaojian Wang, Xiao-Qing Yang and Yimei Zhu; Brookhaven National Laboratory, Upton, New York.

Layer structured oxides with transition metals such as Ni, Co, and Mn have been considered as good cathode materials to replace LiCoO₂ for lithium batteries due to their lower cost and higher capacity. The thermal instability in charged, especially over charged states at elevated temperatures, however, is still a major concern on this class of materials. Recent studies on Co, Al, Mn doped LiNiO₂-based materials using time-resolved X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) with or without the presence of electrolyte show a series of phase transformations during heating [1]. However, due to the averaging nature of X-ray techniques, detailed information about how the structure changes initiated and propagated through new phase nucleation and growth in the microscopic level is quite limited. Therefore further studies using a local probe with high spatial resolution are needed. Here, we present our in-situ transmission electron microscopy (TEM) studies on the structural changes of over charged LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ and LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂ cathode materials during heating. High resolution transmission electron microscopy (HRTEM) and electron diffraction were carried out using JEM-3000F equipped with an ultra high resolution objective-lens pole-piece and a Gatan double-tilt heating stage capable with temperature ranging from room temperature to 1000 °C. The LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ particles harvested from overcharged cell were first examined at room temperature. Electron diffraction and HRTEM show that the main phase is a layered structure with rhombohedral symmetry. Interestingly, rock-salt structure and spinel structure, which only observed at elevated temperatures using X-ray techniques, were presented at the edges and thin areas of the particles, respectively. This implies that after charging, the particles start losing some oxygen atoms near the particle surface, resulting in the structural changes. By heating the sample, we observed that the phase with the spinel structure nucleates and grows more and more into the thick area of the particles, while the rock-salt phase propagates from the surface to the interior of the particles. After heating the sample to 400 °C, the structure of the whole sample completely transformed to the rock-salt

structure. For over charged $\text{LiNi}_0.33\text{Co}_0.33\text{Mn}_0.33\text{O}_2$ sample, spinel structure was also observed on the surfaces of the particles at room temperature. The work was supported by the U.S. Department of Energy, Office of Basic Energy Science, and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under the program of Vehicle Technology Program, under Contract Number DEAC02-98CH10886. [1] K.W. Nam, W.S. Yoon, X.Q. Yang, J. Power Sources 189 (2009) 515.

2:15 PM U2.3

Study of Li-ion Intercalation in MOx by X-Ray Absorption Spectroscopy (XAS) and Inelastic X-Ray Scattering (IXS)

Techniques. Swati V. Pol¹, Mahalingam Balasubramanian¹, Kenneth Nagle², Gerald Seidler² and Christopher Johnson³;

¹Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; ²Physics Department, University of Washington, Seattle, Washington; ³Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, Illinois.

Rechargeable Li-ion batteries are the key components of today's portable electronic technology owing to their high energy and power density. A comprehensive understanding of the local atomic structure and charge transfer mechanism on lithium ion (de) intercalation is of great impact to develop new battery materials with superior properties. The advent of third-generation synchrotron sources coupled with dedicated and specialized instruments for specific-type of x-ray scattering studies has opened a new window to systematically investigate the structure-property relationship of advanced materials under operating conditions. By means of x-ray absorption spectroscopy (XAS) and inelastic x-ray scattering (IXS) methods, we attempt to explore the charge compensation mechanism behind redox chemistry of various metal oxides in operating batteries. The techniques of XAS, namely X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (XAFS), have been used to probe local structural details around specific metal atoms and are used to discern the oxidation states of the metal. The core-shell electronic properties of light elements at the lithium/metal-oxide electrode of a lithium-ion battery were studied using the lower energy resolution inelastic x-ray scattering (LERIX) spectrometer [Ref. 1], which is capable of making simultaneous IXS measurements at nineteen values of momentum transfer. This hard x-ray technique provides soft x-ray absorption-like information but with bulk-sensitivity. In addition, non-dipole transitions that are inaccessible by soft x-ray spectroscopic methods can be investigated at high momentum transfer. Acknowledgments: PNC/XOR facilities at the Advanced Photon Source, and research at these facilities, are supported by the US Department of Energy - Basic Energy Sciences, a major facilities access grant from NSERC, the University of Washington, Simon Fraser University and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. References: 1. T.T. Fister, G.T. Seidler, L. Wharton, A.R. Battle, T.B. Ellis, J.O. Cross, A.T. Macrander, W.T. Elam, T.A. Tyson, Q. Qian, "Multielement spectrometer for efficient measurement of the momentum transfer dependence of inelastic x-ray scattering," Rev. Sci. Instrum. 77 (6), 063901-1-063901-7 (2006).

2:30 PM U2.4

Nuclear Magnetic Resonance Investigation of Structure and Dynamics in Single-ion Conducting PEG600 Ionomers. David

Roach¹, Karl T. Mueller¹ and Ralph Colby²; ¹Chemistry, Pennsylvania State University, University Park, Pennsylvania; ²Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

We are studying a new class of low glass transition temperature ionomers that comprise polyethers with sulfonated anions and either Li^+ , Na^+ or Cs^+ counterions. We aim to thoroughly understand ion conduction mechanisms in this class of materials, with the ultimate goal of being able to design ionomer membranes for facile ion transport. A mixture of neutral dimethyl isophthalate and dimethyl 5-sulfo isophthalate sodium salt were used with $M = 600$ PEG to produce a range of ion contents. Understanding the structure and conduction mechanisms of these single-ion conducting ionomers requires an array of analytical techniques, and in studies reported here nuclear magnetic resonance (NMR) spectroscopy has been utilized for elucidating the structure and dynamics of various components within the ionomer series. Both lithium and sodium series of PEG600 ionomer with varying cation content (0%, 6%, 11%, 17% and 100%) have been investigated using several NMR methods. ^7Li and ^{23}Na magic angle spinning (MAS) assessed that the cationic species are in an aggregated state. Variable temperature (294 to 373 K) ^{23}Na MAS detected a downfield shift and a broadening of the ^{23}Na resonance indicating larger aggregations of cations, consistent with small angle x-ray scattering data. ^{13}C MAS with ^1H decoupling identified the major carbon chemical environments and the overall mobility of the polymer backbone within the samples. Variable temperature (233 K to 353 K) ^1H - ^{13}C cross-polarization MAS (CPMAS) mapped out the motions of the polymer backbone as a function of temperature. ^7Li and ^{23}Na pulsed field gradient (PFG) NMR have also been utilized to investigate the self diffusion of the cations within these ionomer systems. Together, these data present an improved picture of the structure and dynamics in these systems.

SESSION U3: Nanomaterials for Battery Electrodes

Chairs: Yet-Ming Chiang and Keith Stevenson

Monday Afternoon, November 30, 2009

Room 200 (Hynes)

3:15 PM *U3.1

The Opportunity for Nano-materials for Lithium-Ion Batteries. M. Stanley Whittingham, Materials, SUNY, Binghamton, New York.

Transformative changes in chemical energy storage (lithium-ion batteries) demand higher energy densities combined with lower costs. Advances in materials for both the anode and cathode are focusing on the opportunities that nano-sized and nano-structured materials have to offer. Nano-sized materials allow for much higher rates and greater long-term reversibility of the reaction. However, this can come with increased side-reactions and with lower tap density (lower volumetric capacity). Nano-structured

composites can incorporate the positive attributes, whilst minimizing side-reactions and increasing the density. A number of examples from our laboratory will be used to exemplify the opportunities in the field of nanomaterials.

3:45 PM U3.2

Nanostructured Metals and Metal Oxides for Anodes of Li-Ion Batteries. [Ming Au](#)¹, Thad M. Adams¹, Scott C. McWhorter¹, Yiping Zhao² and John Gibbs²; ¹Savannah River National Lab, Aiken, South Carolina; ²University of Georgia, Athens, Georgia.

Currently, carbon base anodes are being used for Li-ion rechargeable batteries through Li ion intercalation process. The theoretic capacity is limited at 372 mAh/g. The volume expansion and breakdown of solid electrochemical interface (SEI) of carbon anodes during overcharging is one of the reasons of thermal runaway and fire ignition. Searching for new anode materials that possesses higher energy storage capacity and inherent fire safety is not only scientist's passion, but the mandate of industries and customers, particularly for plug-in hybrid vehicles and portable power sources. It is found that metal oxides and metals can host Li ions through conversion process that changes lattice structure of metal oxides or forms metal alloys. The theoretic capacity of metal oxides and metals is in the range of 500 ~ 4000 mAh/g. The metal oxides do not react with polymer electrolyte and generate exceed heat. The aligned nanostructure, such as nanorods, creates large inter-rods space that is capable to store the charges and accommodates the volume expansion caused by conversion. It is expected the aligned nanorods of metal oxides will offer high energy density and power density and inherent safety. Growing free standing nanostructured anode materials on current collectors directly without additives and binders represent a new trend of anode fabrication with simplified process and low cost. In other hand, the nanoparticles of metal oxides can be assembled as the hollow spheres that offers unique feature for anodes of Li-ion rechargeable batteries. We will present our experimental results and discuss the aspects related to practical applications in the conference.

4:00 PM U3.3

Free-standing Semiconductor Carbon Nanotube Electrodes for Lithium Ion Batteries. [Roberta DiLeo](#), Matthew Ganter, Arnold Stux, Brian Landi and Ryne Raffaele; NanoPower Research Labs, Rochester Institute of Technology, Rochester, New York.

The advancements in mobile technology have created a considerable demand for high energy density batteries for many applications including for plug-in hybrid electric vehicles, cell phones, and satellite technologies. The higher volumetric and specific energy densities of lithium ion batteries make them a compelling solution for this demand. However, even the current state-of-the-art lithium ion batteries can still be improved through the use of alternative electrode materials. Lithium alloys with semiconductors such as silicon, germanium, and tin are known to have high lithium ion capacities in the range of 500 - 4000 mAh/g; but these semiconductor alloys demonstrate limitations in charge rates and cyclability due to crystal lattice expansion and contraction. The innovative pairing of nanoparticles and nanoscale coatings with CNT electrodes can significantly improve the battery energy density by eliminating the heavy inactive copper substrate. In addition, this structure can provide efficient electron transport through the CNTs and allow for a potential improvement in the crystal structure changes of the nanoparticles. In the present work, a systematic study of semiconductor deposition techniques correlating material properties, such as crystal structure and particle size, with electrochemical performance was completed. A variety of deposition techniques has been used including sputtering, thermal evaporation, and electrochemical reduction to evaluate the ability to control material properties of silicon, germanium, and tin as they are incorporated into CNT papers. Using a conventional half cell setup, the lithium ion capacity of these composites was measured with a LiPF₆ and mixed carbonates electrolyte opposite a pure lithium metal anode. Values of over 800 mAh/g for the initial testing of Ge-SWNT electrodes were demonstrated. Studies investigating concentration, morphology, annealing treatments, and the oxide/reduced state of the semiconductors have been performed using Raman spectroscopy, scanning electron microscopy, and x-ray diffraction to understand more clearly how these material properties influence lithium ion capacity. Raman spectroscopy has shown an upward shift and a narrowing of characteristic peaks from as-deposited to oxidized germanium thin films suggesting the degree of crystallinity can be observed through this technique. Differences in crystallinity through deposition and processing have been monitored to demonstrate the influence of amorphous and crystalline materials on the capacity and voltage profile. In addition, studies on lithium ion capacity as a function of c-rate, ranging from C/10 to 1C, indicate the power capabilities of these semiconductor-nanotube electrodes. Also the influence of electrolyte on capacity and the formation of the SEI are investigated through the use of various mixed carbonates.

4:15 PM U3.4

Design of Resilient Nano-Silicon Anodes. Alexandre Magasinski¹, Bogdan Zdyrko², Benjamin Hertzberg¹, Frank G. Jones¹, Thomas F. Fuller³, Igor Luzinov² and [Gleb Yushin](#)¹; ¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Department of Material Science, Clemson University, Greenville, South Carolina; ³School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Si anodes offer high Li storage capacity, but demonstrate low capacity retention with battery cycling due to large volume changes in Si during Li insertion and extraction. Conventional binders, developed decades ago for graphitic anodes, are not resilient enough to elastically accommodate large changes in spacing between the particles. They quickly become ineffective in holding the particles together and maintaining electrical conductivity within the anode. A few studies on the optimization of anode binders or development of Si-polymer composites have demonstrated enhancement in the cycle life and performance of Si-based anodes, but further improvements in the elastic properties of the polymers and the Si-binder adhesion are required to satisfy the industrial demands. The desired characteristics of novel Si binders include good and stable adhesion to the Si electrode particles and Cu current collectors, chemical and electrochemical stability in conventional electrolytes. The binder should allow a uniform dispersion of Si particles and be able to withstand the large dimensional changes in the anode over a large number of cycles. In this study we systematically investigated the effects of the binder chemistry, its elastic properties, functional groups, swelling behavior, as well as anode density and Si, C and binder content on the electrochemical performance of the produced anodes. Morphology of the

anodes before and after cycling has been analyzed using SEM. The interface between active particles and a binder has been studied using TEM. XPS, FTIR, AFM and tensile-tests were utilized to detect changes in the binder properties. Peel tests have been performed to monitor anode adhesion to Cu current collectors. Specific anode capacity in excess of 1400 mAh/g and stable performance has been achieved for selected nanoSi-nanoC-binder formulations.

4:30 PM *U3.5

What Are the Adjusting Screws for Tuning Materials for Electrical Storage? Joachim Maier, Max Planck Institute for Solid State Research, Stuttgart, Germany.

The contribution discusses the strategies enabling the realization of functional materials for electrochemical devices. Besides synthesizing new compounds and structures, modification of given compounds is of major significance. The classical way of homogeneously doping solids is complemented by a strategy of equal importance, characterized by the purposeful introduction of interfaces ("heterogeneous doping"). The potential of the latter is particularly obvious and even more pronounced in the context of nanostructuring ("nanoionics"). Using the example of Li-based batteries, the applicability of size effects is systematically investigated and the efficiency of this strategy explored.

SESSION U4: Poster Session I
Chairs: Yury Gogotsi and Katsuhiko Naoi
Monday Evening, November 30, 2009
8:00 PM
Exhibit Hall D (Hynes)

U4.1

LiFePO₄ Nanorod Arrays for High Performance Lithium Battery. Xiangyang Kong, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, China.

We employed the oriented nanorod arrays of LiFePO₄ for high capacity and high charge/discharge rate. The nanorod arrays of LiFePO₄ have been prepared without any impurities by using hydrothermal process under the magnetic field up to 2T. The LiFePO₄ nanorod arrays perform the well alignment along the b-axis, which is of benefit for the fast transport for lithium ions. The batteries with the aligned nanorods cathode exhibit higher electrochemical reactivity than the routinely prepared samples, and the discharge capacity was about 165mAh/g measured at a current density of 17 mA/g.

U4.2

Improved Lithium Ion Intercalation Property of Sol-gel Derived Amorphous LiFePO₄-V₂O₅ Films. Yanyi Liu, Dawei Liu, Qifeng Zhang, Anqiang Pan and Guozhong Cao; Materials Science and Engineering, University of Washington, Seattle, Washington.

This paper for the first time reports sol-gel derived amorphous LiFePO₄-V₂O₅ films exhibiting much enhanced electrochemical properties and cyclic stabilities. V₂O₅ and LiFePO₄ sols were synthesized first and then combined to form a stable LiFePO₄-V₂O₅ sol with a molar ratio of LiFePO₄: V₂O₅ =2:1. LiFePO₄-V₂O₅ films were obtained by spreading the sol on FTO substrates followed by ambient drying overnight and nitrogen atmosphere annealing at 500°C for 3 hours. For comparison purpose, pure LiFePO₄ and V₂O₅ thin films were also prepared. Uniform crack-free LiFePO₄, V₂O₅ and LiFePO₄ - V₂O₅ films were readily obtained. While V₂O₅ films are made of orthorhombic vanadium pentoxide phase, both LiFePO₄ and LiFePO₄-V₂O₅ films are amorphous after annealing at 500°C for 3 hours as determined by means of X-Ray Diffractometry. Scanning Electron Microscopy images revealed that the LiFePO₄-V₂O₅ films consisted of two types of homogeneously dispersed and closely packed distinct particles. The electrochemical characterization revealed that the LiFePO₄-V₂O₅ films exhibited the Li-ion intercalation capacity of 252mAh/g at a current density of 100mA/g and 168mAh/g at 200mA/g, which were among the highest up-to-date data according in authors' knowledge. The LiFePO₄-V₂O₅ films also demonstrated an extraordinary cyclic stability of Li-ion intercalation and deintercalation even at high current densities. Both Li-ion intercalation capacity and cyclic stability of the LiFePO₄-V₂O₅ films exceeded that of LiFePO₄ or V₂O₅ films fabricated under the same condition. Such enhanced Li-ion intercalation capacity and cyclic stability could be attributed, at least in part, to the amorphous structure of LiFePO₄-V₂O₅ films, which has a relatively lower density than its crystalline counterpart with more void space allowing easy mass transport and change of volume associated with Li-ion intercalation. Amorphous, as a thermodynamic metastable phase, also has a broader potential range for Li-ion intercalation as its constituent ions possess different local environment compared to its crystalline form. The mixture and coexistence of V₂O₅ and LiFePO₄ during film casting and subsequent thermal annealing prevented the crystallization of both V₂O₅ and LiFePO₄ due to complexity and interferences.

U4.3

Tin (Sn) Whiskers and Nanowires as Negative Electrodes for Li-ion Batteries. Juchuan Li, Fuqian Yang and Yang-Tse Cheng; Chemical & Materials Engineering, University of Kentucky, Lexington, Kentucky.

Sn is a candidate material for the negative electrodes of lithium-ion batteries due to its high theoretical energy capacity. However, bulk Sn electrodes can fracture as a result of lithium insertion and de-insertion, causing mechanical degradation. Recently, it has been shown that whiskers and nanowires can substantially enhance battery cycle life and durability than their bulk counterparts. These observations and theoretical predictions [1] paved the way for developing new materials and structures for high capacity lithium-ion batteries. In this paper, we report three stress-induced growth methods for creating Sn whiskers and nanowires for lithium-ion battery applications. High compressive stresses are generated using substrate bending, indentation [2], and co-

deposition [3]. The characteristics of Sn whiskers, including size, density, crystal structure, and growth rate for each method are investigated and compared. The electrochemical behavior of the whiskers and nanowires as lithium ion battery electrodes will also be reported, including cycle life and energy capacity of the electrodes. [1] Y.-T. Cheng and M. W. Verbrugge. The influence of surface mechanics on diffusion induced stresses within spherical nanoparticles. *J. Appl. Phys.* 104 (8), 083521 (2008). [2] F. Yang and Y. Li. Indentation-induced tin whiskers on electroplated tin coatings. *J. Appl. Phys.* 104 (11), 113512 (2008). [3] Y.-T. Cheng, A. M. Weiner, C. A. Wong, M. P. Balogh, and M. J. Lukitsch. Stress-induced growth of bismuth nanowires. *Appl. Phys. Lett.* 81 (17), 3248-3250 (2002).

U4.4

High Conducting NASICON-like Phases in $\text{InPO}_4\text{-Li}_3\text{PO}_4$ and $\text{InPO}_4\text{-Na}_3\text{PO}_4$ Quasibinary Systems. *Anna Potapova*¹, Irina Smirnova¹, Alexander Mosunov², Andrey Novoselov¹, Sergey Stefanovich² and Galina Zimina¹, ¹Department of Chemistry and Chemical Engineering for Rare and Dispersed Elements, Lomonosov Moscow State Academy of Fine Chemical Technology, Moscow, Russia; ²Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia.

Advances in development of reliable, compact and inexpensive sources of electric current such as Li-ion batteries is an acute problem for further technology progress. NASICON-like phases, e.g. complex phosphates in $\text{ScPO}_4\text{-Li}_3\text{PO}_4$ quasibinary system, were proposed as promising solid-state electrolytes, but obtained data on ionic conductivity were far from expected. In addition, these compounds have complex polymorphism that makes it difficult to obtain NASICON-like ceramics of high phase homogeneity. Looking for the ceramics of better conducting performance and trying to use less expensive metal than scandium, we have investigated quasibinary systems $\text{InPO}_4\text{-Li}_3\text{PO}_4$ and $\text{InPO}_4\text{-Na}_3\text{PO}_4$ at 950 °C. Samples were prepared through every 2-10 mol% and investigated by XRD method to determine phase-formation in the systems. Measurements of ionic conductivity were carried out with impedance spectroscopy method plotting hodographs. $\text{Na}_3\text{In}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{In}_2(\text{PO}_4)_3$ have ionic conductivity of about 10^{-2} S/cm at 300 °C. This value is comparable to that of well-known NASICON-like compounds such as $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$. To improve ionic conductivity, samples were heterovalent Zr-substituted according to scheme $\text{In}^{3+} \rightarrow \text{Zr}^{4+} + v$, where v is a vacancy in cationic sublattice, with solid solutions formation up to 10 mol% Zr. Vacancy formation increases mobility of Na/Li ions and leads to improved ionic conductivity. In these samples ionic conductivity was measured to be of about 10^{-1} S/cm at 300 °C. Further substitution up to 20 mol% Zr results in formation of a secondary phase without any effect on conductivity. We will present the obtained results, demonstrate established regularity of composition-structure-properties and discuss techniques of obtaining high conducting superionic NASICON-like phases in complex phosphate systems.

U4.5

Comparison of Morphology, Particle Size and Pretreatment Effects on Cycling Performance of Si-based Anodes for Li-ion Batteries. *Sigita Urbonaite*, Ida Baglien, David Ensling and Kristina Edstrom; Department of Materials Chemistry, Structural Chemistry, Uppsala, Sweden.

Currently carbon materials are most commonly used as anodes in commercial batteries with an upper capacity limit of 372 mAh/g. The search for new anode materials leading to increased energy density in the battery is one extensive research field. The safety issues with the potential for lithium intercalation in graphite being close to that of metallic lithium leads to inevitable search for more efficient new anode materials. Theoretically, the most promising anode material is silicon which can alloy with 4 lithium ions per silicon. Among the advantages associated to Si-based anodes are properties such as: high capacity - 4200 mAh/g, which is more than ten times higher than that of graphite, abundance, low cost, environmental friendliness, etc. Si-based electrodes were made using three different silicon sources: Si mesh 325 with particle size of 44 micrometers, nano-Si, with particle size of 50 nm and carbon coated nano-Si. Anodes, containing ~80% of silicon and ~12% of carbon black were prepared with CMC binder using water or water/ethanol mixture as a solvent. Each type of silicon required special adjustments of anode preparation procedure, such as specs milling for Si mesh 325, and ethanol treatment or carbon coating of nano-Silicon to achieve best adhesion to the copper current collector. Anode films prepared at different conditions and from different precursors were casted on the current collector trying to avoid cracking of the casted film. It was found that nano-Si based electrode films, more homogeneous and with better adherence, are formed using silicon sonicated in ethanol and using water/ethanol mixture as a solvent, which seems to help avoiding agglomeration of nano-Si and cracking of the pristine coatings. Electrodes, prepared under the above described conditions from different precursors, were cycled and their performance will in this presentation be compared and related to the morphology and pretreatments applied. Ethanol treated nano-Si based anodes exhibited 2-3 times higher capacity over 25 cycles compared with other high silicon content anodes published [1, 2], with a loss of 8% of capacity during the measurement, and the total irreversible capacity being less than 82 mAh/g. The coulombic efficiency is almost perfect at 96%. Responsibility for the increase of nano-Si based electrode capacity falls to the ethanol ultrasonic bath pretreatment and the use of ethanol/water mixture as a solvent. Attempt to understand the role of the ethanol treatment effect on the nano-Si surface was made. The differences of nano-Si surface species before and after ethanol treatment were analyzed by XPS. It seems that some C-O species add to the surface, covering the Si 2p signal; it is probably some kind of functionalisation of the Si (Si-O) surface that takes place. 1. X. Yang, Z. Wen, X. Xu, B. Lin, S. Huang; *Journal of Power Sources*, 2007(164), 880-884. 2. X. He, W. Pu, J. Ren, L. Wang, C. Jiang, C. Wan; *Ionics*, 2007(13), 51-54.

U4.6

Abstract Withdrawn

U4.7

Generation of Manganese Oxide Nanoparticle-Dispersed Porous Carbon Nanofiber Anodes for High-Performance Rechargeable Lithium-Ion Batteries. Liwen Ji, Zhan Lin, Quan Shi, Andrew J. Medford and Xiangwu Zhang; Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, 27695-8301, North Carolina.

In this study, MnOx nanoparticles dispersed to porous carbon nanofibers (C/MnOx) are prepared by thermally-treating electrospun polyacrylonitrile (PAN) nanofibers containing 50 wt% Mn(CH₃COO)₂ (Mn(OAc)₂) salt at elevated temperatures (stabilization in air environment, followed by carbonization in argon atmosphere). C/MnOx nanofibers prepared from this scalable process are mechanically stable. Moreover, the fibers deliver promising electrochemical performance, including high reversible capacity, enhanced cyclability, and excellent rate capability when used as anodes for rechargeable LIBs. Scanning electron microscopy (SEM) images indicate that the electrospun precursor exhibits a very long and straight fibrous morphology with relatively uniform diameter of about 200 nm. After stabilization in air environment, the fibers become slightly more undulated and exhibit significantly larger diameters. When thermally treated in inert gas, the morphology of the carbonized nanofibers became highly uneven and undulate, and more irregular morphology, porous structure and largely decreased average diameter are also clearly shown. These structural changes may be caused by a large weight loss accompanied with gas evolution. Galvanostatic charge-discharge experiments were carried out to evaluate the electrochemical performance of cells using C/MnOx composite nanofibers as the working electrode and lithium ribbon as the counter electrode with a voltage window of 0.01-2.8 V and a constant specific current of 50 mA g⁻¹. The preliminary results indicated that the C/MnOx anode shows remarkably improved lithium-storage capacities, high reversible lithium-storage capacity and also good capacity retention. We are currently carrying out the further experiment to evaluate the rate capability of these C/MnOx nanofibers.

U4.8

Development of Microstructured and Nanostructured 3-D Porous Electrodes via Monolithic Silica Templates. Martin G. Bakker^{2,1}, Franchesca Maddox², Elizabeth Junkin^{2,1}, Amy Grano², Jan-Henrik Smatts³ and Mika Linden³; ¹Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, Alabama; ²Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama; ³Department of Physical Chemistry, Åbo Akademi University, Turku, Finland.

Supercapacitors and advanced batteries capable of rapid charge and discharge need conductive three dimensional porous electrodes. The high conductivities of porous metal electrodes are attractive. However, the surface areas of such electrodes have been well short of those achievable in carbon. Silica monoliths have extremely high surface areas as well as hierarchal porosity. These properties make silica monoliths attractive as templates for formation of porous metal electrodes. Two methods of utilizing monolithic silica templates have been investigated. Electrodeposition potentially allows control of the crystallinity of the resulting metal. Further, by control of the electrodeposition conditions it should be possible to grow metal into only the mesopores or the macropores within the silica monolith. An alternative approach that has proven successful is infiltration of metal nitrate solution into the silica monoliths followed by drying and calcination to precipitate and then decompose the metal nitrate into metal oxide. In the case of silver nitrate this results in formation of silver replicas of the monolith silica structure. For other metals such as nickel, the nickel oxide formed can be reduced to nickel metal under mild hydrogenation conditions.

U4.9

Electrodeposition of Mesoporous Silica on 3-D Scaffolds as Templates for 3-D Porous Metal Electrodes. Martin G. Bakker^{1,2}, Nikolaus Cordes¹, Caleb Hill^{1,2} and Katrina Staggemeier²; ¹Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama; ²Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, Alabama.

Supercapacitors and advanced batteries capable of rapid charge and discharge need conductive three dimensional porous electrodes. The high conductivities of porous metal electrodes are attractive. However, the surface areas of such electrodes are still well short of those achievable in carbon. One approach to formation of high surface area porous metal electrodes is to electrodeposit metal into nanostructured templates on 3-D scaffolds such as nickel foam. By careful control of composition and voltage thin films of mesoporous silica can be deposited onto 3-D scaffolds such as nickel foam. Removal of the templating surfactant produces a very high surface area mesoporous coating. Metal can be plated into the mesoporous silica, which after removal leaves a high surface area 3-D porous electrode.

U4.10

Templating of Porous Metal Nanostructures with Non-ionic Surfactants on 2-D and 3-D Substrates. Martin G. Bakker^{1,2}, Elizabeth Junkin¹, Franchesca Maddox¹, Allison Hu^{1,2} and Christopher Redden^{2,1}; ¹Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama; ²Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, Alabama.

Supercapacitors and advanced batteries capable of rapid charge and discharge need conductive three dimensional porous electrodes. The high conductivities of porous metal electrodes are attractive, and are used as current collectors in Ni-Cadmium and Ni-metal hydride batteries. However, the surface areas of such electrodes are still well short of those achievable in carbon. We have been assessing the use of non-ionic surfactants of the Triton X series as soft templates for the electrodeposition of nickel, cobalt and copper on both planar electrodes and on nickel foam. High surface area nickel nano-wire networks are observed on planar substrates. On nickel foam a thin film of ca. 10 nm pores is observed. On planar electrodes cobalt forms two nanowire network structures. Copper also forms nanostructures on both substrates. Differences in the nanostructure are also observed for different ion concentrations.

U4.11**Using Soft X-ray Absorption Spectroscopy to Study the Phase Transition of LiFePO₄ during Lithium De-intercalation.**

Xiaoqian Wang^{1,3}, Cherno Jaye², Bin Zhang³, Yongning Zhou¹, Kyung-Wan Nam¹, Hong Li³, Xuejie Huang³, Daniel Fischer² and Xiao-Qing Yang¹; ¹Brookhaven Nat. Lab., Upton, New York; ²National Institute of Standards and Technology, Gaithersburg, Maryland; ³Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Since the pioneering work of Goodenough's group [1], olivine-structured LiFePO₄ has been studied intensively as cathode material for lithium ion batteries due to its excellent safety characteristic and high thermal and chemical stabilities. In-situ XRD shows the lithiation/delithiation of LiFePO₄ is a two-phase transition between LiFePO₄ and FePO₄. However, the details of how the new phase is nucleated and propagated are still being debated. One description uses the shrinking-core model [1]: during charge, the FePO₄/LiFePO₄ interface migrates from the surface to the core simultaneously in each particle, accompanied with the increase of lithium-deficient phase and the decrease of Li-rich phase. It is reversible process for discharge. On the other hand, using electron microscopy, Chen et al., [2] and Laffont et al.[3], reported their observation of the formation of FePO₄ and LiFePO₄ domains in platelet-like primary particles (platelet-type model). By X-ray diffraction and high resolution transmission electron microscopy, Delmas et al., observed the co-existence of fully intercalated and fully deintercalated individual particles at a certain charged state, and proposed a domino-cascade model [4]. Recent X-ray Photoelectron Spectroscopy (XPS) results [5] also revealed a continuous evolution of the Fe³⁺/Fe²⁺ ratio at the surface of the particles upon charge, corresponding to the average content of electrochemical reaction. Although XPS serves as an excellent tool for obtaining chemical information of surfaces, it has a limitation of providing information only at the surface (analysis depth of about 5 nm). Therefore for studies involving bulk properties, XPS may not provide a full picture. In this study, we use synchrotron-based near edge x-ray absorption fine structure (NEXAFS) at the metal L-edges to simultaneously probe the surface and bulk electronic structure of Li_xFePO₄ during Li ion deintercalation. The work was supported by the U.S. Department of Energy, Office of Basic Energy Science, and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under the program of Vehicle Technology Program, under Contract Number DEAC02-98CH10886. [1] Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. J. Electrochem. Soc. 144 (1997) 1188. [2] Chen, G.; Song, X.; Richardson, T. J. Electrochem. Solid-State Lett., 9 (2006) A295. [3] Laffont, L.; Delacourt, C. et al., Nat. Mater., 18 (2006) 5520. [4] Delmas, C.; Maccario, M. et al., Nat. Mater. 7 (2008) 665. [5] Dedryvere, R.; Maccario, M. et al., Chem. Mater., 20 (2008) 7164. [6] Yoon, W. S.; Balasubramanian, M. et al., J. Electrochem. Soc. 151-2 (2004) A246.

U4.12

Single-Wall Carbon Nanotubes as Conductive Carbon Additives in Li-Ion Batteries. Arnold Stux, Matthew Ganter, Robyn Schwartz, Anthony Castiglia, Brian Landi and Ryne Raffaele; RIT - NanoPower Research Labs, Rochester, New York.

There are ongoing efforts to incorporate high-aspect-ratio conductive carbon additives into Li-ion batteries in order to improve the physical percolation network for enhanced electronic transport and matrix integrity over conventional carbon additives. Enhanced electronic transport can lead to an increase in capacity, high-rate performance, and cycle life which are important metrics for Li-ion batteries. In the present work, Li-ion coin cells with mesocarbon microbead (MCMB) anodes as the active material have been studied utilizing high purity single wall carbon nanotubes (SWCNTs) as a replacement for the standard conductive carbon. SWCNTs are proposed to interact with MCMB particles such that improved electronic transport and mechanical stability of the coating is achieved during cycling. Preliminary electrochemical performance has been systematically evaluated as a function of SWCNT content within the MCMB anode between 0.1 and 1.0% w/w SWCNT loading. The anode properties were probed by electrochemical impedance spectroscopy (EIS), differential scanning calorimetry (DSC), 4-point probe conductivity, and scanning electron microscopy (SEM) to study the effects of SWCNT loading. Specific capacities exceeding 300 mAh/g for MCMB anodes have been measured with SWCNT additives at an order of magnitude less mass than conventional carbon black additives. The electrochemical performance of the SWCNT-enhanced anodes was also measured as a function of charge/discharge rates to monitor the effect on rate capability. Overall, the incorporation of SWCNTs into the Li-ion anode is shown to enhance the structure-performance relationship by improving electron transport.

U4.13

Chemical and Structural Stability of the Chemically Delithiated Li_{0.95}[Fe_{2+0.70}Fe_{3+0.10}Cu_{0.15}Li_{0.05}]PO₄ Single Crystal.

Shailesh Upreti¹, Natalya A. Chernova¹, M. S. Whittingham¹, Olga Yakubovich², J. Cabana³, Clare P. Grey³ and Janice L. Musfeldt⁴; ¹Chemistry and Materials, State University of New York at Binghamton, Binghamton, New York; ²Geology, Moscow State University, Moscow, Russian Federation, Russia; ³Chemistry, SUNY Stony Brook, Stony Brook, New York; ⁴Chemistry, University of Tennessee, Knoxville, Tennessee.

The adoption of electric vehicles and renewable energy, based on solar or wind, demands chemical energy storage, probably based on low-cost batteries. LiFePO₄ provides a green battery technology that in principle should be low cost. However, this class of material still has a number of technological limitations such as cost and volumetric energy density. In addition, its reaction mechanism is still not fully understood. A greater electronic conductivity would be a great asset, as would additional lithium capacity. The role of substitution on any of the atom sites is not at all well understood, with recent studies suggesting that isovalent substitution such as Mg on the Fe site or V on the P site enhances the capacity and increases the tap-density by forming a denser nanostructure. In nature, lithium-deficient olivine phosphates are stabilized by isovalent substitutions of ions, such as Mg²⁺ or Ca²⁺, on the Fe sites of the structure. This inspires us to produce a series of doped olivine phosphates and study their structure, electrochemical behavior and diffusion kinetics. In this work, the chemistry of dark brown single crystals of composition Li_{0.95}[(Fe₂₊)_{0.70}(Fe₃₊)_{0.10}Cu_{0.15}Li_{0.05}]PO₄ grown under hydrothermal condition at 400C and autogenous pressure, is reported. A remarkably high level of Cu-substitution is achieved compared to earlier reports. A systematic single crystal x-ray examination revealed Pnma space group with unit cell dimensions a = 10.226(2) Å, b = 6.012(1) Å, c = 4.682(1) Å and V = 287.8(1) Å³. In order

to ascertain the presence of Li ions at the transition metal sites, a detailed solid-state Li NMR study was performed. Optical properties have been examined confirming that the electronic excitations are p-p and p-d in nature. Temperature dependent magnetic studies further validate the oxidation states expected from the reported composition and show an antiferromagnetic behavior below 49.5 K with magnetic moments aligned along [010]. This compound delivers a discharge capacity over 100 mAhg⁻¹ when cycled between 2 and 4.5 V at a current density of 0.1 mAcm⁻²; this capacity is sustained at higher current rates. A 3.4 V plateau is observed at the charge curve, indicating that Li removal occurs mostly as a two-phase reaction. Chemical delithiation, executed on single crystal in a bromine acetonitrile solution, allowed a comparative X-ray structural characterization on delithiated samples. Furthermore, in situ and ex situ chemical delithiation studies, using time resolved synchrotron diffraction tools with a goal of screening Li diffusion pathway, are in progress. This work is supported by the US Department of Energy, Office of FreedomCAR and Vehicle Technologies through the BATT program.

U4.14

3D Nano- and Micro- Templated Composite Electrodes for Use in Electrochemical Capacitors. Michael T. Brumbach, Mark Roberts, Bruce Burckel, Ronen Polsky, Bonnie McKenzie, David Wheeler, Susan Brozik and Bruce Bunker; Sandia National Laboratories, Albuquerque, New Mexico.

This work has focused on advanced electrode design through material deployment in templated electrodes for use in pseudo- and electrochemical- capacitors. The intent is to understand material and nanofunctional design of electrodes for high power delivery. Templates evaluated include nanoscale polymeric structure, sacrificial or inert oxides, as well as ordered 3-dimensional porous carbon films. Pseudocapacitive properties were evaluated by creating metal oxide electrodes with nanoscale architectures to: 1) maximize interfacial contact area with electrolyte, 2) increase solution access to electroactive material, and 3) decrease diffusion distances for charge compensating cations. Electrochemical and electroless deposition of electroactive metal oxides and conducting polymers was employed to develop complex, composite electrodes for enhanced charge/discharge behavior. Several challenges are imposed by the coupling of electroactive metal oxides and conducting polymers for charge storage including the need for a suitable electrolyte which effectively utilizes both electrode components. Cyclic voltammetry and impedance spectroscopy were used to evaluate electrode compositions and the efficacy of certain nanoscale architectures for increasing capacitance. Mechanisms for charge storage were investigated using materials characterization including XRD, SEM, and XPS. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

U4.15

Lipon Coated LiCoO₂ Particles by RF-magnetron Sputtering. Yoonqu Kim, Gabriel M. Veith and Nancy J. Dudney; Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

A solid polymer electrolyte suffers from oxidation problems in batteries employing a high voltage cathode over 4.0 V. A recent study indicates that a partial coating of Li₃PO₄ electrolyte layer on LiCoO₂ powders acts as an oxidation barrier in lithium batteries with a solid polymer electrolyte [1]. Use of this Li₃PO₄-coated LiCoO₂ cathode enables reversible cycling up to 4.6 V. Glassy lithium phosphorus oxynitride (Lipon) film electrolytes have both higher ionic conductivity (~1×10⁻⁶ S/cm) and higher voltage windows (~5.5 V) than a Li₃PO₄ film electrolyte [2,3]. Previously, catalyst coatings on powder materials have been done by RF-magnetron sputtering method [4]. Here, we report a similar coating technique for Lipon electrolyte on micron size LiCoO₂ powders. We will describe optimum vapor deposition conditions and effects of the Lipon electrolyte coatings on performances of rechargeable polymer lithium batteries. References [1] Yo Kobayashi, Shiro Seki, Atsushi Yamanaka, Hajime Miyashiro, Yuichi Mita and Toru Iwahori, J. Power Sources 146 (2005) 719-722. [2] J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury and C. F. Luck, J. Power Sources 43-44 (1933) 103-110. [3] Xiaohua Yu, J. B. Bates, G. E. Jellison, Jr. and F. X. Hart, J. Electrochem. Soc. 114 (1997) 524-532. [4] Gabriel M. Veith, Andrew R. Lupini, Stephen J. Pennycook, Gary W. Ownby and Nancy J. Dudney, J. Catal. 231 (2005) 151-158. Acknowledgement This work was supported by DARPA Defense Sciences Office and by the Division of Materials Sciences and Engineering, U.S. Department of Energy.

U4.16

Observation of Overpotential Dependent Phase Transformation Sequences in Nanoscale Olivines and a Model for their Prediction. Ming Tang¹, Yu-Hua Kao², Nonglak Meethong², James F. Belak¹, W. Craig Carter² and Yet-Ming Chiang²;

¹Condensed Matter and Materials Division, Lawrence Livermore National Laboratory, Livermore, California; ²Dept. of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Recent extensive experimental study has revealed a rich variety of unusual phase transition behaviors in nanosized lithium metal olivine cathodes during electrochemical cycling. In particular, amorphous phase formation was observed to be increasingly significant as particle sizes shrink, a phenomenon not seen in larger particles. In a companion theoretical study, we developed a diffuse-interface model to rationalize experimental observations and to further predict the electrochemically-driven phase transition behavior of nanoscale olivines. Due to the preference of disordered structure by the particle surface energy, our model predicts the existence of a critical particle size below which amorphization is favored. The critical size increases considerably with the misfit strain between LiFePO₄ and FePO₄ olivine phases. Furthermore, the electrical overpotential applied on cathodes is identified as an important parameter that controls the transition behavior. Three regimes with distinct transition pathways were found at different overpotential levels. At low overpotentials, cathode particles undergo the conventional crystalline transition between LiFePO₄ and FePO₄ olivines. Spontaneous amorphization is the main transition pathway at intermediate overpotential values. However, the crystalline transition becomes dominant again at higher overpotentials due to 1) the recrystallization of amorphous phase and 2) the kinetic limitation of amorphization. The model predictions have been verified by recent in-situ X-ray diffraction experiments.

U4.18**Layer-by-Layer Assembled TiO₂ - Multiwall Carbon Nanotube Nanostructures for Lithium-Ion Battery Electrodes.** Betar M.

Gallant¹, Seung Woo Lee², Jung Ah Lee², Paula T. Hammond² and Yang Shao-Horn¹; ¹Mechanical Engineering, MIT, Cambridge, Massachusetts; ²Chemical Engineering, MIT, Cambridge, Massachusetts.

While a large number of metals and metal oxides can react with lithium by intercalation or displacement reactions, large chemical strains associated with lithium uptake and surface film growth upon electrolyte decomposition often result in considerable capacity loss during cycling. Nanomaterials can better accommodate volumetric strains resulting from lithium insertion, and therefore offer one opportunity for improving electrode lifetime. In addition, the high surface area to volume ratio enables faster charging and discharging, and can therefore address a critical limitation of typical bulk materials. However, in conventional composite electrodes, significant amounts of conductive additive and insulating binder are needed to ensure that active nanoparticles remain electrically connected, and this can reduce the electrochemically active surface area. It is therefore of interest to develop nanostructures that are additive-free and in a 3D network with facile electronic and ionic conduction. Such electrodes can not only allow fundamental understanding of size effects on lithium reaction mechanisms but also potentially lead to enhanced power capability of lithium batteries. In this study, we create thin-film nanostructures that combine the high theoretical capacities of metal oxides with good electrical conductivity and high surface area of multiwall carbon nanotubes (MWNTs). In particular, we employ anatase TiO₂ nanoparticles, a promising negative electrode material with reported capacities of 170 mAh/g and higher, a redox potential (1.8 V vs. Li) outside the voltage window for surface film formation (below 1 V vs. Li), low cost, and widespread availability. We prepare TiO₂-MWNT thin films using the layer-by-layer (LbL) technique, which utilizes electrostatic interactions between positively charged anatase TiO₂ nanoparticles and negatively charged functionalized MWNTs. MWNT-TiO₂ film growth and quality are investigated in terms of electrical conductivity and film roughness as a function of electrode thickness. Cyclic voltammogram and galvanostatic testing data of MWNT-TiO₂ electrodes in lithium cells will be presented and the effect of electrode thickness and microstructure on lithium reaction kinetics will be discussed.

U4.19**Abstract Withdrawn****U4.20****Abstract Withdrawn****U4.21****Analysis of Active Materials Debonding from Polymeric Binders caused by Insertion Reaction in Lithium-ion Batteries.**

Nanshu Lu^{1,2}, Joost J. Vlassak¹ and Zhigang Suo¹; ¹SEAS, Harvard University, Cambridge, Massachusetts; ²Beckman Institute, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois.

In a lithium-ion battery, both electrodes are atomic frameworks that host mobile lithium ions. When the battery is being charged or discharged, lithium ions diffuse from one electrode to the other. Such an insertion reaction deforms the active materials, and may cause the active particles to debond from the polymeric binders, resulting in loss of electrical conductivity of the electrode. Using fracture mechanics, we show that the volume fraction of the active materials and the stiffness of the polymeric binder have significant effects on the driving force of partial-binder debonding. Critical conditions are determined to avert debonding.

U4.22**Silicon-Carbon Nanocomposite Anodes for Li-ion Batteries.** Benjamin Hertzberg, Patrick Dixon, Alexandre Magasinski and Gleb Yushin; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The specific capacity of Si exceeds that of graphite, the conventional anode in Li-ion batteries, by an order of magnitude. However, achieving stable performance of Si anodes is a challenge. Recent experiments suggest that individual Si nanoparticles and thin films below a critical size do not fracture and exhibit high reversible capacity for Li. The often observed rapid degradation of Si-based anodes is related not to the intrinsic property of Si but to the loss of electrical contact within the anodes caused by the large volume changes that takes place during Li insertion and extraction. In this project we have produced high capacity nanocomposite Si-C particles that do not exhibit volume changes during Li insertion and extraction. According to our approach Si thin films are deposited on the internal pore walls of porous carbon and expand within the available pore volume during electrochemical alloying with Li. The predicted cost of the nanocomposite is comparable or lower than that of the graphite. Morphology of the anodes particles has been analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Charge-discharge, cyclic voltammetry and electrochemical impedance spectroscopy studies have been performed in 2016 coin cell and pouch cell configurations. Charge-discharge experiments have been performed in the 0.01-2 V range vs. Li/L⁺. Specific anode capacity in excess of 700 mAh/g and stable performance of up to 40 cycles has been achieved.

U4.23**Improvement of Battery Performance by Controlling Electrode/Electrolyte Interface Structure of All Solid-State Lithium Secondary Batteries.** Kyosuke Kishida¹, Haruyuki Inui¹, Yasutoshi Iriyama² and Zempachi Ogumi³; ¹Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; ²Department of Materials Science & Chemical Engineering, Shizuoka University, Hamamatsu, Japan; ³Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan.

Solid state lithium-ion conductors have received a considerable amount of attentions as solid electrolytes for all solid-state lithium rechargeable batteries, which have great advantages in terms of safety, thermal stability and resistance to shocks and vibrations. In the case of the all solid-state batteries, structure of interface between the electrode and solid electrolyte must have great influences on the battery performance such as resistivity and mechanical stability of the interface. However, the relationship between the interface and electrochemical properties has not been studied in detail. Recently, we have studied influences of microstructures of the electrolyte/cathode interfaces on electrochemical properties using model assemblies with a perovskite-based lithium lanthanum titanate (LLT: $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$) solid electrolyte and a HT-LiCoO₂ cathode with a layered rock-salt type structure). Our previous results suggest that the resistivity and mechanical stability of the interface can be controlled mainly by two factors, namely nano-scale defect regions such as amorphous LLT at the interface and geometrical configuration of Li layers in LiCoO₂ crystal against the interface plane. In the present study, we prepared various model samples each composed of LiCoO₂ cathode thin film deposited on polycrystalline LLT solid electrolyte with different type of surface finishes or single crystalline LLT with different surface orientations. Microstructures of the various LLT/LiCoO₂ interfaces and their influences on the electrochemical properties of the model cells were investigated in order to elucidate the influence of the two structural factors on the battery performance. LiCoO₂ thin-film cathode with a thickness about 100nm is epitaxially grown with the orientation relationships: $\{110\}_{\text{LLT}}//\{11-20\}_{\text{LiCoO}_2}$ and $\langle 001 \rangle_{\text{LLT}}//\langle 4-401 \rangle_{\text{LiCoO}_2}$. LiCoO₂ domains with their layered structure aligned perpendicular to the interface are dominantly formed when the interface is parallel to (110) of a single crystalline LLT, whereas those with the layered structure inclined about 20° against the interface are dominantly grown when the interface is parallel to (112) of a single crystalline LLT. CV tests of these two assemblies reveal that the former sample exhibits much better battery performance in terms of the interfacial resistivity and the cycle stability, which stems from the advantageous geometrical configuration of the layered structure of LiCoO₂ and the fine-scale domain size. In addition, improvement of battery performance is confirmed by the experiments using assemblies prepared on ion-irradiated or shot-peened surfaces of polycrystalline LLT, both of which have a layer of thin amorphous LLT at the interface. These results confirm that the apparent interface resistivity can be lowered partly by controlling the surface plane of LLT and also by the introduction of amorphous LLT layer through surface modification processes for LLT surface.

U4.24

Transferred to U13.59

U4.25

Tunable Mechanical and Electronic Properties of Nanoporous Foams. [Tony van Buuren](#)¹, Juergen Biener¹, Ted Baumann¹, Sergei Kucheyev¹, Jon Lee¹, Morris Wang¹, Alex Hamza¹, Ln Shao^{2,3}, Raghavan Nadar Viswanath², Dominik Kramer², Joerg Weissmueller^{2,3}, Arne Wittstock⁴ and Marcus Baeumer⁴; ¹LLNL, Livermore, California; ²Institute of Nanotechnology Forschungszentrum, Karlsruhe, Germany; ³Technische Physik, Universität des Saarlandes, Saarbrücken, Germany; ⁴Institut für Angewandte und Physikalische Chemie, Universität Bremen, Bremen, Germany.

Understanding the correlations between electronic structure, surface chemistry, and surface energy is of fundamental importance to the development of new nanoporous materials for energy storage applications. Nanoporous solids are unique in a way that their macroscopic properties can be determined by surface properties. For example, charge-transfer induced changes of the surface stress have been shown to trigger macroscopic and reversible strain effects in nanoporous carbon and nanoporous Au. We will report on our first attempts to measure changes in the electronic structure of nanoporous materials by in situ x-ray adsorption and emission spectroscopies, and correlate these results with macroscopically measurable properties such as capacity and strain.

U4.26

Synthesis of SnO/carbon Nanotube Nanocomposites for an Anode of Lithium-ion Battery. [Ken Sakaushi](#)¹, Yuya Oaki¹, Eiji Hosono², Haoshen Zhao² and Hiroaki Imai¹; ¹Faculty of Science and Technology, Keio University, Yokohama, Japan; ²Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

At the present, tin is one of the most interested elements for the anode of lithium-ion battery. Especially, tin oxides are greatly focused of all other tin based materials since they have large theoretical maximum reversible capacity: tin monoxide SnO has 875 mAh/g and tin dioxide SnO₂ has 790 mAh/g. However, it is difficult to commercialize SnO or SnO₂ anode because of their poor cycle properties caused by a large volume expansion (ca. 300%). Nanosizing, morphological control and integrating with other materials are clues of enhancing electrochemical properties of the elements that making alloy with lithium. There are a lot of reports about nanostructured SnO₂ composites, such as composites with carbon nanotubes (CNTs) or carbon hollow spheres. They show good electrochemical properties. Particularly, they succeeded to develop cycle performance. From this point of view, fabrication of nanostructured SnO composites with carbon materials may also be able to improve electrochemical performances of SnO. However, a few reports about nanostructured SnO composites are studied since SnO is difficult to fabricate in nanostructured materials. Therefore, it is necessary to find fabrication routes to synthesize nanostructured SnO composite materials. Our group has studied synthesis of SnO in the aqueous solution by controlling the value of pH and amount of starting materials. Our focus for this study is fabrication of SnO/CNT composite. Therefore, we studied crystal growth of nanostructured SnO by homogeneous nucleation on substrates. In consequence, SnO nanosheets were successfully obtained on CNTs that are ca.100 nm in diameter and ca.5 μm in length. Thermal decomposition of urea was utilized to control supersaturated condition with gradual increase in pH. SnO nanosheets that were grown in c axis oriented was ca.5 nm in thickness and ca.200 nm in size. The specific surface area of SnO/CNT composite was 42.5 m²/g. This SnO/CNT composite material is expected as excellent anode material for lithium-ion battery because long CNTs that have good electronic conductivity would act as smooth electronic paths.

U4.27

Electrical Transport Properties of Graphite Nanosheets Doped Polyvinylidene Fluoride Composites. Yuchao Li, Sie Chin Tjong and Robert Kowk Yiu Li; Physics and Material Science, City University of Hong Kong, Hong Kong, China.

Graphite nanosheets (GN) were introduced into piezoelectric polyvinylidene fluoride (PVDF) via solution mixing technique. The nanocomposites were then subjected to compression molding for electrical measurements. Solution mixing enabled homogeneous dispersion of GN within PVDF matrix. The electric transport behavior of such nanocomposites was studied by means of impedance spectroscopy in a wide frequency range from 10^2 to 10^7 . The results showed that the dielectric constant and conductivity of the composites are frequency dependent and well obeyed with the scale law ($\sigma \propto \omega^u$ and $\epsilon \propto \omega^{-v}$) in the vicinity of percolation threshold ($\Phi_c = 2.4$ wt%). A large dielectric constant of 173 with a low loss tangent of 0.65 was found for PVDF/GN 2.5 wt% composites at 1 KHz. Such enhancement in dielectric constant could be interpreted in terms of the formation of mini-capacitors associated with the dispersion of graphite nanoplatelets in insulating PVDF matrix.

U4.28

Pore Width Dependence of Hydrated Ca^{2+} Structure in Hydrophobic Nanopore. Natsuko Kojima, Tomonori Ohba, Hirofumi Kanoh and Katsumi Kaneko; Graduate School of Science, Chiba University, Chiba, Japan.

The structure of molecules or ions in solid nanospace is often different from their bulk structure^{1,2}. Especially, the structure of aqueous solution in nanopore is not understood regardless of the importance in the wide area of science and technology. We have studied the structure of Ca^{2+} aqueous solution in slit-carbon space with canonical ensemble Monte Carlo simulation. The pore width of the hydrophobic nanopore was changed from 0.6 to 1.8 nm and the concentration of solution was 1.0 mol dm^{-3} . The parameters of ions were determined by lattice enthalpy of CaCl_2 crystals and the TIP5P potential model³ for water was used. The interaction energy of molecules and ions with graphite pore was calculated with Steele potential⁴. Water molecules form the layered structure of which thickness depends on the pore width. Ca^{2+} ions are distributed near the central region of the pore. The radial distribution function analysis showed that the Ca^{2+} ion had a planer hydration structure in the 0.6 nm slit-pore, being completely different from the hydrated structure of the Ca^{2+} ion in the wider pores and the bulk Ca^{2+} ions. ¹ Kaneko, K. *Adsorption* **1997**, *3*, 197. ² Ohba, T.; Kaneko, K. *Mol. Phys.*, **2007**, *105*, 139. ³ Mahoney, M. W.; Jorgensen, W. L. *J.Chem.Phys.* **2000**, *112*, 8910. ⁴ Steele, W. A. *Surf. Sci.* **1973**, *36*, 317.

U4.29

Abstract Withdrawn

U4.30

Abstract Withdrawn

U4.31

Synchrotron Based X-ray Studies on the Thermal Decomposition Mechanism of Charged Cathode Materials for Li-ion Batteries. Kyung-Wan Nam¹, Xiao-Jian Wang¹, Yong-Ning Zhou¹, Won-Sub Yoon², Otto Haas¹ and Xiao-Qing Yang¹; ¹Chemistry department, Brookhaven National Laboratory, Upton, New York; ²School of Advanced Materials Eng, Kookmin University, Seoul, Korea, South.

The research and development of hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) are intensified due to the energy crisis and environmental concerns. Having the highest energy density among all rechargeable batteries, lithium-ion battery is considered as the best candidate of rechargeable batteries for transportation applications. In order to meet the challenging requirements of powering HEV and PHEV, the safety characteristics of lithium battery need to be thoroughly studied and significantly improved. The thermal stability of the cathode materials is one of the key issues of the safety characteristics, which is related to the occurrence of exothermic reactions in charged batteries at elevated temperatures that can result in thermal runaway and catastrophic failure of the battery. The thermal runaway has been attributed to the reactions between the charged electrodes and the electrolyte. Therefore, in-depth understanding of the structural changes of the charged cathode material during thermal decomposition, with or without the presence of electrolytes and their relationship to the thermal stability of the cathode material is very important. We have developed techniques using the combination of a high intensity synchrotron X-ray beam and fast detectors (image plate or position sensitive detectors) to do time resolved X-ray diffraction (TR-XRD) during the thermal decomposition of charged cathode materials. Recently, we have developed synchrotron based hard X-ray absorption (XAS) techniques to study the oxidation state and local structural changes of each element during the thermal decomposition of charged cathode materials. In addition, the in situ soft XAS techniques we have developed allow us to distinguish the structural differences between the surface and bulk of electrodes using both partial electron yield (PEY) and fluorescence yield (FY) detectors simultaneously during heating of charged cathode materials. In this presentation, we will report our studies on the structural changes of layered nickel based cathode materials (e.g., $\text{Li}_1\text{-xNiO}_2$, $\text{Li}_1\text{-xNi}_0.8\text{Co}_0.15\text{Al}_0.05\text{O}_2$ and $\text{Li}_1\text{-xNi}_1/3\text{Co}_1/3\text{Mn}_1/3\text{O}_2$) during thermal decompositions. The combined results from these synchrotron based X-ray techniques will provide valuable information for synthesizing thermally stable cathode materials and improving the thermal properties of the materials being used currently. TR-XRD spectra were recorded as a set of circles on a Mar 345-image plate detector in the transmission mode at beamline X7B at National Synchrotron Light Source (NSLS). Soft and hard XAS spectra were measured at beamline U7A and X19A&X18B at NSLS, respectively. ACKNOWLEDGMENT The work done at Brookhaven National Lab. was supported by the

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U4.32

Abstract Withdrawn

U4.33

High-Throughput Computational Search for New Li-ion Battery Cathode Materials. Anubhav Jain¹, Geoffroy Hautier¹, Charles Moore¹, Christopher Fischer¹, Kristin Persson², Robert Doe¹, Byoungwoo Kang¹, Xiaohua Ma¹, Jae Chul Kim¹, Hailong Chen¹, Denis Kramer¹, Timothy Mueller¹, Shirley Meng³ and Gerbrand Ceder¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Lawrence Berkeley National Laboratory, Berkeley, California; ³University of Florida, Gainesville, Florida.

Ab initio computational methods have been critical in understanding properties of existing battery materials and predicting trends useful in the design of next-generation compounds[1]. High-throughput ab initio computations, performed over tens of thousands of compounds, can use these developments to potentially screen new Li-ion battery cathode materials on an unprecedented scale. To date, our group has performed via density functional theory over 50,000 total energy computations and 7,000 voltage predictions. These calculations have covered the space of materials in the Inorganic Crystal Structure Database[2], as well as variations on these materials generated using data-mined crystal structure prediction methods[3]. The infrastructure needed to generate, manage, store, and analyze such large computational data sets composes a major portion of our project and is briefly described. Our calculations have recovered the properties of known battery materials, validating our approach towards the search for new cathode materials with high capacity, high rate capability, and high stability. Synthesis efforts are now underway on novel compounds suggested by our computational screening procedure. In addition to its application for materials discovery, high-throughput computational data can serve as a knowledge base which can be data mined for cathode design principles. We show in particular how existing theories describing the tuning of redox couple voltage via the inductive effect can be combined with our large data set to create voltage prediction models which hold across several structure types, redox couples, and polyanion chemistries. Such models lead to 'cathode design maps' which show the interesting redox couples for a given polyanion chemistry, based on necessary voltage and energy density constraints. 1. Ceder, G., et al., Identification of cathode materials for lithium batteries guided by first-principles calculations. *Nature*, 1998. 392(6677): p. 694-696. 2. Bergerhoff, G., et al., The Inorganic Crystal-Structure Data-Base. *Journal of chemical information and computer sciences*, 1983. 23(2): p. 66-69. 3. Fischer, C.C., et al., Predicting crystal structure by merging data mining with quantum mechanics. *Nature Materials*, 2006. 5(8): p. 641-646.

U4.34

Multifunctional Zeolite-like Materials for Energy Applications. Victoria Soghomonian, Physics, Virginia Tech, Blacksburg, Virginia.

Electrically conducting zeolite-like frameworks are largely unstudied as electronic materials, but may offer new avenues in energy applications, ranging from electrical energy storage to catalysis. Zeolitic materials are characterized by the presence of nanoscale channels and cavities delineated by their crystalline framework. As a function of the structure, the specific surface area in zeolitic materials is high. Thus, for instance a novel avenue for realizing higher energy density capacitive electrical storage capabilities can be addressed by a materials system that combines the structural properties of well known but electrically insulating microporous zeolites, with an electronically active framework, as our work indicates. We present a 3-D oxo-vanadium arsenate electrically conducting zeolite-like material, isolated by hydrothermal methods. The vanadium arsenate framework crystallizes in a cubic space group, and we discuss the crystal structure, the thermal stability and the microporous properties of the framework. We then present the experimentally measured electronic and ionic conductivities on single crystals, the temperature dependences of the conductivities, and discuss possible electronic and ionic conduction mechanisms at play in the material, in the empty framework and in the ion-exchanged framework. Measurements suggest that the ionic conductivity occurs through channeling of ions through a sublattice, mediated by phonon-assisted hopping, whereas the electronic conductivity indicates non-metallic behavior. In a zeolite-like material, the pore density is high, due to the regular crystalline arrangement and the small pore size, allowing the packing of large number of ions into the framework. If the framework is electrically conducting, an electrical double-layer may form between a charge in a pore and the framework, resulting in electrical double layer capacitive electrical energy storage. The distance between the charge and the microporous and electrically conducting framework is atomic in scale and this property combines with the high pore density to yield very high capacitances. Thus higher energy per unit volume is realized. Our preliminary calculations and measurements for the vanadium arsenate suggest up to an 8-fold increase in energy density over existing mesoporous carbon implementations.

U4.35

Electrocatalytic Activity of Oxygen Reduction Reactions on Platinum and Glassy Carbon for Li-Air Batteries. Yi-Chun Lu^{1,4}, Hubert A. Gasteiger⁴, Robert McGuire^{3,4}, Ethan Crumlin^{2,4} and Yang Shao-Horn^{1,2,4}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁴Electrochemical Energy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Li-air batteries replace the traditional intercalation electrode with a catalytic porous electrode (air electrode), which can absorb and reduce O₂ from the air. During discharge, Li ions can react with dissolved oxygen to form insoluble reaction products such as

lithium (per)oxide within the pores of the air electrode. Upon charging, lithium (per)oxide can decompose to oxygen and lithium. Li-air batteries have much greater energy density compared to traditional lithium ion batteries based on lithium intercalation compounds. However, current Li-air batteries have low reversibility, low power capability, and short cycle life, which is limited primarily by the reaction kinetics and transport resistances in the air electrode. Kinetics of O₂ reduction and evolution in the air electrode is poorly understood. In this study, we examine the electrocatalytic activity of the oxygen reduction reaction (ORR) on platinum and glassy carbon model electrodes in lithium-conducting nonaqueous electrolyte using rotating disk electrode (RDE) measurements. Well-defined model surfaces of polycrystalline platinum and glassy carbon (5 mm OD x 4 mm thick, mirror polished) were studied via RDE to identify the various transport/reaction processes occurring on the catalytic surfaces and uncover the true catalytic activity of the materials toward the interested reactions. Cyclic voltammogram for polycrystalline platinum and glassy carbon electrode were studied in 1M LiClO₄ in PC:DME (1:2, by volume) under argon or in the presence of oxygen, with sweep rate equals to 5 or 20 mV/s and at various rotation rates. Initial RDE results have shown that (i) the catalytic activity of ORR for the 1st cycle is higher than the subsequent cycles due to the accumulation of lithium (per)oxide on the surfaces. The catalytic activity will then reach steady state soon after the first two cycles, (ii) the lithium (per)oxide-poisoned surfaces can be regenerated by holding the potential at ~ 4.4 V(vs. Li) for a few minutes to get back to the same activity as the clean surface in the first cycle, (iii) the ORR behavior is highly correlated with the accumulation rate (controlled by scan rate) of lithium (per)oxide during oxygen reduction reaction and (iv) the glassy carbon surfaces seem to have higher catalytic activity toward oxygen reduction than the polycrystalline platinum surfaces in the Li-air battery system. Mechanisms of the reaction kinetics on these model surfaces will be discussed.

U4.36

Electronic Properties of Polypropylene Capacitor Dielectrics from First Principles. M. Stournara and R. Ramprasad; Institution of Materials Science, UConn, Storrs, Connecticut.

Polypropylene, being one of the fastest growing engineering plastics, has wide industrial and everyday life applications due to attractive properties such as low density, high melting point, high tensile strength, and a high resistance to chemical attack. A major application area where (biaxially oriented) polypropylene has already found a niche is in high density energy storage capacitor dielectric systems. Still, demands for ever higher electrical energy density continues. Since the energy density scales with the square of the electric field in the dielectric, significant improvements of energy density for a given dielectric can only be achieved by increasing the electrical breakdown strength, and consequently through a fundamental understanding of the factors controlling the breakdown strength and high field electrical conduction. These considerations provide the motivation for the present ab initio density functional theory (DFT) study of the electronic properties of defect-free and defective isotactic polypropylene (iPP). Our DFT calculations have focused on single chains of iPP as well as bulk iPP in the α form (α -iPP). These bulk calculations constitute the first-ever DFT calculations of this system. Our results for the physical structure (in terms of C-C and C-H bond lengths, C-C-C and C-C-H bond angles, and lattice parameters of α -iPP) are in excellent agreement with experiments. We have computed the band structure of α -iPP, and using the self-consistent local electronic potential, we have also determined the electron affinity of this system to be 0.31 eV; this is in contrast to the small but negative electron affinity values of polyethylene. Furthermore, we have also studied various types of chemical imperfections in α -iPP, and have assessed the impact of these defects on its electronic structure. Specifically, hydroxyl, carbonyl and double bond defects were considered. In each of these cases, a doubly occupied state and an unoccupied state were created in the band gap of α -iPP (constituting hole and electron traps, respectively). We find that the carbonyl defects cause the most significant impact to the band structure, resulting in the deepest electron and hole traps. Finally, we have also studied the interface between metal electrodes and iPP, and have determined the interface barrier heights as a function of the atomic-level structure of the interface.

U4.37

A Comparison of the Li-M-P-O₂ (M=Fe, Mn) Phase Diagrams from First Principles Calculations. Shyue Ping Ong, Byoungwoo Kang, Anubhav Jain and Gerbrand Ceder; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We present a comparison of the phase diagrams of the quaternary Li-M-P-O₂ (M = Fe, Mn) systems developed from first principles calculations. These phase diagrams are of interest to material scientists developing synthesis routes for the well-established positive electrode material, LiFePO₄, as well as the potentially promising LiMnPO₄. Using the methodology outlined in our earlier work, the phase diagrams were constructed as a function of oxidation conditions, with the oxygen chemical potential, μ_{O_2} , capturing both temperature and oxygen partial pressure dependence. The Li-Fe-P-O₂ phase diagram shows LiFePO₄ to be stable over a wide range of oxidation environments. The predicted phase relations and reduction conditions compare well to experimental findings on stoichiometric and Li-off-stoichiometric LiFePO₄. Kang et al. subsequently showed that the phase diagram can be applied to identify off-stoichiometric synthesis routes which led to LiFePO₄ with very high rate capabilities. In comparison, the Li-Mn-P-O₂ phase diagram shows LiMnPO₄ to be stable over an even wider range of oxidation environments. Consistent with experimental evidence, LiMnPO₄ is first formed at more oxidizing conditions than LiFePO₄. LiMnPO₄ is also reduced at more reducing conditions than LiFePO₄, again consistent with the experimental observations of Ellis et al. We will also highlight salient differences between the two phase diagrams under various oxidation environments.

U4.38

Heavy Doping of Li⁺ ion into NiO Epitaxial Thin Films via Unequilibrium Room-temperature Processing for New Functionalization. Naoki Shiraishi¹, Yushi Katou¹, Yuki Sugimoto¹, Hideki Arai¹, Nobuo Tsuchimine², Susumu Kobayashi², Masahiko Mitsuhashi³ and Mamoru Yoshimoto¹; ¹Department of Innovative and Engineered Materials, Yoshimoto laboratory, Tokyo Institute of Technology, YOKOHAMA-SHI, KANAGAWA, Japan; ²TOSHIMA manufacturing company, HIGASHIMATSUYAMA-SHI, SAITAMA, Japan; ³Kanagawa Industrial Technology Center, EBINA-SHI, KANAGAWA, Japan.

NiO is a typical material for new p-type oxide semiconductors. Conductivity of NiO can be raised with Li⁺ doping. In case of Li-heavy doping, we can obtain Li_xNiO₂ (0.5 < x < 1.0). Recently the importance of LiNiO₂ has been increased as an electrode material for rechargeable lithium cells. In this work, we tried to fabricate a novel NiO material with Li⁺-heavily doped by applying the pulsed laser-induced room temperature (R.T.) film process. Previously, we have succeeded in the epitaxial growth of various oxide thin films at R.T. such as Sn-doped In₂O₃ transparent electrodes [1]. Although the many studies have been made on the deposition of NiO epitaxial thin film at low temperatures [2], there are few reports on fabrication and the conductive characteristic for Li-heavy doped NiO epitaxial films. The film deposition at R.T., which is the nonequilibrium vapor phase process, is expected to result in different crystal structure and characteristics from the films grown at high-temperatures. A composition-adjusted thin film of Li_xNi_{1-x}O (0.10 < x < 0.40) was deposited on a sapphire (α-Al₂O₃)(0001) or MgO(100) substrates by pulsed laser deposition (PLD) technique in 10⁻⁶ Torr of oxygen at R.T. and the high temperatures of 350 and 515°C. Crystalline properties of thin films deposited at R.T. or high temperatures were examined using reflection high energy electron diffraction (RHEED) and X-ray diffraction. For the Li-heavy doped NiO films (x > 0.30) grown at R.T., a clear streak RHEED pattern showing epitaxial growth was observed. But the Li-heavy doped NiO films grown at high temperatures, exhibited the ring RHEED pattern, which indicates the polycrystal growth of films. Electric conductivity of various Li-doped NiO thin films deposited at R.T. or high temperatures on sapphire (0001) substrates were measured by two-probe method. The interesting results were obtained that conductivity of the film was increased remarkably with an increase of Li-doping for R.T. deposition, but was not changed so much regardless of Li-doping for high-temperature depositions. [1] J.Tashiro et al., Thin Solid Films 415(2002)pp272 [2] A.Matsuda et al, Appl. Phys. Lett. 90.182107(2007)

U4.39

Olivine Electrode Engineering Impact on the Electrochemical Performance of Lithium Ion Batteries. Wenquan Lu, Andrew Jansen and Dennis Dees; Argonne National Laboratory, Argonne, Illinois.

Introduction In order to improve the power capability of lithium iron phosphate, several approaches, such as carbon coating, doping, and/or particle size reduction, have been successfully utilized to mitigate the poor electronic conductivity and slow lithium ion diffusion. However, electrode engineering is also very critical, but easily overlooked, to fully optimize its electrochemical performance in lithium ion batteries. Electrode engineering becomes increasingly important when the active material is less electronically conducting and has a very small particle size, such as LiFePO₄. In this work, a carbon coated LiFePO₄ with sub-micron particle size is investigated for high power applications, such as a hybrid electric vehicle (HEV) and a plug-in HEV (PHEV). This study will focus on how the engineering process affects the cell impedance and its electrochemical performance. Results and Discussion Active lithium iron phosphate (LiFePO₄) (including 6 wt.% carbon coating) was mixed with 4 wt.% SFG-6 graphite, 4 wt.% acetylene black, and 8 wt.% PVDF binder. The cast electrode laminate was calendared into different thickness, corresponding to various porosities. The electronic conductivity of the electrode was checked using a four point probe method, which indicated that the electronic resistance increased with increasing electrode porosity. In general, the electronic resistance of the cast electrode can be attributed to the carbon/olivine, carbon/carbon, and electrode composite/current collector contact resistances. In order to elucidate the contribution of the electronic resistance to the overall impedance, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM) were carried out. It is obvious from SEM images that the low porosity olivine electrode has better contact. The EIS results indicate that the high particle/particle electronic contact resistance seems to be a major contributor to the overall impedance of the sub-micron carbon coated olivine electrode with less calendaring. Direct Current (DC) studies on Lithium/LiFePO₄ half cells, fabricated using the electrodes with various porosities, were also conducted. The cells were subjected to the hybrid pulse power characterization (HPPC) test for electrochemical performance evaluation. Lower area specific impedances were obtained for the electrodes with correspondingly lower porosity (i.e. more extensive calendaring). The studies indicate that the sub-micron carbon coating olivine, when optimized, is a very promising cathode material for HEV/PHEV applications once the electrode is properly prepared.

U4.40

High Performance Supercapacitor based on Polyaniline Nanowires /Carbon Cloth Flexible Electrode. Ying-Ying Horn^{1,2}, Yi-Chen Lu^{1,2}, Yu-Kuei Hsu³, Chia-Chun Chen^{1,3}, Li-Chyong Chen² and Kuei-Hsien Chen^{3,2,1}; ¹Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan; ²Center for National Taiwan Normal University, Teipei, Taiwan; ³Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

Excellent electrochemical performance was achieved from polyaniline nanowires (PANI-NWs) electrode directly grown onto a porous carbon cloth (CC) via electrochemical technique. The three-dimensional architecture of these nanowires not only showed remarkable increase in the electrochemical performance, but also exhibited high gravimetric capacitance of 1079 Fg⁻¹ at a specific energy of 100.9 Whkg⁻¹ and a specific power of 12.1 kWkg⁻¹. Especially, an exceptionally high area-normalized capacitance of 1.8 Fcm⁻² was achieved. The diffusion length of protons within the PANI-NWs was estimated to be about 60 nm by electrochemical impedance analysis, which indicates that the electrochemical performance of the electrode is not limited by the thickness of PANI-NWs. These results clearly present a cost-effective and simple method of fabrication of the NWs with enormous potential in energy storage device applications.

U4.41

Preparation of Orientation-controlled LiCoO₂ Epitaxial Thin Films. Hideki Oki¹, Taro Hitosugi^{2,3}, Tetsukazu Tsuruhama⁴ and Tetsuya Hasegawa^{3,4}; ¹Battery Research Div., Toyota Motor Corporation, Susono, Japan; ²WPI, Tohoku University, Sendai, Japan; ³Kanagawa Academy of Science and Technology, Kawasaki, Japan; ⁴Department of Chemistry, The University of Tokyo, Tokyo, Japan.

Layered-rhombohedral LiCoO₂, a typical electrode material for Li-ion batteries, has been intensively studied in polycrystalline form due to the easiness of preparation and link to applications. The mechanism of Li-ion and electron conductivity in intra-grain LiCoO₂ has not been elucidated, since polycrystalline samples include many grain boundaries that hide the properties of intra-grain properties. Therefore, investigation of the mechanism of Li-ion and electron conductivity requires high quality epitaxial thin films or large single crystals. In this study, we prepared orientation-controlled LiCoO₂ epitaxial thin films, and cyclic voltammogram was measured. We succeeded in the preparation of LiCoO₂ epitaxial thin films on Al₂O₃(0001) and metal (Au and Pt) substrates using pulsed laser deposition. Annealing precursor films deposited at substrate temperature (T_{sub}) of room temperature, resulted in the formation of LiCoO₂ films with flat surface. In contrast, the surface of the film deposited at T_{sub} = 500°C showed island structures with secondary phase such as Co₃O₄. From X-ray diffraction analysis, we confirmed that LiCoO₂(0001) plane is parallel to the substrate Al₂O₃(0001) surface, indicating that the direction of Li-ion conductivity and the CoO₂ layer is in a plane parallel to the substrate. The pole figure measurement of the LiCoO₂ confirmed epitaxial relation of [10-10]Al₂O₃ // [1000]LiCoO₂. On Pt and Au (100) and (111) substrates, the CoO₂ layer is parallel to the substrates, while on (110), the layer is perpendicular. Although XRD measurement indicates single phase, Raman spectroscopy and transmission electron microscopy reveal that the films include a trace of Co₃O₄. Cyclic voltammogram (CV) measurements were performed on LiCoO₂(110) on Pt(110) and LiCoO₂(001) on Pt (111) // 1M LiClO₄ in EC/DEC // Li metal cell. The latter showed no electrochemical activity, while the former appeared reversible peaks at 3.93 V(D1), 4.08 V(D2) and 4.17 V(D3) on discharge, and at 3.90 V(C1), 4.05 V(C2) and 4.16 V(C3) on charge. The main D1-C1 peaks correspond to de-intercalation/intercalation reaction of Li ion. Other small peaks are attributed to phase transitions. This electrochemical behavior is similar to powder samples, showing that our thin films are capable for the further analysis of the physical and chemical properties of Li-ion conductivity.

U4.42

Electrochemical Lithium Intercalation into Cation-Substituted LiMnPO₄ Electrode. Jong-Won Lee, Jin-Hwan Park, Meen-Seon Paik and Seok-Gwang Doo; Energy Laboratory, Samsung Advanced Institute of Technology, Yongin, Gyeonggi-do, Korea, South.

A lithium manganese phosphate (LiMnPO₄) with an orthorhombic olivine structure shows a redox potential of 4.1 V vs. Li/Li⁺, resulting in a higher energy density when compared with LiFePO₄ operating at 3.4 V vs. Li/Li⁺. These properties combined with good thermal stability and low materials cost make LiMnPO₄ attractive as an alternative electrode to LiFePO₄ and other transition metal oxides. With few exceptions, however, much lower reversible capacities have been typically obtained for LiMnPO₄. Several hypotheses have been proposed in the literature to explain such poor electrochemical performances, including Jahn-Teller instability caused by Mn³⁺ ions, low ionic/electronic conductivities and large mechanical strains developed at the boundary of Li-rich and -poor phases. The present work examines the structural and electrochemical properties of LiMnPO₄ in which various divalent and/or supervalent cations were substituted for part of Mn atoms. The materials were synthesized by a solid-state reaction route in the presence of high-surface area carbons and then were subject to extensive characterizations to evaluate their structures and electrochemical behaviors. The experimental results indicate that the materials are tolerant, to some extent, to cation substitution, and the reversible capacity and polarization resistances strongly depend on the ionic size, oxidation state and concentration of the substituent atoms introduced into the LiMnPO₄ structure.

U4.43

Electrochemical Li-ion Storage in Oriented Anatase TiO₂ Nanotubes Arrays. Jae-Hun Kim, Kai Zhu, Qing Wang, Ahmad A. Pesaran and Arthur J. Frank; National Renewable Energy Laboratory, Golden, Colorado.

Oriented nanostructures arrays (e.g., nanotubes) have shown promise for advanced Li-ion batteries [1,2]. Such batteries are of interest due to their improved energy density, rate capability, and cycling stability. Oriented nanotube (NT) arrays with their linear arrangement of pores are expected to facilitate fast electronic/ionic conduction and to accommodate significant volume changes of the electrode materials during charge/discharge cycling. Among the various electrode materials, TiO₂ has attracted [3-5] attention because of their high rate capability and enhanced safety, which are essential properties of rechargeable Li-ion batteries and supercapacitors for hybrid electric vehicle (HEV) applications. In this presentation, we discuss the electrochemical characteristics of anatase TiO₂ NT arrays as negative electrode materials for Li-ion batteries. The NT arrays, which are aligned normal to a substrate, were fabricated by electrochemical anodization of Ti foil. Galvanostatic charge/discharge measurements show that reversible Li⁺ storage capacities of the NT electrodes at low current rates were higher than the theoretical value for bulk materials. Analyses of cyclic voltammograms indicate that there is significant pseudocapacitive Li⁺ storage associated with the NT surface in addition to the Li⁺ storage within the bulk material. The NT film morphology (e.g., pore diameter, wall thickness, NT length) and pore alignment are found to affect significantly the Li insertion-extraction kinetics (e.g., electrons/ions conduction and interfacial charge transfer) and the performance of the electrodes in Li-ion batteries. These results and others are discussed. [1] C. K. Chan et al., Nat. Nanotechnol. 3, 31 (2008). [2] L. Taberna et al., Nat. Mater. 5, 567 (2006). [3] L. Kavan et al., Chem. Mater. 16, 477 (2004). [4] Y. S. Hu et al., Adv. Mater. 18, 1421 (2006). [5] A. R. Armstrong et al., Adv. Mater. 17, 862 (2006).

U8.44

Sn/SnO_x Core-Shell Nanoparticles as Anodes for Lithium Batteries. Xiao-Liang Wang and Weiqiang Han; Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

Tin is an attractive anode material for lithium batteries, principally due to its high theoretical capacity of 994 mAh/g, far more than that of state-of-art graphite (372 mAh/g). Sony's recent commercialization of a tin-based anode further triggered research in this

material. Besides its high capacity, tin possesses other favorable characteristics: (1) Slightly higher operating potential than graphite; (2) no solvent co-intercalation; and, (3) a high lithium-diffusion coefficient at room temperature. However, its cycling stability is poor, i.e., inferior capacity retention and reversibility. It is also difficult for tin to be fully lithiated and achieve the theoretical capacity. For example, Ui et al. demonstrated that the initial capacity of ca. 750 mAh/g of an electroplated tin anode decreased precipitously to ca. 200 mAh/g just in the second cycle. One cause is its huge volume change upon cycling; another is the slow rate of Li^+ extraction. Among the routes to resolving these problems is employing small-grained tin, especially nano tin. This approach could suppress the absolute volume change, and shorten the diffusion distance for Li^+ . While many studies have demonstrated the merits of nano tin, most dealt with single size-ranges. To understand better the effect of nano size, it is essential to study the cell performance of tin over a wide range of sizes. We synthesized different sized tin particles, from ca. 20 nm to ca. 700 nm. Interestingly, these nanoparticles are Sn/SnO_x core-shell nanostructures; typically, the thickness of the SnO_x shells is about several nanometers, as revealed by TEM and EDS. We discuss the effect of size of this type of core-shell nanostructure on cell performance. This work is supported by the U. S. DOE under contract DE-AC02-98CH10886 and E-LDRD Fund of Brookhaven National Laboratory. We thank Drs. Feng Wang, Jason Graetz, Xiao-Qing Yang, and Yimei Zhu (BNL) for their technical help and valuable discussions.

U4.45

Highly Improved Fe₃O₄ Electrodes for Lithium-ion Battery. Chunmei Ban, Zhuangchun Wu, Jeffrey Blackburn, Dane T. Gillaspie and Anne Dillon; National Renewable Energy Laboratory, Golden, Colorado.

New electrodes with large reversible capacities and high rate capabilities are aimed to accelerate the development of all-electrical vehicles for commercial uses. The classical intercalation electrodes has benefited from nano-technologies to achieve stable performance, however the intrinsic capacities due to inability of insertion more than one Li^+ ion per 3d metal barely satisfy the demand of high capacities. As potential negative electrodes, transition metal oxides having conversion reactions during discharging/charging exhibit large, reversible capacities. But such electrodes using conversion chemistry suffer not only from low ionic and electronic conductivity that other electrodes also forbear with, but also from the volume change and the formation of agglomerated cluster due to conversion reactions. Thus Nano-architected electrodes by employing nano Fe₃O₄-CNTs (carbon nanotubes) composite materials are presented here to prevent the severe fade observed when using commercial Fe₃O₄ materials as an anode in Li-ion cells. High capacities (nearly theoretical capacity of 926 mAhg⁻¹) have been achieved and maintained for hundreds of cycles even at C rate. By using above 95% hydrothermally made nano-Fe₃O₄ materials in the electrodes, high energy densities of the cells have been obtained. The very low amount of CNTs using in the composite nanomaterials, produced by a laser vaporization method, doesn't lessen the advantages of magnetite as a low-cost, environmentally friendly anode material for Li-ion batteries. The synthesis of nano Fe₃O₄-CNTs materials, the surface and structural analysis of the electrodes will be discussed in this presentation,

U4.46

Phase Stability Study of Li_{1-x}MnPO₄ (0 ≤ x ≤ 1) Cathode for Li Rechargeable Battery. Sung-Wook Kim, Jongsoon Kim, Hyeokjo Gwon and Kisuk Kang; Department of Materials Science and Engineering, KAIST, Daejeon, Korea, South.

Olivine-type LiMPO₄ (M = Fe, Mn, Co, Ni) compound is one of the promising cathode materials for Li rechargeable battery due to its high stability originated from strong PO₄³⁻ bonding. While LiFePO₄ is a leading candidate among the olivine-type electrode materials, its intrinsically low energy density has been problematic. LiMnPO₄ can theoretically deliver high energy density than its Fe counter part due to the high redox potential of Mn²⁺/Mn³⁺ vs. Li/Li⁺ (4.1 V). However, the utilization of its theoretical energy density has not been easily demonstrated even in mild operating conditions. Many factors have been considered to contribute to the difficulty in utilization such as low electronic/ionic conductivity, small polaronic conduction of Jahn-Teller active Mn³⁺, sluggish phase boundary movement, high surface energy barrier for Li diffusion, and the metastable nature of the delithiated phase. However, clear understanding of these factors has not yet been established, and intensive research efforts on the LiMnPO₄ system are still in progress. Phase stability of Li_{1-x}MnPO₄ (0 ≤ x ≤ 1) is investigated in this study for different Li compositions and temperatures by electron microscopy and high temperature XRD. The Li_{1-x}MnPO₄ is prepared by chemical delithiation of LiMnPO₄ using NO₂BF₄ in acetonitrile. The clear two-phase reaction between LiMnPO₄ and MnPO₄ is confirmed by XRD during the delithiation. Electron microscopy study indicates the instability of the delithiated phase. The morphology of LiMnPO₄ is found to be severely destructed upon delithiation. The map of stable phases is determined at temperature ranges between room temperature and 410 °C. While pure LiMnPO₄ phase is stable at high temperature, partial phase transformation of MnPO₄ into Mn₂P₂O₇ is observed in delithiated phases above 210 °C with following oxygen evolution reaction. $2\text{MnPO}_4 \rightarrow \text{Mn}_2\text{P}_2\text{O}_7 + 1/2\text{O}_2$ Since it is widely known that PO₄³⁻ bonding in the olivine-type compound is strong, it is noticeable that O₂ gas evolution can readily occur through decomposition at a temperature as low as 210 °C. The irreversible phase transformation of the delithiated phase, if it occurs, will deteriorate the electrochemical performance of a LiMnPO₄ electrode. In comparison, PO₄³⁻ bonding is reported to be stable up to 500 °C in various Li composition of Li_{1-x}FePO₄. The instability of the delithiated phase and the phase transformation into Mn₂P₂O₇ may imply that safety concerns can be raised regarding the LiMnPO₄ cathode, unlike its Fe counterpart.

U4.47

The Effect of Al₂O₃-Coating Coverage on the Electrochemical Properties in LiCoO₂ Thin Films. Yuhong Oh, Donggi Ahn, Seunghoon Nam and Byungwoo Park; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea, South.

The electrochemical properties of nanoscale Al₂O₃-coated LiCoO₂ thin films were examined as a function of the coating coverage. Al₂O₃-coated LiCoO₂ films showed enhanced cycle-life performance with increasing degree of coating coverage, which was

attributed to the suppression of Co dissolution from LiCoO_2 . Moreover, an Al_2O_3 -coating layer with partial coverage clearly improved the electrochemical properties, even at 60°C or with a water-contaminated electrolyte. Even though metal-oxide coating on LiCoO_2 has been actively investigated, the mechanisms of nanoscale coating have yet to be clearly identified. Through the surface analysis, it is suggested that the Al_2O_3 -coating layer had transformed to an $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ layer during cycling, which inhibited the generation of HF by scavenging H_2O molecules present in the electrolyte. [1] B. Kim, C. Kim, D. Ahn, T. Moon, J. Ahn, Y. Park, and B. Park, *Electrochem. Solid-State Lett.* **10**, A32 (2007). [2] Y. J. Kim, H. Kim, B. Kim, D. Ahn, J.-G. Lee, T.-J. Kim, D. Son, J. Cho, Y.-W. Kim, and B. Park, *Chem. Mater.* **15**, 1505 (2003). Corresponding Author: Byungwoo Park: byungwoo@snu.ac.kr

U4.48

The Effect of Synthesis Temperature and Stoichiometry on the Electrochemical Properties of $\text{Li}[\text{Li}_{1/3-2x/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$. Christopher R. Fell and Shirley Meng; Materials Science and Engineering, University of Florida, Gainesville, Florida.

The layered lithium-excess oxide compounds $\text{Li}[\text{Li}_{1/3-2x/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ are of interest as a new generation of cathode materials for high energy density lithium-ion batteries. This series of compounds were first reported by Lu and Dahn, and Ohzuku et al. in 2001.^{1,2} Three Ni^{2+} ions substitute for two Li^+ ions and one Mn^{4+} ion in the layered compound Li_2MnO_3 ($\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$).

Additional Li ions are present in the transition metal layers and results in additional superstructure peaks. Following lithium deintercalation and the associated oxidation of Ni^{2+} to Ni^{4+} , lithium may continue to be extracted from this material despite the fact that all the manganese and nickel ions are in their fully charged (+4) oxidation state. Our research has found that formation of a pure layered material depends on the synthesis conditions. The key processing conditions include stoichiometry, sintering temperature and cooling rate. The electrochemical properties of the synthesized materials depend highly on these parameters. Optimized materials exhibit high capacity at reasonable rates. To improve the rate capabilities of this material it is important to understand the atomistic delithiation mechanisms. We will compare the high voltage phase stability and rearrangement of cation ions through a combination of X-ray diffraction and electron microscopy of the Li-excess electrode materials with varying synthesis conditions. References: 1. Lu, Z. H.; MacNeil, D. D.; Dahn, J. R., *Electrochem. Solid St. Lett.* A200 (2001). 2. T. Ohzuku and Y. Makimura, *Chemistry Letters*, 744 (2001).

U4.49

Using Calorimetric Data in Conjunction with Modeling to Make Inherently Safer Li-Ion Batteries. Peter J. Rabovsky¹ and Elena Moukhina²; ¹Netsch Instruments, Burlington, Massachusetts; ²BU Analyzing & Testing, NETZSCH-Gerätebau GmbH, Selb, Germany.

Accelerating Rate Calorimetry (ARC®) and Differential Scanning Calorimetry (DSC) are commonly used to study the materials used in manufacturing Li-ion cells. Materials are looked at alone and in combination with each other to measure thermal stability and to determine the chemical compatibility of the components with each other. Adiabatic calorimeters have been used to study components but also full operating cells as well. Instruments have been designed to allow the cycling of batteries inside the calorimeter so that exotherms can be monitored. Some instrument manufacturers have even created large scale adiabatic calorimeters to measure large battery and battery packs. This approach is fundamentally flawed. A better approach is to measure kinetics at the small scale (i.e., 18650 size or less) and then use modeling to determine the effects of "bulk" heating of the battery or the thermal effects of shorts within the battery itself. Various calorimetric techniques are used to develop the data for screening components and for proper model development. Adiabatic calorimetry, DSC, Simultaneous Thermal Analysis (STA) coupled with an analytical finish, and isothermal calorimetry are all useful in developing the thermodynamic and kinetic information required for model development. Good thermal property data on the materials is also important.

U4.50

Control of Point Defects in Olivine-Type LiFePO_4 Nanocrystals for High-Power Li Batteries. Sung-Yoon Chung, Materials Sci. & Eng., Inha University, Incheon, Korea, South.

In a number of Li intercalation compounds in which an ordered array of Li is usually maintained, the control of point defects including cation disordering is of major significance for application to electrodes in rechargeable cells. Furthermore, as the chemically different environment induced by point defects leads to breaking of the ordered arrangement of atoms in crystals with a complex structure, mass and charge transport behaviors are also considerably affected by the presence of the defects. A variety of investigations on Li vacancies and cation intermixing have been reported for layered oxides. In contrast, few experimental details revealing the atomic-scale point defects in olivine-type lithium metal phosphates, LiMPO_4 (where $M = \text{Fe, Mn, Ni, Co}$), available in the literature (S.-Y. Chung *et al.*, *Phys. Rev. Lett.*, **100**, 125502 (2008); *Angew. Chem. Int. Ed.*, **48**, 543 (2009)), while these phosphates have attracted a great deal of attention as alternative cathode materials in Li-ion cells over the past decade (S.-Y. Chung *et al.*, *Nature Mater.*, **1**, 123 (2002)). Proper control and direct identification of their distribution in the lattice on the basis of crystal chemistry will be crucial steps toward enhancement of effective Li mobility during the intercalation reaction in olivine phosphates. In this presentation, the observations of a variety of lattice defects in ordered olivine LiFePO_4 crystals after rapid phase transformation during crystallization (S.-Y. Chung *et al.*, *Nature Phys.*, **5**, 68 (2009)) will be presented, showing notable distribution behaviors of the defects. For this direct observation, in situ and ex situ high-resolution transmission electron microscopy is utilized. This analysis suggests that the lattice defects in LiFePO_4 can be adjusted for improved Li ion transport.

U4.51

Process Kinetics During RF Sputtering of LiCoO₂ Thin Films for Micro Battery Applications. Nimisha Cs¹, Venkatesh Gopal², Thulasi Raman Kh¹, Munichandraiah Nookala² and Mohan Rao Gowravaram¹; ¹Instrumentation, IISc, Bangalore, Karnataka, India; ²Inorganic and Physical chemistry, Indian Institute of Science, Bangalore, India.

Sputtering from multi-elemental targets often results in non-stoichiometric films when the target is not conditioned for a stable composition. In this study we present the target conditioning analysis of LiCoO₂ sputter cathodes in terms of the real time monitoring and analysis of neutral and ionic species of elements present in the Rf plasma using Optical Emission Spectroscopy (OES). During these studies it was also seen that the target-substrate distance plays a major role in achieving the required composition in the deposited films. The X-ray photoelectron spectroscopy (XPS) core level spectrum of Li⁺, Co³⁺ and O²⁻ of films sputtered from a conditioned target is presented. Electrochemical data in relation to these process parameters supports the optimum substrate to target distance predicted by OES. The optimized conditions for the deposition of good quality LiCoO₂ films with a capacity of 64 microAmpHr/cm²/μm are given. These conditions are different from the data available in the existing literature, where it was demonstrated that good quality films could be deposited at larger target-substrate distance. Our study shows that due to thermalization distance of different elements, a target-substrate distance of 5 cm is ideal and this was supported by OES data.

U4.52

Abstract Withdrawn

U4.53

Averting Cracks Caused by Insertion Reaction in Lithium-ion Batteries. Yuhang Hu, Xuanhe Zhao and Zhigang Suo; Mechanical engineering, Harvard University, Cambridge, Massachusetts.

In a lithium-ion battery, both electrodes are atomic frameworks that host mobile lithium ions. When the battery is being charged or discharged, lithium ions diffuse from one electrode to the other. Such an insertion reaction deforms the electrodes, and may cause the electrodes to crack. This paper uses fracture mechanics to determine the critical conditions to avert cracking. The method is applied to cracks induced by the mismatch between phases in crystalline particles of LiFePO₄.

U4.54

High-Performance Li-ion Battery Cathodes Using Prelithiated Ferroselite Nanoflowers. Liqiang Mai^{1,2}, Shuang Yang¹, Yuan Gao¹, Lin Xu¹ and Bin Hu¹; ¹State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, Hubei, China; ²Department of Chemistry and Chemical Biology, Harvard University, Boston, Massachusetts.

Recently, considerable attention has been devoted to complex nanostructures with different morphology, orientation, and dimensionality due to their size- and shape-dependent photocatalytic, optical, electrical, photoelectric properties. Ferroselite (FeSe₂) has been investigated as a VIII-VI semiconductor with a direct 1.0 eV band gap and as a model system to explore chemical processes and applications in electronics, optics, optoelectronics, spintronics and batteries. Until now, there are few reports on synthesis of FeSe₂ nanoflowers, and Li⁺ ion insertion and extraction behavior and electrochemical properties for this novel nanomaterial are very poorly understood, which limits their wide application in energy field. In the present work, ferroselite (FeSe₂) nanoflowers have been prepared by a mild hydrothermal method at 170°C with Na₂SeSO₃ and FeC₂O₄ as the raw materials, and prelithiated through a secondary hydrothermal reaction with Li salt solution. The products were characterized by XRD, FE-SEM, EDS, CV and model battery testing. The results show that the as-prepared FeSe₂ nanoflowers composed of uniform nanoplates about 20 nm in thickness and 100 nm in diameter, exhibit high discharge capacity of ca. 431 mAh/g. Notably, the capacity retention rate of FeSe₂ nanoflower electrodes is greatly improved from 45% before lithiation to 63% after lithiation through secondary hydrothermal lithiation modification and this improvement of cycling property is confirmed by CV investigation, probably resulting from increase of structure stability and weakening of electrostatic interaction between FeSe₂ layers and Li⁺ ions in interlayer during the discharge when Li ions occupy the interstitial site of FeSe₂ lattice. It is shown that the prelithiated FeSe₂ nanoflowers exhibit good cycling capability and it is suitable for use as high-property electrode material in rechargeable lithium-ion batteries. Acknowledgements This work was supported by the National Nature Science Foundation of China (50702039), the Research Fund for the Doctoral Program of Higher Education (20070497012), Scientific Research Foundation for Returned Scholars, Ministry of Education of China (2008-890) and Innovation Special Foundation of Excellent Returned Scholars of Wuhan (2008-84). The authors are pleased to thank the strong support and helpful discussion of Prof W Chen and Prof JG Guan of Wuhan University of Technology.

U4.55

Abstract Withdrawn

U4.56

Abstract Withdrawn

SESSION U5: Modeling and Simulation of Battery Materials
Chair: Katsumi Kaneko
Tuesday Morning, December 1, 2009

Room 200 (Hynes)

8:30 AM *U5.1

Ionic Liquids as Electrolytes for Electrical Energy Storage: Insights from Molecular Dynamics Simulations. Grant D. Smith, Oleg Borodin and Jenel Vatamanu; Materials Science and Engineering, University of Utah, Salt Lake City, Utah.

Room temperature ionic liquids (ILs) are receiving increasing attention as electrolytes in lithium battery and supercapacitor applications for a variety of reasons, including a wide electrochemical stability window, low volatility, ability to dissolve lithium salts, ability to form high-capacitive double layers, and not least, the tremendous number of conceivable cation/anion combinations. In both battery and supercapacitor applications, the properties of the interface between the electrolyte and the electrode are of paramount importance in understanding the performance of the electrical energy storage devices and how to improve both power and energy density of the device. We have employed atomistic molecular dynamics simulations utilizing a new electroactive interface methodology that allows us to control the potential of the electrode during the simulation in order to study the structure and dynamics of IL-based electrolytes at the interface with model electrodes for both battery and supercapacitor applications. I will present insights we have gained into these important interfaces from our simulation studies.

9:00 AM U5.2

Mathematical Models for Optimizing Electrode Shape, Size and Charging Conditions for Durable Li Ion Battery. Rutooi D. Deshpande¹, Yang-Tse Cheng¹ and Mark W. Verbrugge²; ¹Department of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky; ²Materials and Processes Laboratory, General Motors R&D Center, Warren, Michigan.

Abstract: Diffusion induced stresses (DISs) in Li ion battery electrodes can cause cracking of the electrodes which limits battery cycle life. We are developing several mathematical models [1, 2, 3, 4] relating DISs with lithium concentration in the electrode material, electrode geometry, and charging condition. In this paper, we show that at nano scale, surface stress and surface tension play an important role in mitigating cracking caused DISs. We model these stresses and strain energy for different operating conditions, such as galvanostatic and potentiostatic charging and discharging. We also consider several electrode geometries, including nanowires, nanotubes, and nano-particles. We show that these models can be used to help develop strategies to increase battery life by optimizing electrode geometry and size, as well as charging conditions. [1] Y.-T. Cheng and M. W. Verbrugge, The influence of surface mechanics on diffusion induced stresses within spherical nanoparticles, *J. Appl. Phys.* 104, 083521 (2008). [2] M. W. Verbrugge and Y.-T. Cheng, Stress Distribution within Spherical Particles Undergoing Electrochemical Insertion and Extraction, *The Electrochemical Society (ECS) Transactions* 16, 127 (2008). [3] Y.-T. Cheng and M. W. Verbrugge, Evolution of stress within a spherical insertion electrode particle under potentiostatic and galvanostatic operation, *J. Power Sources* 190, 453 (2009). [4] M. W. Verbrugge and Y.-T. Cheng, Stress and strain-energy distributions within diffusion-controlled insertion-electrode particles subjected to periodic potential excitations, *J. Electrochem. Soc.* (to be published).

9:15 AM U5.3

Elucidation of Layered Cathode Material from First-principles Computational Studies and its Structural and Electrochemical Behavior. Jose J. Saavedra-Arias¹, Reji Thomas¹, Loraine Torres¹, Yasuyuki Ishikawa² and Ram S. Katiyar¹; ¹Department of Physics, University of Puerto Rico, San Juan, Puerto Rico; ²Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico.

Nowadays, the implementation of combined experimental/computational studies is probably the best way to understand the physical and chemical properties of materials and to discover new materials for different technological applications. Hence, the study of new cathode materials by first-principles calculations and their experimental characterization can be the most efficient way to find the proper substitute for LiCoO₂. In the present study, we first employed ab initio calculations to screen layered cathode materials, and then synthesize and study electrochemical properties of the best candidate. Our first-principles calculations were performed in the local density approximation (LDA) to density-functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP). In order to reduce the number of the plane waves required for simulating the interactions between ions and electrons, ultra-soft Vanderbilt pseudo-potentials have been used. All structures were fully relaxed with respect to external and internal parameters. The substitution of the transition metal atoms was performed by equivalent position replacement for minimizing the energy of the system. By the alloy metal method (D. de Fontaine, *Solid State Physics*; H. Ehrenreich, D. Turnbull, Eds, p. 33, 1994), we analyzed the interactions between the transition metals by examining the energy of the solid solution. The computed energies of the transition metals in Li-layered structure may be obtained by the expression, $\Delta E_{\text{mix}} = E(\text{LiNi}_{(1-x-y)}\text{Co}_x\text{Mn}_y\text{O}_2) - (1-x-y)E(\text{LiNiO}_2) - xE(\text{LiCoO}_2) - yE(\text{LiMnO}_2)$. Based on the phase stability, the composition $\text{LiNi}_{0.66}\text{Co}_{0.17}\text{Mn}_{0.17}\text{O}_2$ revealed the formation energy below zero, suggesting that the compound may be synthesized readily. At full delithiation, the ΔE_{mix} is positive, suggesting repulsion between the transition metals. We carried out phase-stability calculations of the structures up to 50% delithiation, and found that this composition shows the highest stability. These results indicate that the compound $\text{LiNi}_{0.66}\text{Co}_{0.17}\text{Mn}_{0.17}\text{O}_2$ is a potential candidate material for cathode application in Li-ion rechargeable batteries. Therefore, this compound was prepared by sol-gel process. Calcinations conditions (time, ambient and temperature) were optimized for the single-phase formation of the layered structure. The structural properties were investigated using X-ray diffraction (XRD) and Raman Spectroscopy. Electrochemical testing was done on the coin cells (cathode/LiPF₆ electrolyte/Li-foil anode) with Cyclic Voltammetry, and the galvanostatic charge-discharge methods. These results, along with Li⁺ diffusion and cycleability, will be presented.

9:30 AM U5.4

Computational Design of a Hybrid Organic-Inorganic Li-Ion Conductor. Jinhua Zhou and John Kieffer; Materials Science and

Engineering, University of Michigan, Ann Arbor, Michigan.

The role of electrolytes in batteries and fuel cells is to effectively separate the reactants, selectively mediate the transport of specific ions that establish the electrochemical process responsible for power generation, and provide sufficient structural rigidity to ensure the mechanical stability of the device. As these are in effect opposing qualities, promising designs of electrolyte materials are often based on a composite approach. Accordingly, we pursue hybrid materials in which a rigid inorganic and a flexible organic component are linked at the molecular level. To efficiently identify the basic design concepts for such materials, we rely on simulations guiding the experimental developments. We carry out large-scale molecular dynamics (MD) simulations based on a reactive force field that we developed, to first generate realistic structural models of the porous networks by reproducing the self-assembly processes of the hybrid building blocks. Using the models so created, we then study the mechanisms underlying ionic transport and establish the relationship between conductivity, materials chemistry, and pore structure. We present the case study of lithium ion transport in a structure constructed from polyhedral oligomeric silsesquioxane (POSS) cubes functionalized with alkane chains of various lengths. In one case the lithium is donated by a siloxy group connected to the POSS cube and in the other case by a carboxyl group connected to the free tail of the alkane chain. Li⁺ conductivity is significantly higher in the latter case, but not as expected because of the higher range of motion provided by flexibility of the alkane chain. The insights gained from this study suggest a specific synthesis route for electrolyte materials.

SESSION U6: Novel Approaches to Advanced Batteries
Chair: Katsuhiko Naoi
Tuesday Morning, December 1, 2009
Room 200 (Hynes)

10:15 AM *U6.1

Fabricating Genetically Engineered High Power Lithium Ion Batteries Using Multiple Virus Genes. [Angela Belcher](#)^{1,5}, Yun Jung Lee¹, Hyunjung Yi¹, Woo-Jae Kim², Kisuk Kang^{3,4}, Dong Soo Yun¹, Michael Strano² and Gerbrand Ceder¹; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea, South; ⁴Institute for Eco-Energy, Korea Advanced Institute of Science and Technology, Daejeon, Korea, South; ⁵Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Development of materials that deliver more energy at high rates is important for high power applications including portable electronic devices and hybrid electric vehicles. For lithium ion batteries, reducing materials dimensions can boost Li⁺ ion and electron transfer in nanostructured electrodes. By manipulating two-genes, viruses were equipped with peptide groups with affinity for single-walled carbon nanotubes (SWNTs) on one end and peptides capable of nucleating amorphous iron phosphate (a-FePO₄) fused to the viral major coat protein. The virus clone with the greatest affinity towards SWNTs enabled power performance of a-FePO₄ comparable to that of crystalline lithium iron phosphate (c-LiFePO₄) and showed excellent capacity retention upon cycling at 1C. This environmentally benign low temperature biological scaffold could facilitate fabrication of electrodes from materials previously excluded because of extremely low electronic conductivity.

10:45 AM U6.2

Kinetics of the Lithium (Per)Oxide Decomposition in Lithium-Air Batteries. Yi-Chun Lu^{2,3}, [Hubert A. Gasteiger](#)^{2,3}, Ethan Crumlin^{2,3}, Robert McGuire^{4,3} and Yang Shao-Horn^{1,2,3}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Electrochemical Energy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁴Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

In lithium-air batteries, the traditional positive intercalation electrode is replaced by a porous air electrode, which catalyzes the formation of lithium (per)oxide (discharge reaction) and its decomposition into oxygen and lithium ions (charging reaction). Battery tests with these air electrodes were shown to exceed the energy density of conventional positive intercalation electrodes, promising the development of sufficiently light-weight lithium-air batteries for plug-in electric vehicles. However, the overpotential for the charging reaction, i.e., the oxygen evolution reaction (OER), is very large and significantly reduces the efficiency of the battery. Therefore, improved OER catalysts are required for lithium-air batteries, but little is currently known about the kinetics of this reaction. Unfortunately, determination of the reaction kinetics of the OER in actual lithium-air batteries is compromised by undefined mass transport losses, caused by plugging of electrode pores with solid lithium (per)oxide and by undefined contact between the catalytically active surfaces and the lithium ion conducting electrolyte. Therefore, we developed a novel rotating disk electrode (RDE) approach which allows to determine the OER kinetics on model electrode surfaces in the absence of undefined mass transport resistances. Applying this method, we will present a detailed study of the lithium (per)oxide decomposition reaction in a lithium ion conducting organic electrolyte (PC:DME (1:2, by volume) and 1M LiClO₄) on glassy carbon and noble metal disk electrodes as well as on oxide electrodes prepared by thin-film deposition methods. Mechanisms of the reaction kinetics on these model surfaces will be discussed.

11:00 AM U6.3

Design of Free-standing Electrodes for 3D Architected Li-ion Micro-batteries. [Emilie Perre](#)^{1,2}, Manikoth M. Shaijumon¹, Pierre-Louis Taberna¹, Torbjorn Gustafsson², Kristina Edstrom² and Patrice Simon¹; ¹CIRIMAT, Université Paul Sabatier, Toulouse cedex 9, France; ²Materials Chemistry, Uppsala Universitet, Uppsala, Sweden.

Due to increasing demand of faster, better, smaller energy storage systems research onto Li-ion batteries is facing new challenges. New batteries not only based on new materials but also on new designs are now considered in order to fulfil the upcoming energy and power requirements. In this context, the conception of 3-dimensional nano-architected micro-batteries is being explored. Such battery designs have been considered in order to maintain the advantages of thin films, especially fast kinetics, while greatly increase the content of active material, thus the capacity available, onto a small foot-print area(1). Different designs have already been presented and show improved performances compared to 2D batteries(2,3,4,5). We propose a 3D-battery design based on templated-growth of free-standing arrays of metallic current collector and subsequent deposition of active material and separator onto the 3D nano-structure. While electrodeposition appears as a tool of choice for the preparation of free-standing forest-like metallic current collectors, different synthesis techniques can be considered for the preparation of the subsequent coatings of active material and separator. Keeping in mind that the quality of the interfaces between the different battery components is of crucial importance, we are exploring different in-situ synthesis techniques being not only electrodeposition but also ALD or sol-gel methods. The advantages of the different techniques for the synthesis of 3D micro-batteries will be discussed. Experimental difficulties and electrochemical performances obtained for the 3D-structured cells will be presented and compared to those for 2D cells. Further, the synthesis of a thin, conformal and pinhole-free separator coating will be presented and its effect on the cell stability will be addressed. References (1)J. W. Long, B. Dunn, D. R. Rolison, H. S. White, Chem. Rev. 104 (2004) 4463. (2)D. Golodnitsky, V. Yufit, M. Nathan, I. Shechtman, T. Ripenbein, E. Strauss, S. Menkin, E. Peled, J. Power Sources 153 (2006) 281. (3)H. S. Min, B. Y. Park, L. Taherabadi, C. L. Wang, Y. Yeh, R. Zaouk, M. J. Madou, B. Dunn, J. Power Sources 178 (2008) 795. (4)P. L. Taberna, S. Mitra, P. Poizot, P. Simon, J. M. Tarascon, Nature Materials 5 (2006) 567. (5)S.-K. Cheah, E. Perre, M. Rooth, M. Fondell, A. Harsta, M. Boman, L. Nyholm, P. Simon, T. Gustafsson and K. Edström, Accepted by Nano Letters.

11:15 AM U6.4

LiCoO₂ with a Novel Concaved Cuboctahedron Morphology Formed from Lithiation of Cobalt Oxide. Hailong Chen¹, Lijun Wu², Lihua Zhang², Yimei Zhu² and Clare P. Grey¹; ¹Department of Chemistry, Stony Brook University, Stony Brook, New York; ²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

Most of the Li-intercalation compounds that have been studied as cathode or anode materials for lithium ion batteries (LIBs) have anisotropic 1-D or 2-D Li diffusion channels/layers. LiCoO₂ [1], the first cathode material to be used in commercial LIBs, has 2-D Li diffusion channels parallel to the *ab* planes of the lattice. LiFePO₄, a cathode material with good rate performance [2-4], has 1-D diffusion channels along the *b* direction, as demonstrated by both theoretical calculation [5] and neutron diffraction experimental observation [6]. Only a few electrode materials, such as LiMn₂O₄ [7] and other spinel materials with a cubic symmetry, have 3-D Li diffusion channels. The anisotropic 1-D or 2-D diffusion of Li in the lattice results in the inactivity of some surfaces of the electrode material particles towards Li-intercalation reactions. Thus, the electrochemical properties, especially the rate performance of these materials, are strongly morphologically dependant. In our previous work [8], we have demonstrated that by controlling the morphology and by forming a 3-D assembled nanostructure, the rate performance of LiCoO₂ can be greatly improved. Here we demonstrate that by choosing an appropriate precursor crystal and reaction conditions, the layered positive electrode material, LiCoO₂, which exhibits rhombohedral symmetry, can grow to form a quadruple-twinned crystal with overall cubic symmetry. The twinned crystals show an unusual, concaved-cuboctahedron morphology, with uniform particle sizes of 0.5-2 μm. On the basis of a range of synthetic and analytical experiments, including solid state NMR and X-ray powder diffraction analysis and HRTEM, we propose that these twinned crystals are formed via the selective dissolution and an ion-exchange reaction, accompanied by oxidation, of a cubic parent crystal of CoO; this is accompanied by the growth of four LiCoO₂ twin crystals. This "crystal engineering" converts a highly anisotropic, layered material into a pseudo-3-dimensional, isotropic material. Extended study on synthesis of other materials by using this method, such as LiFeO₂, which shows a different type of twinned morphology, implies the possibility of generalizing this approach to other intercalation compounds. Thus, this work opens up new opportunities to control the morphology of electrode materials for LIBs and this crystal engineering method is a promising approach to help improve the rate performance of LIBs in the future. 1. Mizushima, K., et al. Mater. Res. Bull. 1980, 15 (6), 783 2. Padhi, A. K. et al. J. Electrochem. Soc. 1997, 144 (4), 1188 3. Chung, S. Y. et al. Nat. Mater. 2002, 1 (2), 123 4. Kang, B. and Ceder, G., Nature 2009, 458 (7235), 190. 5. Islam, M. S., et al. Chem. of Mater. 2005, 17 (20), 5085. 6. Nishimura, S., et al. Nat. Mater. 2008, 7 (9), 707 7. Thackeray, M. M. et al. Mater. Res. Bull. 1983, 18 (4), 461. 8. Chen, H. L. and Grey, C. P., Adv. Mater. 2008, 20 (11), 2206.

SESSION U7: Hybrid Devices

Chair: John Miller

Tuesday Afternoon, December 1, 2009

Room 200 (Hynes)

1:30 PM U7.1

Nanohybrid Capacitor: A New Hybrid System, Triply Enhanced Energy Density of EDLCs by use of UC-derived nc-Li₄Ti₅O₁₂/CNF. Katsuhiko Naoi, Institute of Science and Technology, Tokyo University of Agriculture & Technology, Tokyo, Japan.

There is presently a major effort to increase the energy density of EDLCs up to a target value in the vicinity of 20 Wh kg⁻¹. One important alternative approach to meet this goal that is under serious investigation is to develop "Li-ion capacitors". This approach can overcome the energy density limitation of the conventional EDLC because it employs a hybrid system of a battery-like (faradic) electrode and an EDLC-like (non-faradic) electrode, producing higher working voltage and capacitance. However, the Li-ion capacitors based on a carbonaceous Li intercalation negative electrode have some possible disadvantages, such as long-term stability and safety. Here we suggest a novel hybrid system that certainly achieves a high energy density (triple of conventional EDLCs), high stability and high safety at the same time. This is the new lithium-ion based hybrid capacitor using the lithium titanate

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative intercalation electrode that can operate at unusually high current densities. The high-rate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative electrode has a unique nano-structure consisting of unusually small single nano-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nucleated and grafted onto carbon nano-fiber anchors (nc-LTO/CNF). The novel super-high-rate nano-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nested and grafted onto carbon nano-fibers were prepared by a unique technique (UC method) of a mechano-chemical sol-gel reaction under ultracentrifugal force field (65,000 N), followed by an instantaneous heat-treatment under vacuum for very short duration (3 min). These processes are quite simple and require only a few minutes. Actually, the power characteristic of the prepared composite (nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF) made a new bench mark which exceeds greatly the maximum 300C-rate value that has ever been attained anywhere in the world. In the present lecture, the author presents the representative data for the super-high-rate nano-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nested and grafted onto carbon nanofibers for practical supercapacitors.

1:45 PM U7.2

Structure and Properties of Mesoporous C-TiO₂ for Lithium Ion Batteries and Hybrid Super Capacitor. Alessandra M.

Serventi¹, Michel L. Trudeau¹, Zaghbi Karim¹ and David M. Antonelli²; ¹Materials Science, Hydro-Quebec Research Institute, Varennes, Quebec, Canada; ²Chemistry, Windsor University, Windsor, Ontario, Canada.

Li-ion batteries have emerged as one of the most promising technology for energy storage today. To improve safety, cost and the overall battery performance different materials are presently being investigated to replace carbonaceous anodes, a number of which are based on titanium oxides. However, it has been well demonstrated that to obtain optimal performances, the final electrode materials need to be designed at the nanometric level. In this work we studied the anode properties of mesoporous TiO_2 because of its very high specific surface, which can be as high as $1000 \text{ m}^2/\text{gr}$. At the same time, this porous matrix, with variable pore size and wall thickness, offers unique advantages for carbon impregnation, using a patented process that has allowed unsurpassed properties in other systems such as C- $\text{LiTi}_5\text{O}_{12}$, resulting in zero strain material for negative electrode for Li-ion batteries or Hybrid supercapacitors. We will present the analysis of new C- TiO_2 nanocomposites electrode materials, with specific surface around $128 \text{ m}^2/\text{gr}$, that have improved diffusion kinetics and a potential for an increased power density. The final electrode materials were obtained by thermal annealing sequences of C-filled mesoporous TiO_2 in various atmospheres up to $700 \text{ }^\circ\text{C}$. This carbon impregnation was found to have a major influence on the final structure of the material. We have tested this new coated- TiO_2 material in an electrochemical cell by charge-discharge cycles of 24 hours. The response of the materials was found to be very good with a coulomb efficacy (CE) of the order of 95 %. The reverse capacity after 24 hours was excellent and stable. The capacity was around 122 mAh/g . To correctly understand the macroscopic properties of these nanocomposites functionalized materials, together with electrochemical performance analysis, we will present a complete characterization of the structure, as well as of the chemical nature of the different species present at the sub-nanometer level, that was achieved using high resolution transmission electron microscopy combined with nano-diffraction, EDS and EELS analysis. Complementary Raman, XPS, X-ray and specific surface analysis on the same materials will also be presented.

2:00 PM U7.3

New Hybrid Capacitor based on Nanostructured Composite Electrodes. Hakkwan Kim, Dong Hyeok Choi, Hyun Chul Jung and Yong Soo Oh; Central R&D Institute, eMD Lab, Samsung Electro-Mechanics Co., LTD, Suwon (Gyeonggi-Do), Korea, South.

Asymmetric hybrid capacitor has drawn much attention in recent years, because it can increase the overall cell potential, resulting in higher energy and power densities than conventional electrical double-layered capacitors (EDLC). In this research, we developed an asymmetric hybrid capacitor using MnFe_2O_4 /Carbon Derived Carbon (CDC) nanocomposite as positive electrode and carbon based materials such as activated carbon (AC), graphene, multi-walled carbon nanotube (MWCNT) or CDC as negative electrode combined with organic Li ion electrolyte including partial or complete unsolvated ions. This novel asymmetric hybrid capacitor system shows that we can obtain high energy density without losing innate high power density due to the pseudocapacitance of MnFe_2O_4 and electrostatic capacitance of micropore CDC. The electrochemical mechanism has been resolved by in-situ X-ray diffraction (XRD), DTA and energy filtering transmission electron microscope (EFTEM). Pore size distribution, surface area, morphology and elements mapping are also investigated using BET and FE-SEM. This system also demonstrates superior cycling stability as compared with the conventional transition metal oxide supercapacitors due to the relatively small variation in lattice spacing under the charge-discharge cycling.

2:15 PM U7.4

Flexible Supercapacitors Based on Transition Metal Oxide Nanowire/Carbon Nanotube Heterogeneous Films. PoChiang Chen^{2,1}, Haitian Chen², Guozhen Shen², Saowalak Sukcharoenchoke² and Chongwu Zhou²; ¹Material Science and Eng., USC, Los Angeles, California; ²Ming-Hsieh Department of Electrical Eng., University of Southern California, Los Angeles, California.

Due to the increased consumption of energy in recent years, numerous research efforts have been made to develop different kinds of energy conversion and storage devices. Supercapacitors, having higher energy density than conventional capacitors and higher power density than batteries, are widely investigated and become one of the most attractive power solutions for an increasing number of applications. Supercapacitors are usually made from three different materials including electronically conducting polymers, carbon related materials, and metal oxides. Among these materials, nanostructured metal-oxide materials, with the advantages of high surface-to-volume ratio and short diffusion path length to ions, can be one of the best candidates applied in energy storage and conversion devices. In this concern, a supercapacitor with the features of optical transparency and mechanical flexibility has been fabricated using transition metal oxide nanowire / carbon nanotube heterogeneous film, and studies found that

the power density can reach 7.5 kW/kg after galvanostatic measurements. In addition, to study the stability of flexible and transparent supercapacitor, the device was examined for a large number of cycles and showed a good retention of capacity (~88%). This approach could work as the platform for future transparent and flexible nanoelectronics. To increase the cell voltage and power density, a flexible asymmetric supercapacitor has been fabricated by using indium oxide nanowire / carbon nanotube film as an anode and manganese oxide nanowire / carbon nanotube film as cathodes. The cell operation window is 2 V with the specific capacitance of 126 F/g in 1 M Na₂SO₄ electrolyte and the power density can be improved up to 12 kW/kg. These values are comparable with those of standard electrochemical double layer capacitors working in organic electrolytes.

SESSION U8: Pseudocapacitors
Chair: Nae-Lih (Nick) Wu
Tuesday Afternoon, December 1, 2009
Room 200 (Hynes)

3:00 PM *U8.1

Pseudocapacitor Materials Based on Mesoporous Transition Metal Oxides. Torsten Brezesinski^{2,3}, John Wang¹, Sarah H. Tolbert³ and Bruce Dunn¹; ¹Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California; ²Department of Physical Chemistry, Justus-Liebig-University Giessen, Giessen, Germany; ³Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California.

Capacitive energy storage is distinguished from other types of electrochemical energy storage by short charging times and the ability to deliver significantly more power than batteries. A key limitation to this technology is its low energy density and for this reason there is considerable interest in exploring pseudocapacitive charge storage mechanisms which offer the tantalizing possibility of bridging the performance gap between batteries and double layer capacitors. In this paper we review our recent studies on nanostructured transition metal oxides which exhibit increased levels of pseudocapacitance and enhanced energy storage properties. We investigated the pseudocapacitive responses for two different forms of nanocrystalline TiO₂ films; nanoparticle films with particle sizes less than 10 nm and mesostructured films with pore diameters in the range of 15 - 25 nm. We used a detailed cyclic voltammetric analysis to establish quantitatively the dependence of pseudocapacitance on nanocrystalline TiO₂ particle size. At particle sizes below 10 nm, capacitive contributions become increasingly important, leading to greater amounts of total stored charge (gravimetrically normalized) and faster charge/discharge kinetics. We have now extended these studies to consider the pseudocapacitor properties of mesoporous transition metal oxides prepared by using structure-directing agents. The advantage of the interconnected mesoporous network is that it enables greater electrolyte access to the oxide framework than occurs with dense films. In the case of TiO₂, we find that films prepared by co-assembly of TiO₂ nanoparticles with block co-polymers maintain the high capacitive charge storage properties of the isolated nanoparticles. Moreover, such mesoporous crystalline films offer much greater lithium-ion storage capacity and faster kinetics than non-templated films. Mesoporous films of iso-oriented α -MoO₃ exhibit even higher levels of capacitance because of an additional contribution associated with lithium ions being inserted into the Van der Waals gap of the α -MoO₃. The pseudocapacitive behavior exhibited by these mesoporous materials leads to enhanced levels of charge storage and offers the prospect of designing electrochemical capacitors that can achieve both high energy and high power densities.

3:30 PM U8.2

Electrodeposition of Manganese Dioxide for Electrochemical Supercapacitors. Igor Zhitomirsky, Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada.

New methods have been developed for the electrosynthesis and electrophoretic deposition of nanostructured manganese dioxide films for application in electrochemical supercapacitors. Nanostructured manganese dioxide films were obtained cathodically using polymer-mediated electrosynthesis from solutions of Mn²⁺ salts, containing polymers. Thin films were obtained potentiostatically, galvanostatically or in pulsed deposition regime. The deposition yield was studied using quartz crystal microbalance. It was shown that polymer-mediated electrosynthesis resulted in the formation of Mn₃O₄ phase, which was converted into manganese dioxide by electrochemical oxidation. The size of manganese oxide nanoparticles was varied in the range of 2-10 nm, by variation in the concentration of cationic or chelating polymers. Another approach was based on the cathodic reduction of KMnO₄ or NaMnO₄ salts. The increase in KMnO₄ and NaMnO₄ concentration from 20 mM to 100 mM resulted in reducing deposition rate. Porous and crack free films were obtained from 20 mM KMnO₄ or 20 mM NaMnO₄ solutions. The increase in salt concentration resulted in the formation of dense films which exhibited cracking. It was shown that crack prevention in porous films is based on crack tip blunting mechanism. Film porosity can be increased in a pulse deposition mode. Capacitive behavior of the films was studied in the Na₂SO₄ and K₂SO₄ electrolytes using cyclic voltammetry, chronopotentiometry and impedance spectroscopy. The films showed ideal capacitive behavior in a voltage window of 1 V. The specific capacitance of the films was in the range of 200-400 F g⁻¹. The specific capacitance decreased with increasing film thickness and increasing scan rate in the range of 2-100 mV s⁻¹. The films showed good cycling stability. New methods were developed for the fabrication of nanoparticles of manganese dioxide for electrophoretic deposition. Additives have been developed for charging and electrostatic stabilization of manganese dioxide nanoparticles and carbon nanotubes. Composite films containing manganese dioxide and carbon nanotubes were deposited on current collectors and investigated for application in electrochemical supercapacitors. The composite films containing fibrous manganese dioxide nanoparticles showed higher specific capacitance compared to the films containing spherical nanoparticles. Electrophoretically deposited films showed specific capacitance in the range of 250-650 F g⁻¹. The films deposited cathodically showed higher specific capacitance compared to anodically deposited films. The specific capacitance decreased with increasing scan rate in the range of 2-100 mV s⁻¹ and with increasing film thickness in the range of 1-20 microns. The electrochemical behavior of the films deposited by electrophoretic and electrolytic deposition and deposition mechanisms are discussed.

3:45 PM U8.3

Advanced Nanocomposite Material Based on Manganese Oxide Nanowires and Carbon Nanotubes for Capacitive Energy Storage. Tarik Bordjiba and Daniel Belanger; chemistry, Université du Québec à Montréal, Montreal, Quebec, Canada.

The development of advanced composite materials based on metal oxide-carbon nanotubes is a new route for achieving highly efficient electrode for electrochemical power sources such as fuel cells, lithium batteries and electrochemical capacitors. For electrochemical capacitors, active electrode materials include carbon, conducting polymers and transition metal oxides. Manganese oxide is a promising electrode material for electrochemical capacitors due to its low cost, natural abundance, environmental safety and its high theoretical capacitance. If one Mn atom in MnO₂ is assumed to store one electron, then the specific capacitance of MnO₂ should be around 1370 F/g. But, practically, this oxide show a specific capacitance of only one-fifth or one-sixth of the above value. Such low practical specific capacitance is due to the intrinsically poor electronic conductivity and dense morphology of the oxide [1]. Currently, there are mainly two efficient ways to reach high specific capacitance with manganese oxide. The first one is by developing nanostructured manganese oxide, which allows reaching a specific capacitance in the range of 700 F/g [2]. The second one is by the incorporation of carbon nanotubes in the MnO₂ matrix which allows to reach specific capacitance ranging from 325 to 580 F/g [3-5]. We report, for the first time, the synthesis of a new composite electrode based on manganese oxide nanowires and carbon nanotubes (CNTs) by electrophoretic deposition of CNTs on a stainless steel (SS) substrate followed by direct spontaneous reduction of MnO₄⁻ ions to MnO₂ to form the multi scaled SS-CNT-MnO₂ electrode. The resulting material was characterized by scanning electron microscopy, energy dispersive X-ray analysis, cyclic voltammetry and galvanostatic charge-discharge in a 0.65 M K₂SO₄ aqueous solution. The binderless SS-CNT-MnO₂ nanocomposite electrode shows a very high specific capacitance of 869 F/g of CNT-MnO₂ and good stability during long galvanostatic charge-discharge cycling. To the best of our knowledge, this is one of the highest capacitance for manganese oxide electrode ever reported. In addition to its applicability in electrochemical capacitors, this methodology could be extended to develop other high performance nanocomposite material electrodes based on carbon nanotubes and metal oxide for the future generation of electrochemical power sources. This strategy can find application not only in electrochemical power sources devices but also for catalysis, sensors and microelectronics. Reference: 1- M. Toupin, T. Brousse, D. Bélanger, Chem. Mater. 2004, 16, 3184. 2- S. C. Pang, M. A. Anderson, T. W. Chapman, J. Electrochem. Soc. 2000, 147, 444. 3- T. Bordjiba, D. Bélanger, J. Electrochem. Soc. 156 (5), A378 4- C. Y. Lee, H. M. Tsai, H.J. Chuang, S. Y. Li, P. Lin, T. Y. Tseng, J. Electrochem. Soc. 2005, 152, A716. 5- S. B. Ma, K. W. Nam, W. S. Yoon, X. Q. Yang, K.Y. Ahn, K.H. Oh, K.B. Kim, J. Power Sources 2008, 178, 483.

4:00 PM U8.4

High-Capacitance Ultracapacitor Electrodes Based on Novel Conducting Polymers. Mark E. Roberts, David R. Wheeler, Bonnie McKenzie and Bruce C. Bunker; Sandia National Laboratories, Albuquerque, New Mexico.

Ultracapacitors are electrical energy storage devices that combine the high power, rapid switching, and exceptional cycle life of a classical capacitor with the high-energy density of a battery. Power sources based on ultracapacitors are emerging as the preferred option for applications requiring short power pulses, particularly when combined with conventional batteries. In order to maximize capacitance, switching speed, and power, materials for ultracapacitors need to incorporate conductive and redox-active materials into high surface area structures that are engineered to provide intimate contact between the redox sites and the electrolyte. Conducting polymers are well suited to address these challenges owing to the myriad of synthetic and processing methods available which provide a variety of nanostructures and electrical behaviors. In this presentation, we will present novel conducting polymer electrode materials for electrical energy storage devices. Two classes of materials were investigated: conducting polymers with a triarylamine backbone and thiophene-phenazine containing polymers. The monomers were synthesized using Stille coupling chemistry and used to fabricate porous electrode structures via electrochemical polymerization on conductive substrates. The electrodes were characterized structurally with scanning electron microscopy and electrochemically with cyclic voltammetry, charge-discharge and electrical impedance spectroscopy. Electrodes structures fabricated with triarylamine-based conducting polymers exhibited a remarkably high specific capacitance approaching 1000 F/g in 100 mM tetrabutylammonium tetrafluoroborate in acetonitrile with power and energy densities greater than 6 kW/kg and 25 W-hr/kg, respectively. The electrical performance of the electrodes in electrochemical half-cells, reported for highly porous and nanotube electrodes, is used to provide insight into the electrochemical storage mechanism of polymer-based systems. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:15 PM *U8.5

Pseudocapacitance Effects based on Carbon/Hydrogen and Carbon/Iodide Interactions. Elzbieta Frackowiak, Grzegorz Lota and Krzysztof Fic; Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland.

A considerable improvement of capacitance can be obtained by pseudo-capacitive effects connected with quick faradaic reactions. Among many possibilities hydrogen electroadsorbed reversibly in the nanoporous carbons is of great interest. Carbon/hydrogen interactions with a weak chemical character (110 kJ/mol) are responsible for capacitance enhancement of negative electrode operating in aqueous medium. Correlation of hydrogen capacity with microtexture, surface functionality of carbon (heteroatoms) and electrical parameters of charging/discharging process will be presented. Combination of carbon electrode with another positive electrode gives a significant extension of voltage, in turn, higher energy of supercapacitor. As a second pseudocapacitive example, striking electrochemical behaviour of carbon/iodide interface will be shown and used for supercapacitor application. This efficient charge storage is based on specific sorption of iodide ions as well as stable reversible redox reactions connected with various possible oxidation states of iodine from -1 to +5. An intriguing effect of iodide ions has been observed for positive electrode operating in a narrow range of potential and giving extremely high capacitance values exceeding 1840 F/g. Potassium iodide (1 mol/L) plays a bi-functional role, i.e. electrolytic solution with a good ionic conductivity as well as a source of pseudo-capacitive effects. However, the role of carbon texture in efficient charging of this system cannot be neglected. As opposed to typical pseudocapacitive effects, which are often characterized by some diffusion limitations and observed only at moderate regimes, our innovative two-electrode system can be loaded until 50 A/g supplying still 125 F/g. Amazing capacitance of carbon/iodide interface

has also been confirmed during long-term cycling (over 10 000 cycles).

5:10 PM

MEDAL AWARD PRESENTATION: The Opportunities and Challenges for First Principles Materials Design and Applications to Li battery Materials. Gerbrand Ceder, Materials Science and Engineering, MIT, Cambridge, Massachusetts.

The idea of first principles methods is to determine the properties of materials by solving the basic equations of quantum mechanics and statistical mechanics. With such an approach one can in principle predict the behavior of novel materials without the need to synthesize them, and create a virtual design laboratory. By showing several examples of new electrode materials that have been computationally designed, synthesized and tested, I will show the impact of first principles methods in the field of Li battery electrode materials. A significant advantage of computational property prediction is its scalability which we are currently implementing into the Materials Genome project at MIT. Using a high throughput computational environment, coupled to database of all known inorganic materials, we are computing basic information on all known materials and a large number of novel "designed" materials. To predict the crystal structure of hypothetical new materials we have implemented a data mining algorithm that can with high accuracy guess the structure of any new material. With this ability we have obtained several new candidate Li electrode materials. Finally, I will discuss some the challenges that need to be overcome to further enable the impact of first principles methods. BIOGRAPHY Gerbrand Ceder is the R.P. Simmons Professor of Materials Science and Engineering at the Massachusetts Institute of Technology. He received an engineering degree in Metallurgy and Applied Materials Science from the University of Leuven, Belgium, in 1988, and a Ph.D. in Materials Science from the University of California at Berkeley in 1991 at which time he joined the MIT faculty. Dr. Ceder's research interests lie in computational modeling of material properties and the design of novel materials. Currently, much of the focus of his work is on materials for energy generation and storage, including battery materials, hydrogen storage, thermoelectrics, electrodes for fuel cells and photovoltaics. He has published over 220 scientific papers in the fields of alloy theory, oxide phase stability, high-temperature superconductors, and Li-battery materials, and holds 5 current or pending U.S. patents. His most recent scientific achievement has been the development of materials for ultra fast battery charging. He has received the Battery Research Award from the Electrochemical Society, the Career Award from the National Science Foundation, and the Robert Lansing Hardy Award from The Metals, Minerals and Materials Society for "exceptional promise for a successful career." He has also received three awards from the graduate students at MIT for best teaching. He is the founder of Computational Modeling Consultants.

SESSION U9: New Electrode Structures and Architectures for Capacitive Energy Storage

Chair: Bruce Dunn

Wednesday Morning, December 2, 2009

Room 200 (Hynes)

8:30 AM *U9.1

Multifunctional Carbon Nanoarchitectures as Designer Platforms for Electrochemical Power Sources. Jeffrey W. Long¹, Megan B. Sassin¹, Azzam Mansour², Christopher N. Chervin³, Jean M. Wallace³, Jennifer L. Dysart¹, Katherine A. Pettigrew³ and Debra R. Rolison¹; ¹Code 6170, Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia; ²Systems and Materials for Power and Protection Branch, Naval Surface Warfare Center - Carderock Division, West Bethesda, Maryland; ³Nova Research, Inc., Alexandria, Virginia.

We use carbon aerogels and nanofoams as ultraporous, conductive 3-D scaffoldings onto which we incorporate nanoscopic, electroactive functionalities such as metal oxides, metal nanoparticles, and ultrathin polymers. The resulting multifunctional nanoarchitectures are designed to serve as high-performance electrode structures in applications ranging from high-rate Li-ion batteries and electrochemical capacitors to metal-air batteries and fuel cells [1]. For electrochemical capacitor applications, we have developed self-limiting electroless deposition protocols to apply nanoscopic coatings of either manganese or iron oxides onto the exterior and interior surfaces of carbon nanofoams such that the through-connected pore network of the native nanofoam is retained. The nanoscopic morphology of the metal oxide results in charge-storage capacities higher than typically observed for the oxide used in conventional composite electrode structures, while the nanoarchitecture design itself facilitates rapid charge-discharge of the oxide coating. The MnOx-carbon and FeOx-carbon nanofoam structures function as complementary electrodes (positive and negative, respectively) in asymmetric aqueous electrochemical capacitors that exhibit operating voltages approaching 2 V, and deliver an optimal combination of power and energy densities within a 1-100 s charge-discharge timeframe. In related work, multifunctional nanoarchitectures are designed as air-cathodes for metal-air batteries, in which the nanoscopic oxide coating (in particular manganese oxide) enhances the electrocatalytic turnover for molecular oxygen reduction. En route to practical high-performance energy-storage and conversion devices, these multifunctional nanoarchitectures are also convenient platforms with which to investigate fundamental electrochemical processes at nanoscale interfaces using a variety of spectroscopic techniques. [1] D.R. Rolison, J.W. Long, J.C. Lytle, A.E. Fischer, C.P. Rhodes, T.M. McEvoy, M.E. Bourg, and A.M. Lubers, Chem. Soc. Rev. 38, 226-252 (2009).

9:00 AM U9.2

Three Dimensional Carbon Architectures as Electrodes for Capacitors. Francisco del Monte, Maria C. Gutierrez, Daniel Carriazo, Maria L. Ferrer, Fernando Pico and Jose Maria Rojo; ICMM-CSIC, Madrid, Spain.

The main aim of this work was the design of a synthetic procedure for preparation of monolithic carbon aerogels (CA) of utility as three-dimensional electrodes in electrical double layer capacitors (EDLC). 3D monolithic architectures are lately gaining increased interest in energy storage since they can directly assembled into the supercapacitor cell which allows the miniaturization of the device. The synthetic approach that we have used for preparation of the carbon aerogels (CA) is based on the use of pluronic type

surfactants as templates. The use of pluronic type surfactants had been widely described for preparation of mesoporous carbons (as thin films or fine powder) but there is one single report (Chem. Commun. 2008, 2641) on their use for preparation of 3D monolithic CA with well ordered mesopores of ca. 3 nm and macropores of ca. 3 micrometers which, unfortunately, were not useful for EDLC (micropores are required). Thus, in this work, we have further explored the use of PPO-PEO-PPO block copolymers (in this case, having short PPO and PEO segments) for the preparation of hierarchically micro- (rather than meso) and macroporous CA. The achievement of this particular structure has provided remarkable properties to the CA, such high electric conductivity (~2.5 S/cm). structure (micro and macroporous) of the CA obtained in this work, has allowed their (Chem. Commun. 2008, there was only a very recent work (PPO-PEO-PPO type) for the preparation of highly porous (ca. 65%) and ultraweighted (specific gravity 5×10^{-2}) macroporous monolithic carbon aerogels built of sintered microporous carbon colloids. The three-dimensional continuous macroporous network allowed the achievement of a remarkably This hierarchical structure was also highly suitable for EDL, with the macroporous network structure providing an efficient transport of electrolyte throughout the monolith and the microporosity being crucial for the formation of extended double layer at the electrode/electrolyte interface. This feature was indeed reflected in the achievement of remarkable capacitances of up to 225 F/g (normalized by mass of CA monolith) and ~31 microF/cm² (normalized by BET surface area of CA monolith). [1] MC Gutierrez et al. "PPO15-PEO22-PPO15 Block Copolymer Assisted Synthesis of Monolithic Macro and Microporous Carbon Aerogels Exhibiting High Conductivity and Remarkable Capacitance." J. Mater. Chem. 2009, 19, 1236-1240

9:15 AM U9.3

Enhanced Electric Double Layer Capacitance of Poly Sodium 4-Styrenesulfonate/Graphene Oxide Electrodes with High Cyclic Performance. Hae Kyung Jeong, Mei Hua Jin, Eun Ju Ra, Kang Pyo So, Sivaram Arepalli and Young Hee Lee; Physics and Energy Science, Sungkyunkwan University, Suwon, Korea, South.

We have synthesized poly sodium 4-styrenesulfonate intercalated graphite oxide and characterized its chemical and physical properties. We found that the interlayer distance of a PSS-treated graphite oxide increased by about 1 Å compared to that of the precursor graphite oxide. This increase in interlayer spacing was attributed to the intercalation of a monolayer of planar PSS into the graphite oxide interlayers facilitated by a π - π interaction between the aromatic rings of the graphite oxide and PSS. The PSS-intercalated graphite oxide had a higher structural stability than the pristine graphite oxide during thermal treatment because of the high melting point of PSS, resulting in high specific capacitance (189.4 F/g), energy density (26.16 Wh/kg), and momentum density (90.68 W/kg) with high cyclic performance. We will discuss more detail in the talk.

9:30 AM *U9.4

Electrochemical Capacitors Utilizing Single-Walled Carbon Nanotubes. Kenji Tamamitsu¹, Shunzo Suematsu¹, Daisuke Horii¹ and Hiroaki Hatori²; ¹Functional Material Laboratory, Nippon Chemi-Con Corporation, Takahagi, Japan; ²Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

An electric double layer capacitor (EDLC) utilizing a unique single-walled carbon nanotube called as Super Growth(SG)-SWCNT prepared by a highly efficient CVD process will be presented. We have been investigating the SG-SWCNT as a unique capacitor material mainly because of its high specific surface area (ca. 1,100 m²/g), aligned structure and ultrahigh purity (99.98%), as well as higher growth efficiency (ca. 3,000 times higher) as a practical industrial consideration [1]. We have been successfully developing an electrode that consists only of SG-SWCNT and a current collector with a simple preparation method. Probably due to the absence of complicated additives (e.g., conductive agents, binders, and/or agents for adhesion of the carbon sheets with the current collectors) and the high purity of the SG-SWCNT, much better life performances of the EDLCs based on the SG-SWCNT as both anode and cathode (SG-SG-EDLC) compared with conventional activated carbon EDLCs (AC-AC-EDLC) were found under several DC floating conditions (e.g., 3.5V at 40C and 3.0V at 85C)[2, 3]. In energy and power performances for the SG-SG-EDLC, the power density (>10 kW/L on the basis of device excluding the case volume) was superior to that for the AC-AC-EDLC though the energy density was comparable to each other when applied voltages of both EDLCs were equal to be 3.0 V. Considering the life performance of the SG-SG-EDLC and the AC-AC-EDLC, however, the SG-SG-EDLC would exhibit higher energy density because of its higher applied voltage with similar life performance (i.e. less voltage derating for the SG-SG-EDLC). For more practical trial, we also prepared a multi-stacked SG-SG-EDLC to estimate the capacitor performance based on the device including the case mass. The capacitor displayed gravimetric energy and power densities of 16Wh/kg and 10kW/kg, respectively. Some approaches for further improvement in the energy and power densities as well as life performances are ongoing and some of the results would be shown in the presentation. [1] K. Hata et al., Science, 306, 1362-1364 (2004). [2] S. Suematsu et al., Abstract of the 8th International Advanced Automotive Batteries, FL, USA (2008). [3] K. Tamamitsu et al., Abstract of the 18th International Seminar on Double Layer Capacitors & Hybrid Energy Storage Devices, FL, USA (2008). Acknowledgement This work is partially supported by the New Energy and Industrial Technology Development Organization (NEDO) of "Carbon Nanotube Capacitor Project", Japan.

SESSION U10: New Carbon-Based Materials for Electrochemical Capacitors

Chair: Vincent Meunier

Wednesday Morning, December 2, 2009

Room 200 (Hynes)

10:30 AM *U10.1

Nanoporous Carbons for Electrochemical Double Layer Capacitors: Electrochemical Study of the Ion Size Versus the Carbon Pore Size Effect. Patrice Simon¹, Pierre-Louis Taberna¹, John Chmiola^{3,2} and Yury Gogotsi²; ¹CIRIMAT UMR CNRS 5085, Université Paul Sabatier, Toulouse, France; ²Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ³Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley,

California.

Electrochemical Capacitors (EC), also called supercapacitors, store energy using either ion adsorption (electrochemical double layer capacitors, EDLC) or fast surface redox reactions (pseudo-capacitors). They can complement or replace batteries in electrical energy storage and harvesting applications, when high power delivery or uptake is needed. In this talk, we will present the latest results on the electrochemical characterization of nanoporous Carbide-Derived Carbons (CDCs) for EDLC applications. CDCs with controlled pore size ranging from 0.6 up to 1 nm were prepared by the chlorination of TiC powder. A 3-electrode cell set-up has been used to study the adsorption of NET_4^+ , BF_4^- (TEABF₄) and Ethyl-methylimidazolium Trifluoromethanesulfonyl-imide (EMI+, TFSI-) dissolved in acetonitrile and Propylene Carbonate (PC). Using large-electrode cells, we showed that the gravimetric capacitance of the carbons was maximum when the ion size was close to the carbon pore size. Then, a kinetic study in 2M EMI, TFSI in AN or PC electrolytes was conducted with the Cavity Micro-electrode (CME) cell at various scan rates (from few mV/s up to few V/s). Results show that for the smaller carbon pore size (0.68 nm), the ion adsorption kinetics was controlled by the diffusion of the ions inside the pores. For carbon pore size in the same range as the anion size, an extra capacitance was measured on the Cyclic Voltammetry plots. This reversible extra-capacitance is suspected to be issued from an increase of the electrostatic interactions between the ions and the carbon pore walls in this confined environment. These new results confirm that matching the pore size of carbon to the ion size of electrolyte is of vital importance for optimizing specific capacitance, when using either solvated or solvent-free ionic liquid electrolytes.

11:00 AM U10.2

Layer-by-Layer Assembled Multiwall Carbon Nanotube Electrodes for Energy Storage Devices. Seung Woo Lee¹, Naoaki Yabuuchi², Betar M. Gallant², Shuo Chen², Byeong-Su Kim¹, Junhyung Kim², Paula T. Hammond¹ and Yang Shao-Horn^{2,3}; ¹Chemical Engineering, MIT, Cambridge, Massachusetts; ²Mechanical Engineering, MIT, Cambridge, Massachusetts; ³Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Development of novel energy storage devices using nanoscience and technology has been acknowledged as one of the most important technical issues in the recent energy crisis. Since the efficiency of energy storage devices primarily depends on the materials and structures utilized, both synthesizing unique nanomaterials and designing ideal nanostructures are essential to this research. Potential advantages of nanostructured electrodes for batteries and supercapacitors include higher electrode/electrolyte contact area and faster charge/discharge rates, ultimately leading to higher energy and power density of devices. Layer-by-layer (LBL) assembly is a versatile thin-film fabrication technique which consists of the repeated, sequential immersion of a substrate into aqueous solutions of complementary functionalized materials. We recently demonstrated all multiwall carbon nanotube (MWNT) thin electrodes using LBL assembly with functionalized MWNTs¹. The LBL assembled MWNT electrodes are unique in that they yield distinct advantages such as 1) water-based or "green" electrode processing at ambient conditions, 2) elimination of polymeric/insulating binding agents, surfactants and electronic carbon supports, and 3) precise control of electrode thickness. In addition, the LBL method can be adapted to virtually any 2D, 3D, or flexible substrate to increase electrode surface area for increased energy and power. LBL assembled functionalized MWNT electrodes exhibit a high energy density (200 Wh/kg) delivered at a high power of 100 kW/kg in lithium nonaqueous cells. The high energy densities of LBL-MWNT electrodes can be attributed to the Faradaic reactions between lithium ions and surface functional groups on MWNT electrodes rendering high pseudocapacitance. (1) Lee, S. W.; Kim, B.-S.; Chen, S.; Shao-Horn, Y.; Hammond, P. T. *Journal of the American Chemical Society* 2009, 131, 671-9.

11:15 AM U10.3

Enhanced Performance Electrochemical Capacitors from Graphene Nanosheets Having Diverse Physical and Chemical Characteristics. Sanjib Biswas and Lawrence T. Drzal; Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan.

Graphene is considered to be the basic building block for many potential applications because of its exceptional electrical, thermal and mechanical properties. Acid intercalation followed by thermal exfoliation of natural graphite, developed by Drzal research group in Michigan State University, has been shown to be an easy approach to produce graphene nanosheets with an average thickness from 3 to 5 nm and lateral dimensions ranging from sub micron to more than 50 μm . Retention of aromaticity and the absence of significant oxygen functionalities on the graphene basal plane are evident from the thermal stability (only 6 %wt loss) of these nanosheets in the temperature range from 120 to 300°C, where a considerable weight loss is expected for highly oxidized graphene basal plane from the generation of decomposed gaseous products like CO and CO₂. XPS elemental analysis further confirms the high degree of aromaticity with a C/O atomic ratio close to 21.2. For graphene based EDLC application, attaining high capacitance, while maintaining low electronic resistance, can be realized through enhanced particle surface area, porosity and wettability of the active electrode material. With increasing ratio of edge to basal plane area, on going from large to small sized nanosheets, the relative proportion of oxygen functional groups bound to the active edge sites of these nanosheets increases. While the presence of these oxygen functionalities enhances the wettability of the electrode, the decreasing particle size significantly contributes towards a larger electronic resistivity of the electrode from increasing inter particle contact resistances. In order to retain high electronic conductivity of the electrode, large and small sized nanosheets have been combined into a 100% binder-free aligned multilayer composite structure to optimize the electrode performance for high capacitance and superior frequency responses in aqueous 6M KOH electrolyte. In this aligned configuration the highly electrically conductive large sized nanosheets not only contributes towards the double layer capacitance but also acts as a series of current collectors within the bulk electrode structure for facile electronic conduction from the inside to the outside current collector. This aligned configuration exhibits a symmetrical CV response with nearly straight rectangular sides even at a scanning rate 500 mV/sec. A nearly vertical low frequency line and a 'knee' frequency close to 150 Hz point to the suitability of this electrode for high power applications. The average specific capacitance of the aligned composite at 10 A/gm discharge current density is close to 80 F/gm. 1.Fukushima H. "Graphite Nanoreinforcements in Polymer Nanocomposites" PhD Dissertation, Michigan State University, East Lansing, MI, 2003

2. Biswas, S., Drzal, L.T., Nano Lett., 2009, 9 (1), pp 167-172

11:30 AM *U10.4

Tunable Nanoporous Carbons for Supercapacitor Electrodes. Ranjian Dash^{1,2}, John Chmiola², Lawrence Weinstein¹, Patrice Simon³ and Yury Gogotsi²; ¹Y-Carbon, Inc., King of Prussia, Pennsylvania; ²Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ³CIRIMAT, UMR-CNRS 5085, Université de Toulouse, Toulouse, France.

Y-Carbon's tunable nanoporous carbon based on its proprietary Carbide Derived Carbon technology, offers carbon electrodes whose pore size can be tuned to specific electrolyte for use in a supercapacitor. Such material has shown high capacitance and low resistance, and can be advantageous in high-energy, high-power applications. Experimental evidence will be shown that the pore size to ion size ratio determines the efficiency of electrochemical energy storage systems. In addition to pore size control, Y-Carbon's simple and scalable technology allows control of structure and offers high accessible surface area and a wide range of structures that can be potentially be useful in various electrochemical storage devices, including supercapacitors and batteries. Physical, structural and electrochemical properties of highly pure carbide-derived carbons will be presented. References [1] P. Simon, Y. Gogotsi, Nature Materials, 7 (2008) 845. [2] R. Dash, J. Chmiola, G. Yushin, Y. Gogotsi, G. Laudisio, J. Singer, J.E. Fischer, S. Kucheyev, Carbon, 44 (2006) 2489 [3] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, Angewandte Chemie Int. Edition, 47 (2008) 3392 [4] C. Largeot, C. Portet, J. Chmiola, P.L. Taberna, Y. Gogotsi, P. Simon, J. Am. Chem. Soc., 130 (2008) 2730 [5] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna, Science, 313 (2006) 1760

SESSION U11: Electrolyte Confinement in Porous Electrodes
Chair: Patrice Simon
Wednesday Afternoon, December 2, 2009
Room 200 (Hynes)

1:30 PM *U11.1

Graphitic Nanopore-Field Induced Ordering Effect for Molecules and Ions. Katsumi Kaneko¹, Akemi Tanaka¹, Natsuko Kojima¹, Taku Iiyama², Tomonori Ohba¹, Sumio Ozeki², Hirofumi Kanoh¹ and Patrice Simon³; ¹Chemistry, Graduate School of Science, Chiba University, Chiba, Japan; ²Chemistry, Faculty of Science, Shinshu University, Matsumoto, Japan; ³CIRIMAT Laboratory, University of Paul Sabatier of Toulouse, Toulouse, France.

Graphitic nanoporous materials such as activated carbon fiber (ACF), carbide-derived carbon (CDC), single wall carbon nanotube (SWCNT), and single wall carbon nanohorn (SWCNH) show a considerably high electronic conductivity compared with zeolites, ordered mesoporous silicas, and metal organic frameworks. Also the graphitic wall has the high atomic density, providing the strong interaction potential for molecules and ions per unit weight, although the carbon wall is almost penetrable for X-ray. This paper presents special functions of the carbon nanopore spaces that the strong interaction potential field gives rise to a unique high density structure for molecules and ions including the organic electrolytes. For example, alcohol molecules and SO₂ are oriented to the carbon pore-walls. The structure of water in the carbon pores at 303 K is close to that at 140 K. The hydration number around an inorganic ion such as a Rb ion is smaller than that of the bulk ion by 30 %. The addition of TEABF₄ induces the higher population of PC molecules at the carbon walls.

2:00 PM U11.2

Effect of Salt Depletion on Charging Dynamics in Nanoporous Electrodes. David B. Robinson, Benjamin W. Jacobs and Chung-An Max Wu; Energy Nanomaterials, Sandia National Laboratories, Livermore, California.

Double-layer supercapacitors built from nanoporous electrodes can have such a high ratio of electrode surface area to pore volume that charging the capacitor can deplete the salt from the liquid volume. Experimentally, this effect is often masked by external solution resistance or by transport of salt into the pore from an external reservoir. However, in some practical cases, the phenomenon can have an important effect on charging time and linearity. It can be mitigated through attention to those masking effects and to the symmetry of ion mobilities. We have observed salt depletion effects using dealloyed gold, which has well-defined 10 nm pores and a chemically well understood surface, and by minimizing the salt reservoir. Good correspondence is observed with a modified de Levie model that accounts for reduced conductivity due to salt depletion. This work was performed under the Laboratory-Directed Research and Development Program at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:15 PM *U11.3

Theoretical and Computational Modeling of Carbon-Based Supercapacitors. Vincent Meunier, Bobby G. Sumpter and Jingsong Huang; Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Theoretical methods have evolved to a point where the properties of materials can be successfully predicted based solely on their atomic structure. As such, they provide a unique tool, able to help identifying the origins of the properties of a given structure and uncovering principles that can be used to tailor structure for target applications. In this talk, I will present an overview of the theoretical and computational work we have recently performed on capacitive electrical energy storage [1-2]. I will present a heuristic model that avoids the shortcomings of the electrical double-layer capacitor (EDLC) model by considering explicitly pore curvature into account. The density functional theory based model explains experimental observations for a range of pore sizes: from the micropore regime (< 2 nm), mesopore regime (2-50 nm), and macropore regime (> 50 nm); and diverse carbon materials

and electrolytes. The model allows the properties of a supercapacitor to be correlated with pore size, specific surface area, Debye length, electrolyte concentration, dielectric constant, and solute ion size, and lead to a optimization pathway of carbon supercapacitors properties through experiments. **References:** [1] Theoretical Model for Nanoporous Carbon Supercapacitors, J. Huang, B.G. Sumpter, and Vincent Meunier, *Angewandte Chemie* 47, 520 (2008). [2] Universal Model for Nanoporous Carbon Supercapacitors Applicable to Diverse Pore Regimes, Carbons, and Electrolyte, J. Huang, B. Sumpter, and V. Meunier, *Chemistry: A European Journal (CEJ)*, 14, 6014 (2008). *This work was supported in part by the Laboratory Directed Research and Development Program of ORNL, managed by UT-Battelle, LLC, and by the Center for Nanophase Materials Sciences (CNMS), sponsored by the Division of Scientific User Facilities, U. S. Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory.*

SESSION U12: Nanostructured Materials for Batteries and Capacitors

Chairs: Michael Thackeray and Gleb Yushin

Wednesday Afternoon, December 2, 2009

Room 200 (Hynes)

3:15 PM *U12.1

Ionothermal Preparation of Li-based Electrode Materials: A Myriad of Opportunities. Jean-Marie Tarascon, Nadir Recham, Jean-Noel Chotard, Michel Armand and Loic Dupont; Laboratory of Chemistry of Solids, Université de Picardie Jules Verne, Amiens, France.

One of the major challenges of the next decades is undoubtedly the development of new technologies for energy storage in order to better handle our planet's energy resources. Much hope has been put into the Li-ion battery technology. Yet, its success will depend on the chemist's ability to create electrode materials more performing in terms of power, energy density, safety and cost, while following the concept of sustainability. Nature has not been of much help since the most interesting materials (LiFePO₄ for example) are the most insulating, thereby having been left aside for many years. To thwart such difficulties chemists have acted either on the surface of the material (coating technique) or on its size and morphology using low temperature hydrothermal/solvothermal aqueous processes. To simplify this hydrothermal process and free ourselves from working under pressure, we recently implemented the ionothermal synthesis approach to the field of inorganic compounds. We showed, thanks to ionic liquids which do not have vapour tension, the possibility of preparing electrode materials of controlled size and morphology while working at temperatures < 250°C and under atmospheric pressure. Besides, we demonstrated that ionic liquids can act both as reacting medium and structuring agent during the synthesis process. This step forward due to the richness of ionic liquids chemistry, which number of combinations is practically boundless, opens many new opportunities in the synthesis/design of inorganic compounds; opportunities that we have explored to prepare and stabilize known new Li-based electrode materials whose attractive electrochemical properties will be reported.

3:45 PM U12.2

Composite Tin-Carbon Electrospun Nanofibers for Use as Lithium-Ion Battery Anodes. Christopher A. Bonino¹, Liwen Ji², Xiangwu Zhang² and Saad A. Khan¹; ¹Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina; ²Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina.

Composite tin-carbon nanofibers are a promising material for rechargeable lithium-ion battery anodes. The high storage capacity of tin complements the long cycle life of carbon. In addition, the nanofiber structure has a high surface-to-volume ratio, which improves the accessibility for lithium intercalation as compared to traditional graphite-based anodes. In this study, we prepare polymer nanofibers containing tin salts by electrospinning. Subsequent thermal treatment not only carbonizes the nanofiber, but converts the tin salts to metallic tin, thereby providing tin-carbon composite nanofibers all in a one-step protocol. The performance of the fiber mats as anodes is evaluated in Li-ion half cells. The effects of the properties of the precursor polymer solution on the morphology of the electrospun fibers are studied. The conversion of different tin salts is also investigated.

4:00 PM U12.3

High-Dielectric Constant (K) Al₂O₃ / TiO₂ Atomic Scale Multilayers For Supercapacitors for Energy Storage. Wei Li¹, Bernd Kabius², Ramesh N Premnath¹ and Orlando Auciello^{1,3}; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Electron Microscopy Center, Argonne National Lab., Argonne, Illinois; ³Center for Nanoscale Materials, Argonne National Lab., Argonne, Illinois.

Dielectric materials exhibiting high dielectric constants have recently gained considerable attention for their potential applications in microelectronics such as capacitors and memory devices. Recently, a new kind of Pb/Bi-free dielectric material, CaCu₃Ti₄O₁₂ (CCTO), was reported to possess high dielectric constant over a broad temperature range, which shows a step-like decrease with decreasing temperature accompanying the appearance of a Debye-like relaxation loss peak. Al₂O₃ and TiO₂ have been investigated as high-K materials to replace SiO₂ as gate and for high-capacitance oxide-based capacitors for electronics. The dielectric constants of Al₂O₃ and TiO₂ are approximately 7 and 60-70, respectively. Our previous studies indicate that amorphous Ti_xAl_{1-x}O_y films (Ti:Al=75:25 at %, a trading-off between high-K and offset barrier height) demonstrate a dielectric constant of ~ 30. Other work has shown that the dielectric constant of mixtures of Al₂O₃ and TiO₂ varies between 7 and 60-70 depending on the mixture ratio. Here, we report here that high dielectric constants (> 800) can be achieved in Al₂O₃/TiO₂ multilayers with sub-layer thickness ≤ 1 nm, for frequencies ≤ 104 Hz. A step-like decrease in dielectric constant to ~ 50 occurs between 10⁴ - 10⁵ Hz. The high dielectric constant can be attributed to M-W relaxations, which occurs not due to the orientation of dipole but to the electrical heterogeneity of the multilayers. The Ellingham diagram indicates that the Al oxidation is more favored than Ti-oxide since the Al

Gibbs free energy for oxidation is more negative than for Ti. Therefore, O atoms will have a diffusion tendency from TiO₂ to Al₂O₃ sublayers, that can result in reduction of oxygen content in the TiO₂ sublayers, leading to TiO_x stoichiometry, thus electrical conductivity. As a consequence, the conductivities of TiO₂ and Al₂O₃ sublayers become so different that surface charges would accumulate at the interfaces when electric current pass through. The surface charges relax with a.c. field and cause MW relaxation (the equations expressing the dispersion are completely identical to Debye relaxation although the origins are quite different). A discussion will be presented on the use of the ALD process to produce large area capacitors via conformal coating of large area ridge arrays fabricated on Si surfaces. These capacitors can yield $\geq 10 \mu\text{F}$ capacitance. We are exploring these capacitors for applications such as energy storage embedded capacitors in a Si microchip implantable in the human retina, as part of an artificial retina to restore sight to people blinded by genetically-induced degeneration of photoreceptors, and for super-capacitors integrated with ferroelectric-based high-efficiency photovoltaic devices for energy generation/storage systems.

4:15 PM U12.4

Silicon Nanowire/Carbon Composite Electrodes for Lithium-ion Battery Anodes. Candace K. Chan¹, Seung Sae Hong² and Yi Cui³; ¹Chemistry, Stanford University, Stanford, California; ²Applied Physics, Stanford University, Stanford, California; ³Materials Science and Engineering, Stanford University, San Antonio, Texas.

Silicon nanowires (SiNWs) have the potential to perform as anodes for lithium-ion batteries with a much higher energy density than graphite. Previously (1), we have shown that reversible capacities $>3,000 \text{ mAh/g}$ can be obtained by using an electrode geometry consisting of SiNWs grown on metallic current collector substrates using the CVD-based vapor-liquid-solid (VLS) method. These electrodes consisted of SiNWs directly attached and vertically oriented off of the current collector. SiNWs can be synthesized in large quantities using the supercritical-fluid-solid (SFLS) method (2). Slurries were prepared composed of silicon nanowires synthesized using the SFLS method mixed with amorphous carbon or carbon nanotubes and binder and coated onto Cu foil. Recent results regarding the cycling behavior of the SiNWs using different experimental conditions will be presented. The performance of these composite electrodes will also be compared with our previous work using the VLS SiNWs to determine how the electrode architecture affects the electrochemical performance. In collaboration with Reken Patel and Brian A. Korgel, Dept. of Chemical Engineering, The University of Texas at Austin Reference List 1. Chan, C. K.; Peng, H.; Liu, G.; McIlwrath, K.; Zhang, X. F.; Cui, Y. High performance lithium battery anodes using silicon nanowires. *Nature Nanotech.* 2008, 3, 31-35. 2. Hanrath, T.; Korgel, B. A. Supercritical fluid-liquid-solid (SFLS) synthesis of Si and Ge nanowires seeded by colloidal metal nanocrystals. *Adv. Mater.* 2003, 15, 437-440.

4:30 PM U12.5

Nanostructured Mesoporous TiO₂ Electrodes for Energy Storage. Keith J. Stevenson, Jing Wu and Alan May; University of Texas at Austin, Austin, Texas.

Nanostructured, mesoporous materials have shown significant promise for application in batteries. These materials and assembled interfaces are difficult to characterize by ensemble-averaging, bulk experimental methods since they do not exhibit long-range order, contain unique nano-morphological features and possess localized chemical compositions and defect chemistry. This presentation will highlight the development of several high resolution ellipsometric porosimetry and electrochemical methods for studying the properties and reactivity of nanostructured, mesoporous TiO₂ electrodes. Information obtained from these tools provides fundamental understanding of electron and charge transfer processes for materials utilized in energy conversion and storage technologies.

4:45 PM U12.6

Nanoparticles Assemblies for Extreme Power Devices. Maxim N. Tchou^{1,3}, Scott P. Fillery^{1,3}, Hilmar Koerner^{1,2}, Lawrence F. Drummy^{1,4}, Peter A. Mirau¹, Michael F. Durstock¹ and Richard A. Vaia¹; ¹Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio; ²UTC Inc., Dayton, Ohio; ³National Research Council, Washington, District of Columbia; ⁴UES Inc., Dayton, Ohio.

Future applications, such as all-electrical aircraft, require new energy storage technologies with combinations of high energy density ($> 20 \text{ J/cc}$), efficiency (dielectric loss $< 1\text{E-}4$) and discharge rate ($< 1 \mu\text{s}$). These must incorporate innovative materials that combine increased dielectric strength ($> 1000 \text{ V}/\mu\text{m}$) and dielectric constant (> 3) with gradual failure modes and higher temperature durability. Polymeric nanocomposites offer potential material option by combining high dielectric constant of inorganic fillers with high dielectric strength of polymers. Traditional nanocomposites produced by blending of components, however, do not provide sufficient control over morphology, and therefore at high inorganic loadings exhibit a drastic reduction in dielectric strength. Assemblies of core-shell nanoparticles, as a single-component system, offer a possibility for optimization of structure and properties through the modification of the interface. Herein, we report the synthesis and dielectric properties of the assembly of hybrid nanoparticles consisted of titanium dioxide core surrounded by covalently attached polystyrene corona via phosphate coupling and "click" chemistry. The use of mixture of low and high molecular weight polymer in different ratios enabled tuning of nanoparticle density, arrangement, and particle-particle spacing, as well as thermoplastic characteristics of the assembly. Direct solution casting of these hybrid particles without addition of free polymer yielded the solid films of high inorganic content (30-60%) and sufficient robustness. The films exhibited dielectric constants up to 6.5 and flat frequency response up to 100 kHz.

SESSION U13: Poster Session II
Chairs: John Miller and Yang Shao-Horn
Wednesday Evening, December 2, 2009
8:00 PM

Exhibit Hall D (Hynes)

U13.1

Nanoporous SnO₂ as Anode Material for Li-ion Batteries. Rolf Ochs¹, Dorothee V. Szabo¹, Sylvio Indris² and Sebastian Becker²; ¹Institute for Materials Research III (IMF III), Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen, Baden-Wuerttemberg, Germany; ²Institute for Nanotechnology (INT), Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen, Baden-Wuerttemberg, Germany.

Nanomaterials based on tin dioxide (SnO₂) possess very promising potential as anode material in Li-ion batteries because they exhibit in principle much higher specific capacities (790 mAh/g) than currently used carbon anodes (372 mAh/g). Bulk SnO₂ anode material however shows very poor long-term cycle stability due to internal stress caused by the large volume change (>200%) during the alloying process from Li and Sn to Li_{4.4}Sn resulting in cracks and loss of active material. Nanoporous materials could resolve this issue because they feature local free space to compensate this volume change. Bare tin dioxide (SnO₂) nanoparticles and SnO₂/carbon core/shell nanoparticles have been synthesized utilizing the Karlsruhe Microwave Plasma Process (KMPP), a versatile gas phase process. For the utilization as negative electrode material for Li-ion batteries the nanoparticles have been deposited as a film on Ni-Substrates on the one hand by in-situ depositing and on the other hand by a standard powder processing method for comparison. Scanning electron microscopy (SEM) characterization of the in-situ deposited films reveal a highly porous, club-like morphology. Nevertheless, these films exhibit a high mechanical stability. Transmission electron microscopy (TEM) of the particles shows a relatively uniform particle or core size of about 5 nm. The crystal structure of the particles is identified by electron diffraction to be the tetragonal cassiterite structure. Electrochemical performance measurements show specific charge and discharge capacities for the first cycle in the region of their theoretical values. With increasing cycle number the specific capacities actually decrease. This is attributed to the large volume change during the charging/discharging process and resulting in an island formation in the layer. Compared to the powder samples the capacity loss of the in-situ deposited layers is significantly reduced. This may be actually attributed to the nanoporous morphology of these layers. Optimizing the carbon shell thickness should further enhance the cycle stability as this carbon shell acts as a scaffold between the SnO₂ particles. These results indicate that this is a promising approach for high capacity anodes in Li-ion batteries.

U13.2

Abstract Withdrawn

U13.3

Control of Particle Size and Thin Film Surface Morphology using Femtosecond Pulsed Laser Deposition: For Growth of Li-ion Battery Electrode and its Applications. Makoto Murakami, Bing Liu, Zhendong Hu and Yong Che; IMRA America, Inc, Ann Arbor, Michigan.

For battery applications of electrode materials, controlling their particle size and surface morphology is one of the most important approaches to maximize their battery performances. In this presentation, we introduce a novel method to control the particle size and the surface morphology, and a method of pulsed laser deposition (PLD) using a femtosecond pulsed laser with burst-mode, which is a multi-pulse mode of selected number of pulses with very short time separation (20 ns) in between the pulses (**Burst-PLD**). This method enables controllability for thin-film morphologies, ranging from nanoparticle aggregates to epitaxial thin films with completely droplet-free and atomically smooth surfaces [1]. Using the Burst-PLD, we are potentially design the electrode materials to overcome the problems such as overvoltage which is dominated by solid-state diffusion of lithium in positive electrode. As for demonstrations, we have grown several cathode (LiMn₂O₄ and LiCoO₂) and anode (Li_xTiO₂, Li_xSnO₂) and their composite thin films for lithium ion battery electrode materials using the Burst-PLD. A fiber based femtosecond laser (FCPA μJewel™ D-1000 laser developed by IMRA America, Inc.) is used for generating burst-mode laser pulses. The number of burst-mode pulses is selectively controlled from 1 to 20, and the repetition rate of the burst is also tunable in the range of 0.1 - 5 MHz. Ceramic targets placed in vacuum chamber are ablated with different number of pulses. When more number of pulses is used for the ablation (typically more than 10 pulses), smoother thin films free of droplets and clusters are obtained. While by decreasing the number of burst-pulses and/or increasing pulse energy for the ablations, rougher films of nanoparticle aggregates are obtained with increasing particle size. LiMn₂O₄ and LiCoO₂ composite thin films are also grown by switching each targets, and the ratio of the composition are controlled by changing the ratio of ablation time of both targets. Epitaxial LiMn₂O₄ and LiCoO₂ thin films are successfully grown on Al₂O₃ (0001) single crystal substrate. In case of conventional PLD using excimer laser and such, solid solution thin films are successfully obtained; however, when femtosecond pulsed laser is used, we obtained composite of epitaxial LiMn₂O₄ and LiCoO₂ thin films rather than solid solution. We attribute the reason why solid solution thin films cannot be obtained in case using femtosecond PLD is that the particles are created very early stage of the ablation and they fly onto the substrate, and the materials do not have enough energy to react each other on the substrate in the typical growth temperature. [1] M. Murakami et al. Appl. Phys. Express, 2 042501 (2009)

U13.4

Structural Studies of Chemically Delithiated Mixed Olivine Phosphates. Joel K. Miller, Natalya A. Chernova, Shailesh Upreti and Stanley M. Whittingham; Material Science, SUNY Binghamton, Binghamton, New York.

Lithium iron phosphate's value as a cathode material in lithium ion batteries is well known. However, the ionic diffusion in LiFePO₄ and related olivine phosphates is still poorly understood due to essentially two-phase nature of their delithiation and lithiation. For

example, during most of a galvanostatic cycle of LiFePO_4 , a lithium dilute (vacancy rich) phase and a lithium rich (vacancy dilute) phase are present. Therefore, a lithium diffusion coefficient determined for Li_xFePO_4 at a value of $x < 0.90$ and > 0.05 via impedance spectroscopy (IS) or galvanostatic intermittent titration technique (GITT) will reflect diffusion at the phase boundary between these two phases in this miscibility gap region. In this study we suggest the possibility of overcoming this problem by synthesizing olivines with controlled ratios of metals on the M1 site, similar to those observed in mineral olivines. In nature, there are single-phase olivine-type phosphates for which lithium concentration is within the aforementioned miscibility gap of lithium iron phosphate. Nature accomplishes this by incorporating other cations (Mg^{2+} , Ca^{2+} , etc.) on the M1 site to stabilize the structure. One example of such a mineral is simferite, $\text{Li}_{0.5}\text{Mg}_{0.5}\text{Fe}_{0.3}\text{Mn}_{0.2}\text{PO}_4$. According to single crystal x-ray diffraction data of mineral simferite, the Mg^{2+} substitution creates randomly distributed lithium vacancies (*Doklady Akademii Nauk SSSR*, **307**, 1119, 1989). Furthermore, Mn^{2+} substitution might lead to single phase lithium cycling. Such substituted compounds with randomly distributed lithium vacancies can be used to determine the lithium diffusion coefficient as a function of lithium vacancies. We have had success substituting Mg^{2+} and Mn^{2+} on to the M1 site via hydrothermal reaction followed by chemical oxidation with NO_2BF_4 or Br_2 . $\text{Li}_{0.5}\text{Mg}_{0.5}\text{Mn}_{0.3}\text{Fe}_{0.2}\text{PO}_4$ and related $\text{Li}_x[\text{Mg},\text{Mn},\text{Fe}]\text{PO}_4$ were prepared in this manner. Products were evaluated by powder x-ray diffraction, DC-Plasma emission spectrometry, transmission electron microscopy, scanning electron microscopy, and temperature dependent magnetic studies. X-ray diffraction showed that single phase powders were synthesized with lattice parameters consistent with Vegard's law predictions. DCP and magnetic properties confirm the metal contents and oxidation states. Micron particle size limits the electrochemical performance of the compounds, so that only about half of the available lithium can be extracted electrochemically. The nature of delithiation reaction (one-phase vs. two-phase) will be discussed. GITT and impedance spectroscopy studies will be used to estimate the effect of lithium vacancies on the diffusion. This work is supported by the US Department of Energy, Office of FreedomCAR and Fuel Partnership through the BATT program at Lawrence Berkeley National Laboratory.

U13.5

Conversion Reactions Electrodes of Transition-Metal Oxides Using Nanoporous Conductive Scaffolds. John J. Vajo, Adam F. Gross, Elena Sherman and Ping Liu; HRL Laboratories, Malibu, California.

Lithium ion storage based on intercalation reactions in transition-metal oxides is generally limited to one, or at most two, electron reductions. However, compete multi-electron reductions to Li_2O + transition metals, designated as conversion reactions, are possible provided that the reactants and products have the proper nanoscale structure[1]. These reactions can have capacities exceeding ~1000 mAh/g and, therefore, are of interest for advanced lithium batteries. We have studied conversion reactions of Mn, Fe, and Co oxides incorporated into the pore volume of electrically conductive nanoporous carbon aerogels. The aerogels confine the oxide domains to the nanoscale and further provide good electrical contact, electrical conductivity, and electrolyte access. Carbon aerogels were synthesized using resorcinol-formaldehyde condensation followed by pyrolysis. Typically, we used aerogels with a total pore volume of ~1.3 cm³/g and a peak in the pore size distribution at 25 nm, although, pores sizes from 5 nm to 30 nm are possible by adjusting the synthesis conditions. After synthesis, oxides were incorporated using metal nitrate hydrates as precursors. The hydrates were melted at 50 - 100 °C and infiltrated into the aerogels filling the pore volume. Heating was then used to first decompose the hydrates and, subsequently, the nitrate anions within the pores of the aerogel to yield the corresponding nanoscale metal oxides: MnO_2 , Fe_2O_3 , and Co_3O_4 . Oxide mass loadings from 25% to ~50% were achieved. Electrochemical cycling behavior was studied using Swagelok cells against Li metal counter electrodes. When corrected for the capacity contribution from the carbon aerogel (~200 mAh/g), lithium capacities of the oxides approached 1000 mAh/g. These capacities indicate complete reduction to Li_2O + Mn, Fe, and Co. In this presentation, we will describe the preparation, characterization, and cycling behavior of these nanoconfined oxide electrodes. [1] P. G. Bruce, B. Scrosati, J.-M. Tarason, *Nanomaterials for Rechargeable Lithium Batteries*, *Angew. Chem. Int. Ed.* 2008, 47, 2930 - 2946 and references therein.

U13.6

Abstract Withdrawn

U13.7

High Rate, Nanocomposite Zinc - doped LiFePO_4 Cathode for Lithium Ion Batteries. Arun Kumar, Reji Thomas, Maharaj S. Tomara and Ram S. Katiyar; Physics, University of Puerto Rico,, San Juan, Puerto Rico.

The cost effectiveness, environmental benevolently, and thermal stability have made Lithium iron phosphate (LiFePO_4) as one of the most attractive cathode materials for rechargeable Li-ion batteries. LiFePO_4 exhibiting theoretical capacity of ~170 mAh/g and a flat charge/discharge profile at ~ 3.4 V Li^+/Li . However, slow diffusivity of Li^+ in LiFePO_4 ($D_{\text{Li}} \sim 10^{-14}$ - 10^{-16} cm²/s) compared to the widely used layered LiCoO_2 ($D_{\text{Li}} \sim 10^{-12}$ - 10^{-13} cm²/s) allowed only 60% of the capacity to be tapped in the early work. To overcome the poor ionic as well as electronic conductivities of LiFePO_4 , carbon coating has been described to improve the Li-ion kinetics. The control on the particle size in the nano-regime along with a narrow particle size distribution of the synthesized LiFePO_4 cathode materials is found beneficial to increase capacity. Even though, researchers solved the problem of obtaining higher capacity near to the theoretical capacity, but its remarkable capacity loss at larger current density is still a problem. To improve the rate-capability we have studied the effect of the Zinc oxide doping of LiFePO_4 on the electrochemical properties. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical properties were investigated systematically. The XRD pattern demonstrated that an olivine phase of ZnO-doped LiFePO_4 and the structure was indexed to the orthorhombic $Pnma$ space group. The SEM image revealed that the particles were agglomerated and the particle sizes were almost homogeneously distributed. Olivine compound $\text{LiFe}_{1-x}\text{Zn}_x\text{PO}_4/\text{C}$ ($x=0.03$ and 0.06), results indicate that Zn^{2+} does not affect the olivine structure of the cathode but considerably improve its initial capacity and rate capability. The cyclic voltammetry (CV) and galvanostatic charge and discharge test showed the 3% ZnO- doped LiFePO_4 with $x=0.03$ has higher electrochemical reactivity for lithium

insertion and extraction than 6% ZnO- doped LiFePO₄. LiFe_{0.97}Zn_{0.03}PO₄/C showed initial specific discharge capacity of 159.32 and 109.67 mAh/g with C/10 and 12C rate, respectively. This enhancement might be due to increase in the electronic conductivity by Zn²⁺ substitution and carbon coating.

U13.8

Electron Energy-loss Spectroscopy (EELS) Mapping of Lithium Compounds in the Solid-electrolyte Interphase (SEI) on Graphite Anode Materials for Li-ion Battery. Feng Wang¹, Lijun Wu¹, Vyacheslav Volkov¹, Yimei Zhu¹, Xiaoqing Yang¹, Toshihiro Aoki² and Jason Graetz¹; ¹Brookhaven National Lab, Upton, New York; ²JEOL USA, Peabody, Massachusetts.

The formation of a thin and stable solid-electrolyte interphase (SEI) film on the electrodes of lithium-ion batteries is a critical factor determining the battery performance. A comprehensive understanding of how the SEI forms and the composition of the SEI layer is one of the great challenges in lithium battery research, after the three decades of effort [1]. Besides Peled's "mosaic" model, several other different models have been proposed based on various spectroscopic analyses. It is desirable to resolve and visualize the distribution of various lithium compounds in the nanometer-thick SEI film. Unfortunately, not much work on this has been reported so far. Taking the advantage of high spatial resolution of EELS in the TEM [2], we are making progress in mapping main components in the SEI layer for several graphite anode materials for lithium-ion cells. In this study the elemental concentration distribution was extracted from the energy-filtered images. The different lithium compounds were further differentiated by the Li-K near-edge fine structure, electron diffraction and high-resolution TEM imaging. High-vacuum transfer and cryo-holders were used to minimize the air exposure and to reduce the radiation damage. Filtered images and EELS spectra were recorded on JEOL 3000F attached with a GIF spectrometer. Other data were collected on a double aberration-corrected JEOL 2200 MCO equipped with an in-column W filter. Our results for synthetic graphite (from Alfa-Aesar and TIMCAI) and highly oriented pyrolytic graphite (HOPG) cycled in a standard EC/DMC/LiPF₆ electrolyte will be presented. In addition, the issue of radiation damage, the main factor limiting the spatial resolution will also be discussed [3]. The work was supported by the U.S. Department of Energy, Office of Basic Energy Science, and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under the program of Vehicle Technology Program, under Contract Number DEAC02-98CH10886. Reference: [1] P. B. Balbuena, Y. Wang (Ed.), Lithium batteries: solid electrolyte interphase. Imperial College Press (2004). [2] R.F. Egerton, Electron energy-loss spectroscopy in the TEM, Rep. Prog. Phys. 72 (2009) 016502. [3] R.F. Egerton, F. Wang, and P.A. Crozier, Micros. and Microan. 12 (2006) 65.

U13.9

High Conductivity in Carbon Nanotube Array/Ionomer Composite with Aligned Ion Transport Paths. Yang Liu¹, Sheng Liu¹, Junhong Lin¹, Hulya Cebeci², Roberto G. de Villoria², Brian L. Wardle² and Qiming Zhang^{1,3}; ¹Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania; ²Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

In supercapacitors and Li-Ion batteries, the design of the composite electrode morphology is important since the ion transport speed in it determines the charging/discharging period. As electrodes in our supercapacitor, the ionomeric polymer/conductive network composite dominates the charge/discharge speed and the charging capacitance. In this study, CNT forest is applied as conductive network due to its extraordinary electronic and mechanical properties and high stability. Free standing CNT forest enables the possibility of further densifying the forest into high volume fraction, up to about 20%, to enhance its properties. The CVD grown 1% volume fraction multiwall carbon nanotubes generally have 3-5 walls, about 10nm diameter. Higher volume fractions of carbon nanotubes are achieved by mechanical densification. Composite is made by wetting the carbon nanotube array with Nafion solution and evaporating excess solvent with a modified solution-cast procedure to avoid the forming of islands and voids. The electronic conductivity of 1%, 10% and 20% carbon nanotube array/Nafion composite is measured as 0.4 S*cm⁻¹, 2.8 S*cm⁻¹ and 3.5 S*cm⁻¹, respectively. Moreover, compared to the ionic conductivities of neat Nafion membrane 6x10⁻⁴ S*cm⁻¹ and conductive nanoparticle/Nafion composite 1.1x10⁻⁵ S*cm⁻¹, the ionic conductivity of carbon nanotube array/Nafion composite ~10⁻⁴ S*cm⁻¹ holds enormous promise for faster ionic and electronic transports than conductive nanoparticle/Nafion composite. A further impedance analysis of the device structure and the prototype device fabrication are also investigated in the work. With this improvement in charging/discharging speed, there is a huge potential of enhancing the supercapacitor performance in HEV, LEV and etc.

U13.10

Chemically Reduced Graphene Sheets Separated by Layer-by-Layer Assembled Carbon Nanotubes for Electrochemical Capacitor Applications. Hye Ryung Byon¹, Seung Woo Lee², Paula T. Hammond² and Yang Shao-Horn¹; ¹Department of Materials Science and Engineering, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We present high specific capacitance of chemically reduced graphene (CRG) sheets separated by layer-by-layer (LbL) assembled multi-walled carbon nanotubes (MWNTs) in acidic aqueous solution. Amine-functionalized MWNT (MWNT-NH) and graphene oxide (GO) were alternately adsorbed onto ITO-coated glasses via the LbL assembly method, which were then subject to a 24-h hydrazine treatment at 120 C in order to convert GO to CRG. The MWNT/CRG films showed ~10 times greater electronic conductivity in comparison with original MWNT/GO LbL films upon removal of a large number of surface oxygen groups on GO sheets. The specific capacitance of MWNT/CRG films from cyclic voltammetry measurements in 0.5 M HSO was measured to be ~150 F/g, from which the capacitance of CRG layers in the films was estimated to ~230 F/g by excluding the MWNT capacitance contribution. The high specific capacitance of CRG films can be attributed to 1) the availability of electrochemically active surface

area of CRG sheets separated by the MWNTs in the LbL films, and 2) pseudo-capacitive charge storage associated with redox of nitrogen-containing and oxygen-containing surface functional groups on the CRG surface.

U13.11 Transferred to U15.5

U13.12

New Binder Materials for Si Electrode. Gao Liu, Shidi Xun, Xiangyun Song, Honghe Zheng and Vince Battaglia; Environmental Energy Technologies Division, Lawrence Berkeley National Lab, Berkeley, California.

High-capacity electrodes for lithium-ion batteries have to be developed in order to meet the 40-mile plug-in hybrid electric vehicle energy density needs. Si, with a high volumetric and gravimetric density (2446 mAh/mL and 4200 mAh/g at Li_{4.4}Si), may be a viable candidate. Full capacity cycling of Si results in significant capacity fade due to a large volume change during Li insertion and removal. Decreasing the particle size to nanometer scale can be an effective means of accommodating the volume change; however, the repeated volume change during cycling can also lead to repositioning of the particles in the electrode matrix and result in particle dislocation from the conductive matrix. This dislocation of particles causes the rapid fade of the electrode capacity during cycling, even though the Si particles are not fractured. In our opinion, any new approach to enable Si material should be compatible with the current Li-ion chemistry and manufacturing processes. To this end, a new class of binder material was designed and synthesized. These new binders provide improved binding force to the Si surface to help maintain good electronic connectivity throughout the electrode. The electrodes made with these binders have significantly improved the cycling capability of Si.

U13.13

Nanowire Composites for Electrochemical Energy Storage. Zheng Chen and Yunfeng Lu; UCLA, Los Angeles, California.

In order to design a better electrochemical capacitor with both high energy and power density, a common strategy is to construct a hybrid capacitor that integrates both the electric double-layer capacitance and pseudocapacitance within a single electrode. For example, Sato et al. loaded ruthenium oxide onto activated carbon, resulting in a capacity of 308 F g⁻¹ at 7.1 wt % ruthenium loading and a low scanning rate of 2 mV s⁻¹. Dong et al. reported the composite of MnO₂ and the templated carbon with a capacitance of 156 F g⁻¹ at 20 wt-% MnO₂ loading and a scanning rate of 50mV s⁻¹, which is about two times of that of the constituent carbon. Kim et al. dispersed ruthenium oxide nanoparticles on carboxylated CNTs and obtained a total capacitance of 304 F g⁻¹ at a RuO₂ loading amount of 50 wt-%. Similarly, composites prepared by electrodepositing MnO₂ on vertically aligned CNT arrays exhibit a capacitance up to 199 F g⁻¹ (or 305 F cm⁻³) with long cycle life; however, the complex fabrication process may limit their actual use. In spite of extensive research and effort, making supercapacitors with high energy and power density still remains challenging. Herein, we report the synthesis of novel supercapacitor materials based on the composites of low-cost, interpenetrating CNTs and V₂O₅ nanowires. This unique architecture provides several major advantages: 1) the small dimension of the CNTs and the nanowires provide high surface areas, leading to a high EDLC and better utilization of the V₂O₅ active sites (higher specific pseudocapacitance); 2) the interpenetrating nanotube/nanowire structure creates hierarchical porous channels, enabling effective electrolyte transport and active-site accessibility; (3) the nanowires are intimately intertwined with highly conductive CNTs, facilitating a faster electron transport and efficient current collection. Experimentally, these novel composites were readily synthesized using a one-pot hydrothermal approach. Note that V₂O₅/CNT composites were prepared by depositing a thin layer of V₂O₅ (6 nm thick) on a CNT film, exhibiting a high Li-ion capacitance up to 910F g⁻¹ at a scan rate of 10mV s⁻¹. However, such composite thin films with extremely low V₂O₅ loadings may not be suitable for practical applications. This work provides a simple but effective synthesis route and structure design towards better supercapacitors.

U13.14

Abstract Withdrawn

U13.15

Electrical Conductivity Enhanced by Proton Irradiation in Hydrogen-bonded KH₂PO₄. Jin Jung Kweon, In Hwan Oh, Kyu Won Lee and Cheol Eui Lee; Department of Physics, Institute for Nano Science, Korea University, Seoul, Korea, South.

Hydrogen-bonded proton conductors, which can be used in fuel cells in the intermediate temperature range (100 ~ 300 °C), are recently attracting great interest due to their potential as electrolytes in fuel cells. KH₂PO₄ (KDP) may be used as a model system of the proton conducting materials. We have investigated the effects of proton irradiation, with different irradiation energies and doses, on the anisotropic electrical conductivity of KDP. The room-temperature electrical conductivity exhibited a more than an order of magnitude enhancement along the a-axis in proton-irradiated KDP. From the temperature-dependent measurements of the a-axis and c-axis electrical conductivities, the proton irradiation is found to have given rise to changes in the activation energy presumably of the proton intersite hopping. Our work demonstrates the potential of the proton irradiation as a means of controlling the electrical conductivity of the proton conductors for the use of efficient proton fuel cells.

U13.16

Materials Selection Criteria for Mechanically Durable Insertion Electrodes for Lithium Ion Batteries. Yang-Tse Cheng¹ and

Mark W. Verbrugge²; ¹Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky; ²Materials and Processes Lab, General Motors Research and Development Center, Warren, Michigan.

Lithium ion battery electrodes may experience large volume changes caused by concentration changes within the host particles during charging and discharging. Electrode failure, in the form of fracture or decrepitation, can occur as a result of repeated volume changes. In this paper, we present a set of analytic solutions for the evolution of stresses within a spherically-shaped electrode element under several representative charging-discharging conditions, including the ones developed earlier [1-4]. Based on the analytic solutions, we develop a set of criteria for the initiation of cracks in spherical insertion electrodes. These criteria may help guide the development of new materials for lithium ion batteries with enhanced mechanical durability. [1] Y.-T. Cheng and M. W. Verbrugge, The influence of surface mechanics on diffusion induced stresses within spherical nanoparticles, *J. Appl. Phys.* 104, 083521 (2008). [2] M. W. Verbrugge and Y.-T. Cheng, Stress Distribution within Spherical Particles Undergoing Electrochemical Insertion and Extraction, *The Electrochemical Society (ECS) Transactions* 16, 127 (2008). [3] Y.-T. Cheng and M. W. Verbrugge, Evolution of stress within a spherical insertion electrode particle under potentiostatic and galvanostatic operation, *J. Power Sources* 190, 453 (2009). [4] M. W. Verbrugge and Y.-T. Cheng, Stress and strain-energy distributions within diffusion-controlled insertion-electrode particles subjected to periodic potential excitations, *J. Electrochem. Soc.* (to be published).

U13.17

Core-Shell NiSi/Si Nanowires for Li-ion Battery Anodes. Gil-Sung Kim¹, Kibum Kang¹, Geunhee Lee¹, Hyun-Seung Lee¹, Cheol-Joo Kim¹, Donghun Lee¹, Dong An Kim¹, Yong-Mook Kang³ and Moon-Ho Jo^{1,2}; ¹Department of Materials Science and Engineering, POSTECH, Pohang, Gyungbuk, Korea, South; ²Division of Advanced Materials Science, POSTECH, Pohang, Gyungbuk, Korea, South; ³Division of Advanced Materials Engineering, Kongju National University, Cheonan, Chungnam, Korea, South.

There has recently been growing interests in the development of alloy-type anodes with the higher energy capacity and longer cycle life for Li-ion batteries. Si is an attractive alternative to the existing carbonaceous anodes due to the highest theoretical charge capacity (4200 mAh/g) and a low discharge potential (below 0.5 V). Single-crystalline Si nanowires (NWs) can provide further advantages over bulk Si or Si powders, mainly due to their affordable accommodation of large volume-changes upon Li-Si alloying/dealloying and efficient charge collection capability, otherwise they are seen as a major source for the cell performance degradation as in the case of bulk Si or Si powders. In this study, we employ core-shell metallic NiSi/amorphous Si (*m*-NiSi/*a*-Si) NWs on the stainless steel substrates, where the electrochemically inactive, conducting *m*-NiSi core acts as a stable mechanical support and an efficient current collector during the alloying and de-alloying reactions. We have fabricated a coin-type half cell by incorporating *m*-NiSi/*a*-Si NWs, and find the enhanced rate capability and superior cycling performance, compared to monolithic Si NWs. In particular, we have investigated the electrochemical reaction of Li⁺ with *a*-Si NW shells, and discuss the roles of the *m*-NiSi core on the cycling performance, in terms of the structural deformations and the reaction kinetics.

U13.18

Abstract Withdrawn

U13.19

Cubic Mesoporous TiO₂ for Next Generation Electrochemical Capacitors: Templated Sol-Gel vs. Nanocrystal Based Films. Torsten Brezesinski^{1,2}, John Wang³, Bruce Dunn³ and Sarah H. Tolbert²; ¹Physical Chemistry, Justus Liebig University Giessen, Giessen, Germany; ²Chemistry & Biochemistry, University of California at Los Angeles, Los Angeles, California; ³Materials Science & Engineering, University of California at Los Angeles, Los Angeles, California.

Capacitive energy storage has been somewhat overlooked as an energy storage technology. It is based on electrochemical capacitors (ECs), which include double layer capacitors and pseudocapacitors. These energy storage devices are related to batteries, but have different storage mechanisms. Capacitive storage offers a number of desirable properties, such as charging within seconds and the ability to deliver up to 10 x more power than batteries. The limiting feature that prevents more widespread usage of ECs has been the relatively low energy density of the materials employed. Here, we present methods to overcome the limitations of ECs through the use of nanoporous transition metal oxides. A significant feature occurs as materials approach nanometer-scale dimensions. The charge storage from faradaic processes occurring at the surface becomes increasingly important.[1] However, capacitive energy storage in bulk materials is hindered by slow molecular transport of solvent and ions through the network. To address this problem, we turn to nanoporous films. In recent years, it has been shown that such materials can be readily formed by co-assembly of inorganic oligomers with amphiphiles. However, despite the fact that a broad range of ordered porous materials can be made, the majority of the templated materials do not allow the inorganic walls to be crystallized while retaining nanoscale order. Here, we report the fabrication as well as pseudocapacitive characteristics of block copolymer templated anatase TiO₂ thin films synthesized using either sol-gel reagents or preformed nanocrystals as precursors. Both materials are 100 % crystalline and have large surface areas; yet, the structure of the porosity is not identical. Following our previously reported approach, we are able to use the voltammetric sweep rate dependence to determine quantitatively the capacitive contribution to the current response.[1] Considerable enhancement of the electrochemical properties results when the films are both made from nanocrystals and mesoporous. Such materials show high levels of capacitive charge storage and high insertion capacities. By contrast, when nanoscale porosity is created in a material with dense walls rather than porous walls derived from the aggregation of nanocrystals, insertion capacities comparable to templated nanocrystal based films can be achieved, but the capacitance is much lower. The results presented here underscore the importance of pseudocapacitive behavior that develops in mesoporous oxide films. Also, they suggest that both a mesoporous morphology and the use of nanocrystals as the basic building blocks are very promising for the rational development of metal oxide capacitors. Through this combination, it may become

possible to attain greater power densities while maintaining energy density in next generation electrochemical capacitors. [1] Brezesinski, T.; Wang, J.; Polleux, J.; Dunn, B.; Tolbert, S. H. J. *Am. Chem. Soc.* 2009, 131, 1802.

U13.20

Binding Site of Li⁺ Ions in 1D Nanostructured β -MnO₂ Probed by ⁷Li MAS-NMR Spectroscopy. In Young Kim, Hyung-Wook Ha, Tae Woo Kim and Seong-Ju Hwang; Dpartment of Chemistry and Nano Sciences, Center for Intelligent Nano-Bio Materials (CINBM), Ewha Womans University, Seoul, Korea, South.

We have found that the formation of 1D nanostructures increases remarkably the charge capacity of β -MnO₂ phase for lithium secondary batteries. To elucidate the origin of the capacity increases after the nanostructure formation, we have carried out systematic ⁷Li magic angle spinning-nuclear magnetic resonance (⁷Li MAS-NMR) analyses for lithiated β -MnO₂ nanorod and its bulk microcrystalline homologue. The β -MnO₂ 1D nanorods were synthesized by the hydrothermal treatment of diverse manganese oxide precursors. The electrochemical measurements clearly demonstrated that the electrode performance of the β -MnO₂ nanorod is much superior to that of bulk β -MnO₂, confirming the positive effect of nanostructure formation. According to ⁷Li MAS-NMR analysis, the lithiated β -MnO₂ shows a strong peak near 0 ppm, underscoring that the Li⁺ ions are mainly adsorbed on the surface of lithiated β -MnO₂ nanorod. Based on the present MAS-NMR results, we could conclude that the increase of the surface area upon the nanostructure formation is mainly responsible for the obtained excellent electrode performance of the β -MnO₂ nanorod.

U13.21

Highly Reversible Li Storage in Si Nanowires with the Maximum Capacity. Kibum Kang¹, Dong-Wook Han⁴, Hyun-Seung Lee¹, Gil-Sung Kim¹, Donghun Lee¹, Geunhee Lee¹, Yong-Mook Kang³ and Moon-Ho Jo^{1,2}; ¹Materials Science & Engineering, POSTECH, Pohang, Gyungbuk, Korea, South; ²Division of Advanced Materials Science, POSTECH, Pohang, Gyungbuk, Korea, South; ³Division of Advanced Materials Engineering, Kongju National University, Cheonan, Chungnam, Korea, South; ⁴Department of Materials Science & Engineering, Korea Advanced Institute of Science & Technology, Daejeon, Korea, South.

The electrochemical Li_xSi intermetallics form various crystalline compounds with x up to 4.4, correspondingly symptomatic of the largest known gravimetric charge capacity of 4,200 mAhg⁻¹ in the bulk limit, thus can represent an interesting anodic system for the high capacity Li-ion battery. Here, we show direct evidence of reversible phase transitions during the Li-Si alloying/dealloying in Si nanowire (NW) hosts at the full electrochemical cycle by the electron diffraction and energy loss spectroscopic observations at the individual NW level. Concomitantly, we report highly reversible Li charge/discharge capacity whose corresponding composition is Li_{4.4}Si upon the full electrochemical lithiation in a coin-type Si NWs half-cell. Specifically, we have found that an amorphous Si shell/crystalline Si core NWs initially transformed into crystalline and amorphous Li₁₃±Si₄ NWs, followed by crystalline and amorphous Li₂₂Si₅ NWs. Upon the delithiation, the Li₂₂Si₅ NWs progressively transformed into Li₁₂±Si₇ NWs in the radial direction, followed by a recovery to crystalline and amorphous Si NWs.

U13.22

The Change of Elastic Properties in Graphite Anode During Li Intercalation. Yue Qi¹, Haibo Guo³, Louis G. Hector¹ and Adam Timmons²; ¹Materials and Processes Lab, GM R&D Center, Warren, Michigan; ²Chemical and Environmental Science Lab, GM R&D Center, Warren, Michigan; ³Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina.

Stresses induced by lithium diffusion can lead to fracture of electrode materials resulting in capacity and voltage decreases in Li ion rechargeable batteries. The diffusion-induced stress field is often derived from an analytical formulation in which coupling between the mechanical and diffusion problems is based upon an analogous thermal stress problem. Here, we demonstrate that this analogy is invalid for anode materials where diffusion induced staging and phase transition occur. The elastic properties of Li intercalation graphite compounds (Li-GIC) at various stages were predicted from first principles density functional calculations. The results show that Li intercalation significantly increases the elastic moduli perpendicular to the graphite basal planes, and slightly decreases the elastic moduli along the basal planes. Changes in elastic moduli can be accounted for by the changes in bonding nature due to Li intercalation. Inter-plane bonding is strengthened by the additional ionic bonds formed between positively charged Li ions and negatively charged carbon atoms; while the extra charge on C atoms occupies the anti- π bonding thereby weakening the intra-plane bonds. The predicted elastic constants were input to a core-shell model with a moving phase boundary. A two phase coexisting state is predicted wherein the Li-rich region is under compression and Li-deficient region is under tension. This study suggests that the assumption of constant material properties, used in many current battery models is inappropriate.

U13.23

Synthesis and Electrochemical Characterization of 0.5Li₂MnO₃-0.5Li[Mn_{0.375}Ni_{0.375}Co_{0.025}]O₂ Cathode Materials for Li Rechargeable Batteries. Sivaprakash Sundaresan and S. B. Majumder; Materials Science Center, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India.

For lithium rechargeable battery, composite cathodes with high discharge capacity, rate capability, cycleability and stability are one

of the most attractive material candidates. In the present work, using self combustion route, we have successfully synthesised $0.5\text{Li}_2\text{MnO}_3$ (inactive)- $0.5\text{Li}[\text{Mn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.025}]\text{O}_2$ (active) composite layered cathode for lithium rechargeable batteries. The synthesized cathodes were characterized in terms of their phase formation behaviour, microstructure evolution and electrochemical properties. X-ray Rietveld refinement analyses confirm the hexagonal layered structure of these cathode materials. In the cut-off voltage between 4.6 to 2.0 V, using a discharge current ~ 10 mA/g, the charge and discharge capacity of the synthesized cathode material was measured to be 340 and 180 mAh/g respectively. By analyzing the charge and discharge profiles in conjunction with Nyquist plots we have investigated the lithium intercalation behaviour of these composite cathode materials. Through these analyses, it has been postulated that during charging these cathode beyond 4.5 V, lithium is extracted simultaneously both from active as well as inactive components while during discharge part of the lithium is intercalated back which leads to the observed irreversible loss in capacity. In the subsequent charge-discharge cycles, the irreversible loss in capacity was found to be reduced and these cells yield excellent cycleability.

U13.24

TiO₂ Nanotubes with the Controlled Morphology as High Performance Anode Materials in Rechargeable Lithium Ion

Battery. YoungJin Yoon¹, Changdeuck Bae², Hyunjun Yoo¹, Jooho Moon², Joosun Kim³, Won-Sub Yoon¹ and Hyunjung Shin¹; ¹School of Advanced Materials Engineering, Kookmin University, Seoul, Korea, South; ²Department of Materials Science and Engineering, Yonsei University, Seoul, Korea, South; ³Center for Energy Materials Research, Korea Institute of Science and Technology, Seoul, Korea, South.

One-dimensional nanostructures such as nanowires, nanorods, and nanotubes (NTs) are actively being investigated as efficient charge collectors for energy storage and conversion applications. TiO₂ NTs has been confirmed as a safe anode material in lithium ion batteries due to its intrinsic higher chemical stability. They also show higher lithium insertion potential in comparison with the commercialized carbon anode materials. Nanotubular structures of TiO₂ allow for better accommodation of the large volume changes without the initiation of fracture that can occur often in bulk or micron-sized TiO₂. Each of TiO₂ NTs is electrically connected to the metallic current collector so that all the NTs contribute to the capacity as direct 1-D electronic pathways allowing for efficient charge transport. We have studied the electrochemical characteristics of TiO₂ NTs as anodes for lithium ion batteries that have large surface area, high aspect ratio as well as high areal density. TiO₂ nanotubular anodes have been fabricated by template-directed atomic layer deposition (ALD) process onto porous alumina membranes. With the ALD process, in principal, all of the physical dimensions including diameter, length, and wall thickness of TiO₂ NTs are readily adjustable. In particular, the electrochemical characteristics of TiO₂ NTs with different crystallinity and structural dimensions were investigated in this work. As a result, the optimum structures of NTs are determined as follows: With the same morphological feature, rate capacity of TiO₂ NTs with thinner wall was much higher than that of thicker wall of TiO₂ NTs. The thinner TiO₂ NTs (i.e., 5nm-thick) show especially high specific capacity (typically 312mAhg⁻¹ with C/10) and ultrafast discharge rate (typically 50mAhg⁻¹ with 370C). Higher specific capacity (typically 200mAhg⁻¹ with C/10) is obtained from the crystalline TiO₂ NTs compared to the amorphous ones (typically 138mAhg⁻¹ with C/10). This is probably due to disordered structures and lower electronic carrier mobility in amorphous TiO₂ NTs. The modest capacity fading was also observed in accordance with faster C-rates. It is noted that the cell retained full capacity of 200mAhg⁻¹ when more than 300 cycling at C/3, indicating the chemical/mechanical robustness of our NT electrodes. We have also controlled the morphology of TiO₂ NTs to improve further their electrochemical performances. Upon the demonstration of the capability with pristine, smooth NTs, a few approaches might be possible to improve the design of the NTs' morphology. We have fabricated the branched TiO₂ NTs obtained by a mild alkali treatment. It shows extremely fast cycling time with high specific capacity (typically 100mAhg⁻¹ with 300C). The proposed nanoarchitectures should make our nanotubular TiO₂ NTs ideal in lithium ion battery applications with significantly high capacity as well as ultrafast lithium ion intercalation.

U13.25

Layer-by-Layer Assembled Thin Films for Battery Electrolytes. Lang Sui¹, Arthur A. Feldman¹, Nicholas A. Kotov^{1,2} and John Kieffer¹; ¹Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ²Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Battery electrolytic thin films were fabricated using exponentially grown layer-by-layer (eLBL) assembly method. In eLBL, poly (ethylene oxide) (PEO), poly(acrylic acid) (PAA) and fumed silica (f-SiO₂) were combined through weakly opposite charge attractions between polymers or through hydrogen bonding. This way, relatively thick films of 40-60 microns were made using few deposition steps. Unlike traditional LBL, eLBL films have high levels of interpenetration where each layer is not easily distinguishable. [(PEO/PAA)_x/SiO₂]_y films were fabricated with a total of 30 PEO/PAA bilayers. The amount of SiO₂ is varied by changing the PEO/PAA thickness between each SiO₂ deposition. The amount of deposited SiO₂ was measured using thermogravimetric analysis. NaCl salt was dissolved into PEO solution and incorporated into the film during deposition. Fluorescence spectroscopy of tagged PEO and PAA showed that homogeneously blended films were created during exponential growth. The in-plane and out-of-plane elastic moduli were measured using Brillouin light scattering and found to be of comparable magnitude, indicating the elimination of interfaces between layers. Ionic conductivities of the films were measured using impedance spectroscopy. Impedance spectroscopy showed an improvement in ion conductivity for eLBL as compared to cast films. Furthermore, the addition of f-SiO₂ layers also resulted in an increase of conductivity.

U13.26

Carbide-derived Carbon for Thin Film Supercapacitors. Min Heon¹, Yury Gogotsi¹, Jeffrey D. Hettinger², Magali Brunet³, David Pech³, Pierre-Louis Taberna⁴ and Patrice Simon⁴; ¹Department of Materials Science and Engineering and A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania; ²Department of Physics and Astronomy, Rowan University, Glassboro, New Jersey; ³LAAS-CNRS, Université de Toulouse, Toulouse, France; ⁴CIRIMAT UMR CNRS, Université Paul Sabatier, Toulouse, France.

Thin film batteries and supercapacitors are potentially capable of providing power to a new generation of advanced power-thirsty electronic devices, portable electronics, sensors, etc. They may also be integrated with solar batteries, storing electrical energy and providing high power density. However, compared to Lithium-ion batteries, very little work has been done to integrate supercapacitors on a silicon chip or produce thin film supercapacitors in general. Carbide-derived carbon has been shown to perform very well in supercapacitor electrodes. In this research, we will demonstrate continuous thin films of carbide-derived carbon formed on various substrates, which were produced by selective etching and vacuum decomposition of Silicon Carbide (SiC) and Titanium Carbide (TiC) films. The synthesis process of CDC thin film has been investigated in details using different carbides on several substrates. Selective etching by chlorine has been optimized for thin-film CDC synthesis on a variety of substrates through analysis of the film growth using Raman spectroscopy and electron microscopy. The electrochemical properties of the thin film supercapacitors using carbide-derived carbon will be discussed as well.

U13.27

Electrochemical Behavior of Amorphous Tin-Cobalt Anode. Ruigang Zhang, Shailesh Upreti and M. Stanley Whittingham; Binghamton University, Binghamton, New York.

Lithium-ion batteries are ideal power sources for portable electronic devices. However, safer and less costly electrodes are the need of next generation rechargeable batteries, particularly for the applications where high pulse charging and discharge is required, example includes; hybrid electric vehicles and all-electric vehicles. Amorphous tin based anodes have attracted much interest due to their higher volumetric capacity than graphite and excellent capacity retention. Here we compare the electrochemical behavior of amorphous and crystalline tin based material. At all cycling depths of discharge, 10% to 100%, the amorphous anode showed no loss of capacity in direct contrast to crystalline Sn foil. Lithium removal was found to show excellent rate capabilities, but lithium insertion was found to be rate limited. An ex-situ X-ray analysis revealed that annealing triggers the crystallization and grain size increase in Sn based material. A detailed in-situ, ex-situ X-ray diffraction, EIS and CV analysis, will be presented with an aim to throw more light on the chemistry and limitations of this class of material. This work is supported by the US Department of Energy, Office of FreedomCAR and Fuel Partnership, through the BATT program at Lawrence Berkeley National Laboratory.

U13.28

Effect of Annealing on the Dielectric Properties of BaTiO₃ - High-k Polymer Nanocomposites. Sai G. Shiva Reddy, Youngjin Choi, William I. Milne and Gehan A. J. Amarutunga; Engineering, University of Cambridge, Cambridge, United Kingdom.

High-k materials find usage in a variety of electronic applications such as high-frequency, high energy density capacitors, transducers, piezo-sensors, etc. Barium Titanate (BaTiO₃) nanoparticles are known to possess a very high dielectric constant, typically in the range of 1- 10000, that largely depends on the particle size and the post annealing temperature. In this paper, we attempt to improve the dielectric properties of BaTiO₃ nanoparticles by post annealing and blending with polymers. Hydrothermally synthesized BaTiO₃ nanoparticles are first annealed and then suspended in a high-k polymer matrix (cyanoethylated cellulose, k of 21 at 1Khz). We report the effect of annealing BaTiO₃ nanoparticles, at various temperatures in the range of 50-1100°C, on the dielectric properties of the nanocomposites. The performances as a function of the fraction of BaTiO₃ filler in the polymer matrix are also investigated.

U13.29

Electrochemical Supercapacitors Confined in Nanopores of Anodic Aluminum Oxide on Silicon Substrate. Juchao Yan, Eastern New Mexico University, Portales, New Mexico.

Electrochemical supercapacitors include electrical double-layer capacitors and/or electrochemical redox capacitors. On demand, electrochemical supercapacitors can supply charge more quickly than batteries, making them ideal for smart cards, displays, implantable medical devices, and hybrid cars. During the past nearly thirty years, electrochemical supercapacitors have evolved through several generations of designs.¹ However, their rational designs on a nanoscale for higher power performance (e.g., higher energy-density) than most batteries are still needed. Nanoporous anodic aluminum oxide (AAO) is a self-ordered, hexagonal array of straight cylindrical pores with tunable diameters (between 5 nm and 300 nm) and depths (up to hundreds of μm). Since 1995,² AAO has been the most popular template for synthesizing one-dimensional metals, semiconductors, inorganic composites, conducting polymers, etc. Surprisingly, there have been very few reports on the fabrication of electrochemical supercapacitors using AAO as a template. Using layer-by-layer assembly in cylindrical nanopores of AAO, Jiang et al.³ reported the first nano-supercapacitor array, consisting of an electro-polymerized polypyrrole (PPy), a porous TiO₂ separator, and a chemo-polymerized PPy. This supercapacitor array forms an excellent concept, but suffers from low capacitance and very limited cycleability (probably due to the difficult control of the electropolymerization process). At Eastern New Mexico University, we have developed a cost-effective, enabling technology to fabricate freestanding AAO membranes with ordered, interconnected pore features. If such

interconnected nanopores were used for electropolymerization, one could experimentally control the depth of the electropolymerized layer on the basis of the sharp change in the electropolymerization parameters. Here, we wish to report a three-step, bottom-up fabrication process to form composite supercapacitors in interconnected nanopores of AAO. We will use pyrrole, thiophene, and aniline respectively as the monomers for the in-pore electro- and chemo-polymerization of the conducting polymers, and to electrodeposit porous TiO_2 , MnO_2 , and RuO_2 respectively on the electropolymerized layer as the separators. High-resolution scanning electron microscopy and transmission electron microscopy will be used to characterize the composite supercapacitors. The electrochemical performance of these composite supercapacitors will be investigated using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. References: 1. Pushparaj, V.L.; Shaijumor, M.M.; Kumar, A.; Murugesan, S.; Ci, L.; Vajtai, R.; Linhardt, R.J.; Nalamasu, O.; Ajayan, P.M. Proc. Natl. Acad. Sci., USA 2007, 104, 13574. 2. Masuda, H.; Fukuda, K. Science 1995, 268, 1466. 3. Liu, L.; Zhao, Y.M.; Zhou, Q.; Xu, H.; Zhao, C.J.; Jiang, Z. Y. J. Solid State Electrochem. 2006, 11, 32.

U13.30

Si Nanoparticle Composites as High-density Energy Storage Material for Li-ion Batteries. Jung-Kyoo Lee², Kurt B. Smith¹, Cary M. Hayner¹ and Harold H. Kung¹; ¹Chemical and Biological Engineering, Northwestern University, Evanston, Illinois; ²Chemical Engineering, Dong-A University, Saha-gu, Susan, Korea, South.

Si is known to have a very high energy storage density when used as a negative electrode for a Li ion battery. However, when used as a simple physical mixture with conducting carbon powder or graphite, nanosize Si particles exhibit very poor cycling stability. The initial high storage density (over 3000 mAh/g) disappears rapidly within a few charge/discharge cycles. Since composites of Si nanoparticles are easy to prepare, they offer a huge advantage on cost of manufacturing compared with highly sophisticated engineered structure. Thus, it is of great interest to find ways to stabilize the Si nanoparticles. We postulate that the cycling stability of Si nanoparticle composite can be enhanced if the particles can be dispersed homogeneously in the composite. Using this guideline, we prepared and tested two types of Si-carbon composites in which the carbonaceous component was derived either from a resorcinol-formaldehyde gel or from graphene sheets. The results show that when the Si nanoparticles are successfully dispersed in the composite, the cycling stability is much enhanced, and capacity loss of less than 0.5% per cycle can be obtained even for deep charge/discharge cycles. For samples prepared using the RF gel, the effect of surface treatment of the Si particles by introducing phenolic groups by hydrosilylation was examined. Introducing the phenolic groups onto Si enabled direct attachment of the Si particles onto the RF gel, which might facilitate contact of the particles with the gel. This surface modification could be followed by FTIR, and isolation of Si particles from each other was confirmed by TEM. Different methods were investigated to prepare samples with graphene sheets. These include using exfoliated graphene oxide sheets with or without pre-reduction and Si nanoparticles with or without surface treatment. The cycling stability depends strongly on the method of preparation. In general, methods that result in better dispersed Si samples show higher stability. Interestingly, even for an electrode thickness less than 1 mm, the initial storage capacity was found to increase with decreasing thickness, suggesting the importance of transport process to access to all Si nanoparticles and possible ways of improvement.

U13.31

The Hydrothermal Synthesis and Characterization of Carbon-Free LiFePO_4 and $\text{Li}(\text{Ti}_x\text{Co}_y)\text{Fe}_{1-x-y}\text{PO}_4$ Powders for Li-Ion Batteries. Gangqin Shao^{1,2}, Xuhui Mao¹, Luis Ortiz¹ and Donald R. Sadoway¹; ¹Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²State Key Laboratory of Advanced Technology for Materials Synthesis & Processing, Wuhan University of Technology, Wuhan, China.

Even though in most situation, LiFePO_4 and the related cathode powders have excess carbon or carbon coating for their applications, the carbon-free powders are needed to have a reduced primary particle size in order to shorten Li^+ diffusion lengths and ohmic drop, as well as a narrow size distribution, in order to ensure a homogeneous current distribution, and achieve a high power efficiency and a long cycle life. The evaluation of ionic and electronic conductivity can be easier processed from carbon-free powders. Besides, the iron-ion in the olivine structure of LiFePO_4 can be partially or wholly substituted by other metal-ion such as the transition metal of cobalt for the application in higher discharge potentials. In this study, LiFePO_4 and $\text{Li}(\text{Ti}_x\text{Co}_y)\text{Fe}_{1-x-y}\text{PO}_4$ powders were hydrothermally synthesized from carbon-free raw materials in aqueous medium. The thermogravimetry analysis (TGA) was conducted to investigate the energy and weight changes. Phase structure was determined from X-ray diffraction (XRD) by using the Rietveld method. The microstructure and the corresponding chemical composition were examined by a scanning electron microscopy (SEM) combined an energy dispersive spectroscopy (EDS). The electrochemical lithium deinsertion/insertion characterization were also performed.

U13.32

Kinetics of Li Ion Diffusion in LiFePO_4 . Gopi Krishna Phani Dathar and Graeme Henkelman; Chemistry & Biochemistry, University of Texas at Austin, Austin, Texas.

Lithium olivine phosphates are one of the most studied cathode materials in Li ion batteries due to their low cost, non-toxic nature, high specific charge capacity and reversibility of lithium insertion. In this work we investigate how Li ions diffuse in the bulk and on the surface of these materials. Diffusion mechanisms that we can anticipate are determined with the nudged elastic band method. The adaptive kinetic Monte Carlo method is also used to directly model the dynamics of Li diffusion over long time scales. This method does not require that the final state of each diffusion event be specified so that we are able to discover complex reaction mechanisms directly from density functional theory.

U13.33

Dielectric Characteristics of Nano-scale, Multilayered Polymer Films Fabricated by Plasma Enhanced Chemical Vapor Deposition. Scott P. Fillery, Jesse O. Enlow, Rachel Jakubiak, Timothy J. Bunning and Michael F. Durstock; Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio.

Polymer films, such as biaxially oriented polypropylene, are widely used as the active dielectric in current capacitor designs due to their low dielectric loss and high reliability. However, higher energy density capacitors are likely to necessitate dielectric materials with improved permittivity or dielectric strength. The current nanocomposite approaches to this challenge have been dominated by random morphologies that exhibit drastic reductions in breakdown strength at higher filler loadings. One promising approach is the creation of a polymer nanocomposite with an extreme density of internal interfaces (500-1000 m²/g) which could effectively trap locally injected carriers, inhibiting the breakdown event. In this contribution, we report on the fabrication and characterization of a multilayer structure, using plasma enhanced chemical vapor deposition, a solvent free process for depositing films with excellent spatial uniformity and thickness control. Polymer stacks of between 10 and 40 alternating layers of benzene and octafluorocyclobutane, with layer thicknesses between 10 and 100nm, were deposited on conductive substrates. Permittivity, dielectric loss and dielectric strength were probed as a function of the relative individual layer thickness.

U13.34

Abstract Withdrawn

U13.35

Electrochemical Evaluation of Melt-Cast LiMPO₄. Dean MacNeil¹, M. Gauthier², C. Michot² and G. Liang²; ¹Department of Chemistry, Université de Montréal, Montréal, Quebec, Canada; ²Phostech Lithium Inc., Montréal, Quebec, Canada.

LiFePO₄ has received a large amount of attention as a positive electrode material for lithium-ion batteries (1,2). It represents a low cost, thermally stable and environmentally friendly substitute for cobalt-based lithium metal oxides currently used as cathodes in the batteries of portable computers and cellular phones. In addition, the realization of high power batteries that have large capacity at high rates of charge and discharge are possible using small particle sized, carbon coated LiFePO₄ (3). Thus far, most commercial LiFePO₄ material has been synthesized using solid-state chemistry methods, while a large amount of work has been devoted to developing hydrothermally prepared LiFePO₄ due to the smaller particle size obtained through this method. These two methods have drawbacks in that they both require long reaction times and costly precursors. We have recently introduced a new method of LiFePO₄ synthesis that has the capability to provide large amounts of samples from a variety of precursors within a short reaction time (4,5). This melt-casting procedure uses typical metallurgical synthesis methods and can easily provide samples in kilogram quantities. The process involves the formation and cooling of a liquid phase from which we obtain ingots of pure crystalline LiMPO₄. Subsequent grinding procedures and carbon coating treatments are critical to prepare LiMPO₄ material with tunable electrochemical performance. This presentation will detail the synthesis and characterization of LiMPO₄ obtained from various precursors in the molten state as well as the preparation of carbon coated LiMPO₄ products and their electrochemical performance. The importance of obtaining material with nano-scale dimensions will be stressed. References 1. A.K. Padhi, K.S. Nanjundaswamy, and J.B. Goodenough (1997). "Phospho-Olivines as Positive Electrode Materials for Rechargeable Lithium Batteries". J. Electrochem. Soc. 144: 1188-1194. 2. B. Ellis, W. H. Kan, W. R. M. Makahnouk, and L. F. Nazar J. Mater. Chem., 17, 3248 (2007). 3. N. Ravet, S. Besner, M. Simoneau, A. Vallee, M. Armand, and J. Magnan, U.S. Pat., 6,962,666 (2005). 4. L. Gauthier, M. Gauthier, D. Lavoie, C. Michot, N. Ravet World Patent 2005/062404 5. K. Zaghib, G. Liang, F. Labrecque, A. Mauget, C. Julien, M. Gauthier, Abstract #582, The Electrochemical Society and The Electrochemical Society of Japan Meeting Abstracts, 214th ECS Meeting, Honolulu, HI, Oct., 2008.

U13.36

Theoretical Improvement in Lithium Ion Battery Energy Density with a Free-Standing Carbon Nanotube Anode. Brian Landi^{3,1}, Cory Cress² and Ryne Raffaele¹; ¹NanoPower Research Labs, Rochester Institute of Technology, Rochester, New York; ²Naval Research Labs, Washington, District of Columbia; ³Chemical Engineering, Rochester Institute of Technology, Rochester, New York.

There is an ever growing demand for electrical energy storage to support mobile electronics, hybrid-electric/full electric vehicles, and utility scale grid management. Lithium ion technology has recently emerged as the premier rechargeable battery chemistry due to the increased energy density over other technologies. Although the cathode is generally the limiting electrode in today's devices, an attractive strategy being investigated to increase the battery energy density is to augment the anode capacity sufficiently to increase the number of active layers contained within an individual battery. This could be achieved with a multi-functional free-standing anode that has both high lithium ion specific capacity and sufficient electronic transport. Since no binder or inactive metal foil collector is used in such a design, the entire mass of the electrode can factor into the usable electrode capacity. The most promising developments to date using free-standing electrodes have been with carbon nanotube (CNT) papers which have capacities ranging from 600-1000 mAh/g depending upon morphology and electrolyte characteristics. In addition, the CNTs can be used to support high capacity anode materials like silicon and germanium with recent measurements exceeding 1000 mAh/g for free-standing silicon-CNT electrodes. At present, however, there currently lacks a quantitative framework to predict the intended impact and relative improvement using free-standing electrodes in a full battery design. The replacement of conventional anode designs which use graphite composites coated on copper foil with a free-standing CNT anode can result in a 200-300% increase in usable anode capacity depending on composite thickness. In the present work, a numerical model has been developed to calculate the relative improvement in battery energy density for any free-standing anode paired with conventional LiCoO₂, LiFePO₄, and LiNiCoAlO₂ cathode chemistries. The results show a nonlinear dependence on battery improvement with anode capacity, density,

and the nominal battery voltage. Overall, performance metrics with optimized cathode conditions and free-standing silicon-SWCNT anodes show energy densities in excess of 300 Wh/kg and 650 Wh/L to be theoretically achievable at the battery level. The expected enhancement in lithium ion battery performance through the use of free-standing anodes represents a dramatic increase in energy density, and potential directions to overcome present-day technical challenges will be highlighted.

U13.37

Abstract Withdrawn

U13.38

Abstract Withdrawn

U13.39

Silicon/Carbon Composite Anode Materials for Lithium-ion Batteries. Wenchao Zhou, Shailesh Upreti and M. Stanley Whittingham; Institute for Materials Research, SUNY-Binghamton, Binghamton, New York.

Silicon has attracted much attention as a possible anode candidate to replace the graphitic carbon materials because of its high capacity. Nevertheless, there are a few issues that prevent its use as a durable active anode in battery commercialization. Notably, the huge volumetric expansion that leads to the quick capacity fade, the irreversible lithium loss in the first cycle due to Si-Li alloying and the electrolytic surface reactions, which are issues that require substantial attention before its viable commercialization. Recently there have been reports on nano-sized Silicon/Carbon (Si/C) composites prepared by high energy mechanical milling that exhibit interesting electrochemical performance. We synthesized nano-sized material using an intrinsically low-cost method where Si is reduced from its oxide by Al during ball milling. Si was subsequently coated with conductive carbon by means of pyrolytic decomposition of Polyacrylonitrile (PAN) at 800C in an inert atmosphere. Electrochemical tests show that this nano Si offers a reversible capacity over 600 mAh/g for more than 30 cycles. The electrochemistry of the material was also collected in carbonate electrolyte with LiBOB additive. It is found that the additive helps to form stable surface film which reduces the electrolyte reaction. The Si/C composite was characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. This work is supported by the US Department of Energy, Office of FreedomCAR and Fuel Partnership through the BATT program at Lawrence Berkeley National Laboratory.

U13.40

Abstract Withdrawn

U13.41

Impedance Spectroscopy of SEI on Porous SnO₂/CNTs Composite Anodes for Lithium Ion Batteries. Abirami Dhanabalan¹, Xifei Li¹, Yan Yu², Kevin Bechtold¹ and Chunlei Wang¹; ¹Mechanical & Materials Engineering Department, Florida International University, Miami, Florida; ²Max-Planck-Institute for Solid State Research, Heisenbergstrasse, Stuttgart, Germany.

Tin oxide based amorphous composites have been studied extensively because of the high theoretical specific capacity compared to the commercialized carbon anode. During charge and discharge, solid electrolyte interface (SEI) film is formed at the interface between the electrolyte and the anode due to the reaction between the anode and the electrolyte. It is a thin lithium ion conductive film which protects the anode from co-intercalation of solvents and consequent exfoliation. The SEI film formed on the anode has important influence on the irreversible capacity, cycle performance and stability of Li⁺ insertion into anode. The significant volume change of the SnO₂ could lead to some cracks on the surface of the anode, which results in the contact between acting anode material and electrolyte again, and new SEI film is possible to be formed on the cracks. The progressive structural changes of SEI film on the SnO₂ strongly affects its electrochemical performance. In this work, impedance studies were carried out on SnO₂/CNT anode which was prepared by means of electrostatic spray deposition (ESD). Tin acetate was dissolved in the glycol and ethanol based solvent as precursor solution in which CNT was homogeneously dispersed using sonication method. The as-obtained precursor solution was pumped through the stainless steel nozzle. The deposition temperature was kept at 200°C, 250°C and 300°C, respectively. The concentration of CNT was also varied. Coin cells were assembled using a SnO₂/CNT working electrode, a Li metal counter electrode, a separator and an electrolyte solution of 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC). The electrochemical impedance spectroscopy (EIS) test was performed by Versatile Multichannel Potentiostat (VMP3), in order to understand the formation and the change of SEI film on SnO₂/CNT anode with subsequent cycling. The equivalent circuit was proposed to fit the EIS plots. The experimental results will be discussed in detail at the conference.

U13.42

Effect of Fe Substitution on the Phase Formation and Charge Storage Characteristic of LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂. Naba K. Karan, Rahul Singhal, Jose I. Lopez, Reji Thomas and Ram S. Katiyar; Physics, University of Puerto Rico, San Juan, Puerto Rico.

Recently, layered LiMn_{0.5}Ni_{0.5}O₂ has drawn attention as an alternate cathode material for secondary lithium-ion batteries due to its lower cost, better stability at high voltages and improved thermal safety characteristics compared with LiCoO₂. However, LiMn_{0.5}Ni_{0.5}O₂ suffers from poor rate capability. Partial substitution of nickel and manganese in LiMn_{0.5}Ni_{0.5}O₂ by cobalt has reduced the Li/Ni intermixing, and has produced improvements in the rate capability and thermal stability properties.²⁻³ One such

compound, $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC), has been investigated extensively, and is a leading candidate for the positive electrode active material in lithium-ion batteries for transportation applications. However, this particular composition also has substantial amount of "undesirable" cobalt. In order to reduce the cobalt content in NMC, it would be interesting to study the effect of iron substitution for cobalt in NMC as iron could potentially contribute actively to the electrochemistry. In the present work, $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Fe}_x\text{Co}_{1/3-x}\text{O}_2$ bulk cathodes ($x = 0.0 - 1/3$) were synthesized using a cost effective chemical solution technique. The structural properties and oxidation state of Mn, Fe, Co and Ni were investigated using X-ray diffraction (XRD), Raman Spectroscopy and X-ray photoelectron spectroscopy (XPS). The morphology was studied using scanning electron microscopy (SEM). The electrochemical measurements (cyclic voltametry, charge-discharge tests) of the synthesized cathodes were performed in a two-electrode coin-cell configuration (CR2032), using liquid electrolyte [1M LiPF₆ in (1EC:1DMC v/v)] and Li-metal as anode. The major peaks in the XRD patterns of the synthesized $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Fe}_x\text{Co}_{1/3-x}\text{O}_2$ cathode materials could be indexed to R-3m symmetry. Minor peaks from an additional phase also appear in the data, especially for the higher iron content oxides. These features are visible as shoulders to the main R-3m peaks on the higher angle side. The crystal structure of this impurity phase has not been conclusively determined at this time; the various possibilities include rocksalt or ordered rocksalt-type structures. The first charge and discharge capacity for $x=0$ were 178 and 154 mAh/g, respectively correspond to a coulombic efficiency of 86%. Both charge and discharge capacity decreased with increasing x , for $x=1/6$ the charge and discharge capacity were 170 and 108 mAh/g, respectively. The effect of Fe substitution on the phase formation and electrochemical behavior of $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Fe}_x\text{Co}_{1/3-x}\text{O}_2$ along with the effect of annealing conditions upon electrochemical properties will be presented and discussed in conjunction with structure of the as prepared and electrochemically cycled electrode materials using ex-situ Raman spectroscopy and XRD.

U13.43

Synthesis of Electrochemically Active LiMnPO_4 via a Novel Precipitation Method. [Jie Xiao](#), Wu Xu, Daiwon Choi and Ji-Guang Zhang; Pacific Northwest National Laboratory, Richland, Washington.

LiMnPO_4 was synthesized from $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ precursor precipitated via a spontaneous reaction. These $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ nano-plates reacted easily with lithium source forming LiMnPO_4 pure phase with excellent electrochemical properties providing a low cost manufacturing process. The morphology of the $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ precursor varied in different solvents used in washing process and affected the electrochemical behavior of the LiMnPO_4 accordingly. Different lithium salts were used in the precursors and TGA was applied to understand their reaction mechanisms. Their corresponding LiMnPO_4 products were then compared in terms of structure, morphology, electrochemical performances and magnetic properties. The weight percent of carbon in the LiMnPO_4/C composite was adjusted between 10 % and 20 % to optimize the electrode composition while still maintaining high performances. This work is supported by US Department of Energy, Office of Vehicle Technologies through the BATT program and Laboratory Directed Research and Development Program at the Pacific Northwest National Laboratory (PNNL).

U13.44

Abstract Withdrawn

U13.45

New Electrode Architecture For Enhancing Energy Density In Rechargeable Batteries. [Can K. Erdonmez](#), Wei Lai, Chang-Jun Bae and Yet-Ming Chiang; MIT, Cambridge, Massachusetts.

Current lithium-ion batteries are based on thin, large area ("2D"), laminated, composite electrodes with highly optimized compositions, microstructures and geometries that minimize and trade off various kinetic limitations to cell operation. While yielding impressive rate capabilities, this approach also severely limits volumetric and gravimetric utilization of active materials, due both to the significant volume of inactive additives present in the electrodes, and to cell components whose amounts scale with electrode area (e.g. collectors, separators) or volume (e.g. external packaging). Here, we pursue an alternative electrode architecture, demonstrating thick, three-dimensionally porous, high-density intercalation cathodes that are largely free of the electrochemically-inert additives which are conventionally employed. We show that such structures can have sufficient electronic conductivity and are surprisingly tolerant of the substantial, cyclic stresses that accompany electrochemical cycling of intercalation compounds. For LiCoO_2 -based cathodes of this configuration, discharge capacity vs. C-rate has been systematically characterized as a function of porosity and thickness for several distinct microstructures. At low discharge rates ($\sim C/50$), full capacity utilization is obtained in cathodes with thicknesses up to 800 microns and densities up to 87% by volume, providing ~ 8 times the capacity per area of conventional cathodes. At $C/3$ to $C/2$ continuous discharge rates, 80% of the theoretical capacity can be obtained in cathodes of 74% density and 400 micron thickness. These and other experimental methods used in conjunction with existing theoretical models allow us to identify the most relevant rate-limiting processes. Microstructure modifications to measurably enhance rate capability are demonstrated. Small prototype cells show that specific energy and energy density can be more than doubled compared to conventional technology.

U13.46

Metal Oxide Nanofiber Structures for Energy Storage. Lukas Rubacek, Jiri Duchoslav and [Jan M. Macak](#); Research and development, Elmarco, Ltd., Liberec, Czech Republic.

The presentation deals with the use of nanofiber materials in lithium-ion batteries. These nanofiber materials are produced by electrospinning that has recently attracted a lot of attention as a progressive method for production of a range of materials. In the present case, the NanospiderTM technology has been used for the hundreds of nanometers. The as-produced material has a

specific surface area of about 35m²/g. We have investigated charging-discharging properties by means of cyclic voltammetry. The achieved results have demonstrated very promising features that suggest the suitability of electrospun nanofibers for advanced high-rate batteries.

U13.47

Three Dimensional Microsupercapacitors: As-Pyrolyzed and Porous Carbon Structures. Majid Beidaghi, Wei Chen and Chunlei Wang; Mechanical and Materials Engineering, Florida International University, Miami, Florida.

Due to their efficacy as high power density energy storage devices, electric double layer capacitors (EDLCs) have been the subject of much research and consideration in recent years. In this study, the Carbon-Microelectromechanical system (C-MEMS) technique is used to fabricate microsupercapacitors with high aspect ratio three dimensional (3D) carbon electrodes at a small footprint. C-MEMS technique is a simple process for fabricating carbon electrodes, in which patterned photoresist can be pyrolyzed and converted to carbon under high temperature in inert atmosphere. In our microsupercapacitor design, we employed an improved electrode design by placing carbon posts as electrodes on interdigitated carbon strips as current collectors on a single SiO₂ coated Si substrate. Two different carbon structures, one with solid pyrolyzed carbon and the other with porous carbon, were fabricated and their performance were compared. Also, the effect of pyrolysis temperature profile and amount of porosity on the capacity of the microsupercapacitors were investigated. Electrochemical performance of the microsupercapacitor was tested by AC impedance and cyclic voltammetry (CV) methods. Detailed result will be presented at the conference.

U13.48

Structure and Electrochemical Performance of Reduced Spinel Li₄Ti₅O₁₂. Natalya A. Chernova, Jian Hong and Stanley M. Whittingham; MSE, SUNY at Binghamton, Vestal, New York.

Li₄Ti₅O₁₂ is a well-known zero-stress anode material for lithium batteries, which combines virtually unlimited cycle life with safe operation; the latter is due to high working potential (1.55 V vs. Li/Li⁺). Nano-Li₄Ti₅O₁₂ anode combined with LiFePO₄ cathode provides high power capability making this system a viable candidate to replace electrochemical super-capacitors and for use in electrical vehicles. However, low tap density of nano-powders and low electronic conductivity of Li₄Ti₅O₁₂ requiring addition of conductive carbons limit the volumetric energy density of the material. Here we explore the possibility to enhance the electronic conductivity of Li₄Ti₅O₁₂ by partial reduction. Li₄Ti₅O_{12-δ} spinels were synthesized by high-energy ball milling followed by heat treatment in reductive He/H₂. In some samples carbon black (3~5 wt %) was added at the ball-milling stage to control the particle size; the annealing temperature and time were varied. In the resulting dark-blue products, some Ti⁴⁺ is reduced to Ti³⁺, introducing oxygen vacancies as suggested by the Rietveld refinement of the x-ray diffraction data and a weight gain upon TGA in oxygen. The magnetic tests indicate the presence of 1-2% paramagnetic Ti³⁺. An increase of the magnetic susceptibility at high temperatures suggests that strongly antiferromagnetically coupled Ti³⁺ clusters might also be present. The electronic conductivity of the reduced spinels is improved by many orders of magnitude as compared to Li₄Ti₅O₁₂, but is still low, 10⁻⁸-10⁻⁷ S/cm, which is consistent with small amount of isolated Ti³⁺ ions. The powders synthesized in the presence of carbon show excellent electrochemical performance and power capability exceeding those of nano-Li₄Ti₅O₁₂. The particle size of these powders is several hundred nanometers and the tap density is 2.1 g/cm³. The exact amount of Ti³⁺ and the nature of charge-compensating defects are currently under investigation. This work is supported by the US Department of Energy, Office of FreedomCAR and Fuel Partnership, through the BATT program at Lawrence Berkeley National Laboratory.

U13.49

Doping Effects on LiFePO₄ Cathode Materials for Lithium-Ion Batteries. Hui Fang¹, Travis Neeley¹, Thomas Murphy¹, Erica Cerda¹, Gan Liang¹ and Mark Croff²; ¹Department of Physics, Sam Houston State University, Huntsville, Texas; ²Department of Physics, Rutgers University, Piscataway, New Jersey.

LiFePO₄ cathode materials doped with various elements, Al, Cr, Ti, Nb, Zr, and W, at both Li and Fe sites for lithium-ion batteries are synthesized by two different methods, solid-state reaction and template method. X-ray diffraction, X-ray absorption, cyclic voltammetry, and constant current charge/discharge measurements are employed to characterize the structural, electronic, and electrochemical properties of the samples. The effects brought by doping on both Li and Fe sites will be discussed and presented.

U13.50

Carbon Nanotubes grown on Cu Substrates using a Ni Catalyst for Battery Anode Applications. Gowtam Atthipalli¹, Prashant N. Kumta^{1,2,3}, Wei Wang⁴, Alexander Star⁵, Brett L. Allen⁵, Yifan Tang⁵ and Jennifer L. Gray¹; ¹Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ³Department of Bioengineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ⁴Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; ⁵Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania.

Carbon nanotubes with their unique 1-D character and their large aspect ratio are ideal candidates for anodes on suitable conducting substrates for battery applications. We studied the growth of carbon nanotubes on copper substrates using a nickel thin film as a catalyst. The catalyst was sputtered in a chamber having a base pressure in the ultra-high-vacuum regime. By adjusting the sputtering parameters including sputtering time, power, and pressure, the effects of the morphology and the structure of nickel catalyst on the growth of carbon nanotubes have also been investigated. Multiple hydrocarbon sources were used as carbon feedstock and the corresponding catalyst precursors, during the chemical vapor deposition (CVD) of the carbon nanotubes to determine the ideal conditions for carbon nanotube growth on copper. Correlations between the thickness of the thin film nickel

catalyst and the carbon nanotube diameter and alignment are also presented in the study. A hypothesis for critical catalyst thickness range below which no carbon nanotube growth is observed is also postulated. The structure and morphology of the carbon nanotubes and the thin film nickel catalyst were studied using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Results will also be presented on experiments designed to yield aligned carbon nanotubes on copper substrates.

U13.51

Abstract Withdrawn

U13.52

Silicon Based High Capacity Anode for Li-Ion Battery Applications. Jiguang Zhang, Jie Xiao, Donghai Wang, Jun Liu, Daiwon Choi, Chongmin Wang, Zhenguo Yang, Wu Xu and Graff Gordon; Pacific Northwest National Laboratory, Richland, Washington.

Si-based lithium alloys are well known for their potential to attain high specific energies. Silicon has a theoretical specific capacity of nearly 4,200 mAh/g ($\text{Li}_{21}\text{Si}_5$), which is 10 times larger than that of graphite (LiC_6 , 372 mAh/g). However, the high capacity of silicon is associated with huge volume changes (up to 300 percent) when alloyed with lithium, which can cause severe cracking and pulverization of the electrode and lead to significant capacity loss. We have investigated the electrochemical properties of Si-based anode by several approaches. First, electrochemical properties of carbon coated nano-porous Si powder were investigated. The Si powder with nanosized pores is the ideal starting materials for high capacity anode because the nano pores in these particles can tolerate large volume expansion during the charge and discharge process. The main barrier for battery application of these porous silicon samples is their poor electrical conductivity. To solve this problem, the micron size nano-porous Si particles were coated with ~6% weight of carbon by CVD process. The morphology change of the original Si and carbon coated Si before and after electrochemical cycling has been investigated. In a separate effort, self-assembling approach has been used to prepare Si-graphene superstructures. Unlike mechanical mixing, self-assembling process produces a new class of nanocomposites in which the conductive and mechanically robust graphene sheets are uniformly distributed in the ordered domains of silicon powders, representing a new concept in the design and synthesis of nanocomposite materials. Such materials can be further assembled into free standing papers for direct macroscopic use of self-assembled nanomaterials in energy storage devices. The graphene sheets can also be dispersed into three dimensional, ordered nanoporous networks, forming conductive, high surface area nanoporous materials. The third approach to prepare high capacity Si based anode is the gas induced 3D-growth (or Solid-Liquid-Solid growth) of silicon nanowires. Si-based anodes prepared by these three approaches have demonstrated an initial capacity of exceeding 1,000 mAh/g, but their long term stability strongly depends on the preparation conditions, binder, and cycling conditions. Electrochemical performances of Si-based anode prepared by these approaches will be compared in this report. This work is supported by DOE Office of Vehicle Technologies (OVT) through Batteries for Advanced Transportation Technologies (BATT) Program and PNNL Laboratory Directed Research and Development (LDRD) Project. * Corresponding author. Tel.: 509-372-6515; fax: 509-375-3864. E-mail address: jiguang.zhang@pnl.gov

U13.53

Synthesis and Characterization of LiFePO₄ Nanoparticles as Cathode Material for Lithium Ion Batteries. Hui Zhou, Natasha Chernova, Shailesh Upreti and Stanley M. Whittingham; Materials Science Program, State University of New York at Binghamton, Binghamton, New York.

Lithium transition metal phosphate olivines such as LiFePO₄ have been recognized as promising electrodes for lithium-ion batteries due to their outstanding electrochemical and thermal stability. Several synthesis techniques have been explored so far with the goal of improved electrochemical behavior and lower cost. Our laboratory pioneered the hydrothermal method which leads to a uniform particle size and good electrochemical performance. However, alternative solvents might lead to smaller particle sizes and lower costs, by using a continuous process. In the present work, LiFePO₄ nanoparticles were synthesized through the polyol process under N₂ atmosphere, where pressurized vessels are not needed. The polyol medium itself acts not only as a solvent in the process, but also as reducing agent and as a strong stabilizer, limiting particle growth. A N₂ protective atmosphere is helpful in getting a pure LiFePO₄ phase. With increasing reaction time, the purity and electrochemical property becomes better. X-ray and TGA analysis revealed the presence of a few amorphous organic impurities in the sample; a post-heat treatment eliminated these impurities. This treatment improved the electrochemical capacity and rate capability. A reversible specific capacity of 130 mAh/g was achieved at 0.4 mA/cm², significantly less than hydrothermal samples. Efforts to optimize the synthesis and post-treatment conditions are under progress. Particle morphology, composition, magnetic properties and detailed electrochemical performance will be discussed. This work is supported by the US Department of Energy, Office of FreedomCAR and Fuel Partnership through the BATT program at Lawrence Berkeley National Laboratory.

U13.54

Facile Approach to Prepare Porous Ni Foam Supported-porous NiO Anode for Lithium Ion Batteries. Xifei Li, Abirami Dhanabalan, Kevin Bechtold, Chiwon Kang and Chunlei Wang; Florida International University, Miami, Florida.

The graphite with the theoretical capacity of 372 mAhg⁻¹ is commercialized as the first generation anode for lithium ion batteries. However, its limited capacity cannot match with the recent request of lithium ion batteries with the high energy density and the high power density. So the second generation anode materials are coming with the high theoretical capacity. In 2000, Tarascon et.al were the first to propose the transition-metal oxides (M_xO_y , M=Ni, Co, Cu etc.) as anode materials for lithium ion batteries. NiO shows the high capacity up to 718 mAhg⁻¹. Furthermore, its density, 6.81 g/cm³, is much higher than that of graphite, 2.268 g/cm³. The volumetric energy density of NiO anode is about 5.8 times as large as graphite. However, during charge/discharge process,

the formed nanosized Ni and NiO particles are easy to aggregate. NiO also has the inherent bad electric conductivity. Both of these cause the poor cycle performance of NiO anode. In this research, we report a simple yet efficient method to create NiO films on the porous nickel foam substrate. By controlling the preparation process nickel foam was partly oxidized to prepare the special structure of porous nickel foam substrate supported porous NiO films. This material design has been demonstrated with good adhesion and good electric contact between the NiO film and the Ni substrate. The special porous structure can effectively reduce the aggregation of nanoscale particles during cycle. As-prepared porous Ni foam supported-porous NiO film can be used as anode materials for lithium ion batteries, and no conductive agent and binder are needed, therefore, the anode resistances are efficiently reduced and the energy density of lithium ion batteries can be tremendously increased. In an argon-filled glove box the thin films were assembled as the electrochemical cells using lithium sheet as the counter electrode. Cyclic voltammetry and electrochemical impedance spectroscopy were performed on Versatile Multichannel Potentiostat (VMP3) at a scan rate of 0.2 mV s^{-1} over a potential range of 0.02 and 3.0 V (vs. Li/Li^+). All cells were galvanostatically cycled between 0.02 and 3.0 V (vs. Li/Li^+) at room temperature by NEWARE BTS-610 battery tester. The experimental results will be discussed in detail.

U13.55

Macroporous Composite Anodes for Lithium Ion Batteries. Wu Xu, Nathan L. Canfield, Jie Xiao, Deyu Wang, Zimin Nie and Ji-Guang Zhang; Energy and Efficiency Division, Pacific Northwest National Laboratory, Richland, Washington.

Lithium ion batteries to power plug-in hybrid electrical vehicles (PHEV) need to have higher energy density, longer cycle life and calendar life, higher safety and lower cost than the state-of-the-art lithium ion batteries. The currently commercially available lithium ion batteries mainly use carbonaceous materials especially graphite as anode material which has a theoretic specific capacity of 372 mAh/g and good cell performance. Alternative anode materials that are being investigated include silicon, tin, aluminum, alloys, metal oxides, and others. Although silicon, tin, aluminum, and tin oxide as anode materials have much higher theoretical specific capacities (4,200 mAh/g, 993 mAh/g, 993 mAh/g, and 782 mAh/g, respectively) than graphite, they have not been practically used because of the poor cycle life and fast capacity fade resulted from the electrode cracking and pulverization due to the high volume change associated with lithium alloying and de-alloying during charge and discharge. Extensive efforts have been made on these alternative anode materials by reducing electrode cracking and pulverization during charge and discharge. It has been reported that porous 3D substrates are helpful to accommodate the volume changes of these high capacity anode materials during the charge/discharge cycles. Conventional approach to prepare anode active materials inside the porous substrate is to use electrochemical deposition, which is difficult to make thick and uniform deposition coatings and generates a lot of wastes harmful to environment and more efforts and costs are needed on waste treatment. Here we report a new approach to prepare macroporous composite anodes, which is versatile and suitable to produce large quantity of porous composite anode sheets for battery applications. The macroporous composite anodes developed in this method have shown improved discharge capacity and cycle life than those from conventional tape-casting method. Acknowledgement This work is sponsored by PNNL Laboratory Directed Research and Development (LDRD) Project and DOE Office of Vehicle Technologies (OVT) through Batteries for Advanced Transportation Technologies (BATT) Program.

U13.56

Development of Novel $\text{Li}_2\text{MPO}_4\text{F}$ (M = Mn, Co) Cathode for Li Ion Battery Applications. Deyu Wang, Jie Xiao, Wu Xu and Ji-Guang Zhang; Energy and Efficiency Division, Pacific Northwest National Laboratory, Richland, Washington.

LiFePO_4 has been widely used in batteries for portable tools and will also be used in plug in electrical vehicles because of its high stability, low cost, and high power rate. However, its practical specific energy is limited by both low voltage ($\sim 3.4\text{V}$) and moderate capacity ($\sim 150 \text{ mAh/g}$). To further improve the capacity of olivine phosphate based cathode materials, $\text{Li}_2\text{MPO}_4\text{F}$ (M = Mn, Co) is investigated in this work. In addition to the stability and safety of phosphate based cathodes, $\text{Li}_2\text{MPO}_4\text{F}$ (M = Mn, Co) exhibit higher voltage than LiFePO_4 and has a theoretical capacity of $\sim 290 \text{ mAh/g}$, which is 70% higher than current olivine phosphate based cathode materials. Although $\text{Li}_2\text{FePO}_4\text{F}$ has been reported before, its theoretical capacity is only 145 mAh/g due to the absence of Fe (IV) and only one lithium can be extracted from $\text{Li}_2\text{FePO}_4\text{F}$. Various synthesis approaches for $\text{Li}_2\text{CoPO}_4\text{F}$ and $\text{Li}_2\text{MnPO}_4\text{F}$ have been investigated. Their structure, morphology, and electrochemical properties will be reported in this work. Acknowledgement This work is sponsored by DOE Office of Vehicle Technologies (OVT) through Batteries for Advanced Transportation Technologies (BATT) Program and PNNL Laboratory Directed Research and Development (LDRD) Project.

U13.57

Investigation of Battery Materials Using Scanning Probe Microscopy. Nina Balke, Yoongu Kim, Nancy J. Dudney and Sergei V. Kalinin; CNMS, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The electrochemical energy storage systems based on Li-based insertion and reconstitution chemistries are a vital aspect of energy technologies. A distinctive feature of these systems is a significant change of molar volume, which can be as large as tens of percent, during electrochemical processes. This expansion is highly anisotropic; e. g., in LiCoO_2 it is the most pronounced in the c-axis direction and smallest in the direction of the CoO_2 layers. Here, the strong strain-bias coupling in electrochemical materials is used to develop the capability for mapping electrochemical reactions on the nanometer scale, and hence get insight into the mesoscale mechanisms of battery operation. In one approach, a Scanning Probe Microscopy tip is used to detect local surface strains developing in the operational battery with a thin (10-100 nm) top electrode. The use of the top-electrode system allows measurements to be taken reversibly, while spatial localization of the process on the top interface suggests this method has the potential for high spatial resolution. In parallel, the tip-electrode studies has been used to study local tip-induced processes and we demonstrate the mapping of local Li mobility within the material.

U13.58

Directing the Growth of Nanoscale Hybrid Architectures for Electrical Energy Storage. Erik D. Spoecke, Erica S. Martin, Mark Roberts, Michael T. Brumbach, David Wheeler and Bruce C. Bunker; Sandia National Laboratories, Albuquerque, New Mexico.

The growing demand for electrical energy storage currently surpasses existing technologies, driving the need to develop new materials and technologies. One area of expanding exploration in the electrochemical community is focused on the development and integration of nanoscale electroactive oxide materials and functional organics for incorporation into technologies such as lithium ion batteries or ultracapacitors. We describe here a materials synthesis strategy that utilizes both organic and inorganic templates to synthesize and assemble mesoporous electroactive nanocomposites with promising electrochemical behaviors. By integrating both organic templates, such as functional amphiphilic molecules or electroactive polymers, and inorganic templates, such as zinc oxide, we can produce nanostructure electroactive oxides, such as ruthenium oxide or molybdenum oxide, with texture and porosity on multiple length scales. This process furthermore directs the in situ growth of these nanostructured materials on electrodes, dramatically simplifying electrode preparation and improving electrical and ionic transport across the active material. Electrochemical characterization reveals these templated, functional metal oxides to be promising candidates for incorporation into next generation electrical energy storage applications. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

U13.59

Metal Oxide-Graphene Hybrid Materials for Li-Ion Battery. Donghai Wang¹, Daiwon Choi¹, Juan Li¹, Zhenguo Yang¹, Zimin Nie¹, Rong Kou¹, Chongmin Wang¹, Laxmikant Saraf¹, Jiguang Zhang¹, Ilhan Aksay² and Jun Liu¹; ¹Pacific Northwest National Laboratory, Richland, Washington; ²Princeton University, Princeton, New Jersey.

Electrochemical energy storage has been receiving great attention for potential applications in electric vehicles and renewable energy systems from intermittent wind and solar sources. Currently, Li-ion batteries are being considered as one of the leading energy storage techniques for the applications. However, many potential electrode materials (e.g., oxide materials) in Li-ion battery are limited by slow Li-ion diffusion, poor electron transport in electrodes, and poor cycling stability due to phase transformation and volume change during charge/discharge process. A promising approach to improve electrode performance is to develop multifunctional nanocomposites that combine high redox activity, good mechanical properties, and good electron and ion conductivity of different functional materials with controlled architectures. In this presentation, we discuss synthesis and characterization of metal oxide-graphene hybrid materials and their application in Li-ion battery. The hybrid materials were directly synthesized by assembling in-situ grown metal oxide nanocrystals with graphene sheets and characterized using XPS, Raman, XRD, TEM, and SEM techniques. Li-ion insertion properties of the graphene-TiO₂ (rutile or anatase) hybrids were investigated showing superior Li-ion insertion capacity with good retention at high charge/discharge rate. In particular, the hybrid material is able to reversibly accommodate Li up to 85 mAh/g at 1-3 V versus Li+/Li at charge/discharge rate of 30C, which is much higher than 43 mAh/g capacity of nanocrystalline TiO₂. Other nanocrystalline metal oxide-graphene hybrid materials have also been studied in terms of capacities and stability as anode materials. The self-assembled metal oxide-graphene hybrid materials are expected to be used for studying synergetic properties and improving performance of materials and devices in electrochemical energy storage and conversion. Ref: Wang, D. et al. Self-Assembled TiO₂-Graphene Hybrid Nanostructures for Enhanced Li-Ion Insertion. ACS Nano 3, 907-914, (2009).

SESSION U14: *In-Situ* Studies
Chair: Jean-Marie Tarascon
Thursday Morning, December 3, 2009
Room 200 (Hynes)

8:30 AM *U14.1

In and Ex situ NMR Spectroscopy: Applications to Anode Systems: Intermetallics, Conversion Reactions and Li Metal Dendrite Formation. Baris Key, Rangeet Bhattacharya, Hailong Chen, Meng Jiang, Dongli Zeng and Clare P. Grey; Chemistry, SUNY Stony Brook, Stony Brook, New York.

This presentation will describe the application of new in situ NMR approaches to identify processes that are very difficult to detect directly by ex-situ methods will be discussed. For example, we can detect side reactions involving the electrolyte and the electrode materials, and follow structural transformations that occur during extremely fast charging and discharging. We will discuss the approach for a series of anode materials, including Li metal. For example, a combination of in- and ex-situ NMR is used to study the anode material Si. This material has been the subject of much recent investigation, because of its extremely large gravimetric and volumetric capacity. This material undergoes a crystalline-to-amorphous phase transition on electrochemical Li insertion into crystalline Si, during the first discharge, hindering attempts to link structure in these systems with electrochemical performance. We apply a combination of static, in-situ and ex-situ MAS 7Li and 29Si NMR studies to investigate the changes in local structure that occur in the actual working LIB. The first discharge occurs via the formation of isolated Si ions and smaller Si-Si clusters embedded in a Li-ion matrix; the latter are broken apart at the end of the discharge forming isolated Si ions. A spontaneous reaction of the lithium silicide with the electrolyte is directly observed in the in situ NMR experiments; this mechanism results in self-discharge, and potentially capacity loss, if Si-based LIBs are discharged to low potentials. This reaction is slowed down considerably, for Si particles coated with CMC. The effect of rate on dendrite formation will be explored for graphite and Li metal, by using in situ NMR methods. We exploit the fact that the Li rf used to excite the NMR spins can only penetrate the 1st few microns of a metallic particle, to explore the formation of Li metal dendrites. For conversion and extrusion reactions, we follow both Li and Cu extrusion. Acknowledgements: We thank Mathieu Morcrette, Jean-Marie Tarascon, Adam Best, and Stephen Harris for their help in the Si and Li projects. This work was partially supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. DOE under Contract No. DE-AC03-76SF00098, via subcontract No

6517749 with the Lawrence Berkeley National Laboratory.

9:00 AM U14.2

In-Situ TEM Study of Interfacial Layer Formation in Li-Ion Battery. Chongmin Wang¹, W. Xu², Lax Saraf¹, B. Arey¹, J. Liu³, Z. G. Yang², J. G. Zhang², S. Thevuthasan¹ and D. R. Baer¹; ¹Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington; ²Energy and Environmental Directorate, Pacific Northwest National Laboratory, Richland, Washington; ³Fundamental and Computational Science Directorate, Pacific Northwest National Laboratory, Santa Barbara, California.

One of the fundamental challenges facing the Li-ion battery development is the understanding of the fading mechanism of the active electrode materials during the repeated charging and discharging. In-situ transmission electron microscopy (TEM) and spectroscopy will be ideal tools for probing the structural evolution of the electrode materials during battery operation. However, related to the high vacuum operation of a TEM as well as the requirement of electron transmission through the sample, a prototype battery must be sealed with thin membrane that enables the electron transmission at the interested region. It is known that electrolytes based on ionic liquid have a low vapor pressure. Therefore, it is generally expected that using ionic liquid as electrolyte, the prototype battery may be operated in vacuum without sealing the whole system using a thin membrane. In this work, we report our exploratory work on developing in-situ TEM devices that will eventually enable direct and high spatial resolution observation of the structural evolution of the interface between the electrolyte and the electrode materials. In a model experiment, a prototype Li-ion battery was developed in the system of using SnO₂ nanowire as anode, an air stable salt LiTFSI in a hydrophobic ionic liquid as electrolyte, and LiCoO₂ as cathode. Focused ion beam (FIB) manipulation of a single nanowire enables the assembling of a prototype battery. Furthermore, due to the low vapor pressure of the ionic liquid, the whole system can be directly loaded into a TEM without sealing. The interface across the solid-ionic liquid was studied during charging and discharging using TEM imaging and electron energy loss-spectroscopy (EELS). It has been observed that during the initial charging, the ionic liquid drifts along the nanowire (anode) surface and the thickness of the liquid reaches an equilibrium value. At the same time, electrodeposition occurs on the anode, leading to the formation of a thick layer that covers the anode. It has been found that Li concentration is much higher within this deposited layer as compared with the initial electrolyte. Due to the deposition of this layer, lithiation of SnO₂ is dramatically retarded. This directly correlates with the observed fast fading of the battery when this type of ionic liquid is used for the battery as compared with that uses a standard liquid electrolyte.

9:15 AM U14.3

The Fastest High Definition Raman Imaging of Compositional Distribution on the Lithium-ion Battery Electrode. Tomoya Uchiyama, Taisuke Ota and Minoru Kobayashi; Nanophoton corporation, Suita, Osaka, Japan.

Analyzing the degradation of lithium-ion battery electrode is very important for the increase in performance, longer operating life and improving security of secondary batteries. Raman spectroscopy is one of the most appropriate methods to investigate the degradation of electrode because the compositional change and becoming are most obvious on the Raman spectrum. We developed a new laser Raman microscope by combining the line illumination and multi-spectrum simultaneous measurement. By using this method, the incident laser can excite the Raman scattering from the sample surface along the line illuminated area and measure it as 400 Raman scattered lights while each light is dispersed spectrally by 1340-400 pixels electrically cooled CCD detector. Additionally, our Raman microscope scans the line-shaped laser by laser beam scanning method and realizes high-speed and vibration-free imaging compared to the stage scanning method. We developed original optics (patented) to avoid a non-uniform intensity illumination along the line caused by the cylindrical lens (conventional line illumination method). Also, we adopted slit confocal optics to keep the three-dimensional spatial resolution when we use line illumination. By these means, we succeeded in speeding up the Raman imaging speed about several hundred times faster than that of conventional method while keeping the high definition imaging performance. By using our Raman microscope, we obtained the high definition Raman image which shows the distribution of LiCoO₂ and carbon black clearly in only 20 minutes. Also we observed the production of Co₃O₄ induced by high power laser beam scanning on the electrode.

SESSION U15: Electrolytes and Separators for Batteries and Capacitors

Chair: Grant Smith

Thursday Morning, December 3, 2009

Room 200 (Hynes)

10:00 AM U15.1

Transport Properties of Ionic Liquids for Lithium Battery Applications: Insights from Classical Molecular Dynamics Simulations. Oliviero Andreussi and Nicola Marzari; Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Room Temperature Ionic Liquids (RTILs) have attracted much of the attention of the scientific community in the past decade, mostly due to their novel and highly customizable properties. Applications of RTILs have been proposed in the most different fields, and a particular attention has been devoted to their possible use as electrolytes in lithium batteries. Nonetheless, their high viscosities, especially in the presence of dissolved lithium salts, pose serious problems to the use of RTILs in practical applications. To elucidate some of the physical aspects behind transport properties of RTILs, extensive classical molecular dynamics (MD) calculations are reported. Bulk viscosities and ionic conductivities of buthyl-metil-imidazole based RTILs are presented over a wide range of temperatures. The dependence of the properties of the liquids on the kind of anion is analyzed. The effect of adding a lithium salt to the considered RTILs is described. In particular, as a result of lithium addition, the formation of extended percolated

network is reported for two of the considered anions. Moreover, the presence of a density dependent percolation threshold is found and the effect of this structural reorganization on lithium transport is analyzed.

10:15 AM U15.2

Organosilicon Electrolytes for Safe Lithium-Ion Batteries. Monica L. Usrey¹, Xin Chen¹, Michael Pollina², Robert West^{1,2}, Mark Zager², Lingzhi Zhang^{1,2} and Robert Hamers^{1,2}; ¹Chemistry, University of Wisconsin-Madison, Madison, Wisconsin; ²Silatronix, Inc, Madison, Wisconsin.

While the safety of lithium ion batteries has been improved through the use of new electrode materials, significant safety issues and technical performance limitations remain due to the current use of flammable electrolytes, such as alkyl carbonates and acetonitrile. Organosilicon compounds are very attractive electrolytes for lithium ion batteries because they have very low vapor pressures, high flash points (185°C and higher), low viscosity, low toxicity, and electrochemical stability up to 5 V (vs. Li/Li+). We have been investigating organosilicon (OS) compounds as the basis for a new generation of safer lithium ion batteries. Using both commercial and non-commercial electrodes and cell designs, the electrochemical performance of several organosilicon compounds has been evaluated. Of particular importance is the formation of the solid-electrolyte interphase (SEI) layer on the graphitic anode. Unlike traditional alkyl carbonates, where the SEI layer is formed by the carbonate, the SEI layers from OS electrolytes arise primarily from decomposition of the salt. Using FTIR spectroscopy and SEM imaging, we have investigated SEI layer formation and correlated this with relevant electrochemical properties and OS molecular structure. With suitable formation of an SEI layer, we demonstrate that OS compounds can serve as the foundation for highly stable, rechargeable batteries with excellent performance.

10:30 AM U15.3

Carbon Based Supercapacitors in Protic Ionic Liquids. Francois Beguin¹, Roman Mysyk¹, Encarnacion Raymundo-Pinero¹, Meriem Anouti² and Daniel Lemordant²; ¹Research Center on Divided Matter; CNRS/University, Orleans, France; ²Laboratory CIME, University Francois Rabelais; Tours, France.

The amount of electrical energy accumulated in a supercapacitor (SC) is proportional to capacitance and square of voltage. SC in aqueous electrolytes can work at a maximum voltage of 1 V, while 2.7 V can be reached in organic electrolytes. Although the latter are preferred in commercial SC, they present many disadvantages because they are expensive, poorly conductive and environment unfriendly. We propose to use protic ionic liquids (PILs) as new electrolytes in carbon based SC. PILs are relatively cheap, highly conductive and environment friendly. Moreover, due to their proton exchanging capabilities, a pseudo-faradaic enhancement of capacitance can be expected, as in aqueous electrolytes, while operating in a larger voltage window.

The presentation will show the electrochemical performance of two pyrrolidinium based PILs (pyrrolidinium formate and pyrrolidinium nitrate) in presence of two different carbon electrodes: i) a commercial activated carbon, AC; ii) the same oxidized in order to increase the amount of surface functionalities without modifying the porous texture, ACox. The contribution of pseudo-faradaic charge transfer reactions to the capacitive response is demonstrated by the shape of the voltammograms in three-electrode cells, the pseudocapacitive effect being more pronounced for the carbon ACox. As a consequence, higher capacitance values can be obtained when using PILs with oxygen-enriched carbons. Additionally, for the considered carbons, the values of capacitance in PILs are comparable to the values in aqueous electrolytes, while the cells can be advantageously used at larger voltage, providing gains in energy density.

10:45 AM *U15.4

The Characteristics of Organic Electrolytes Using Spiro-ammonium Salt. Kazumi Chiba^{1,2}, Tsukasa Ueda¹, Hideo Yamamoto¹ and Katsuhiko Naoi²; ¹R&D center, Japan Carlit Co., Ltd., Shibukawa, Gunma Pref., Japan; ²Institute of science and Technology, Tokyo University of Agriculture & Technology, Koganei, Tokyo Met., Japan.

1. Introduction The development of a high performance electrolytic solution is an essential requirement in fabricating an electric double-layer capacitor (EDLC) with excellent characteristics. To successfully develop such an electrolytic solution, the characteristics both of its primary components—the electrolyte and the solvent—need to be improved. 2. SBP-BF₄, a new electrolyte In this study, the solubility of various types of quaternary ammonium tetrafluoroborates in propylenecarbonate (PC) was compared. This comparison was performed using quaternary ammonium tetrafluoroborates that had been synthesized and were considered to show desirable characteristics, as well as those had already been commercialized. Each salt was dissolved in PC, and the EDLC characteristics of the resultant electrolytic solutions were studied by comparing the internal resistance from -40°C to +20°C and discharging rate from 2 mA/cm² to 560 mA/cm² at 20°C for each solution. The results show that SBP-BF₄ exhibited the most desirable characteristics for many of the evaluation items, exceeding those of an electrolytic solution made by dissolving EMI-BF₄ (an ionic liquid) in PC. The results of the comparison indicate the following: spiro-type SBP-BF₄, which is composed of two pentacyclic rings, is an excellent electrolyte; TEA-BF₄, which is widely used, presented exceptionally poor characteristics compared to the other compounds under consideration; and electrolytic solutions obtained by mixing ionic liquids with a solvent are not superior to those obtained by dissolving a solid electrolyte (except for TEA) in a solvent. 3. New, voltage resistant solvents One significant weakness of EDLCs is their low energy density, partly due to their low withstanding voltage of 2.5 to 2.7 V, which is much lower than the approximately 4 V that can be obtained with a rechargeable lithium-ion battery. However, very few studies have approached the issue of enhancing the withstanding voltage for EDLCs by studying electrolytic solutions. In this study, therefore, we focused on the possible applicability of linear-structure sulfone compounds, which have rarely been studied. In general, linear-structure sulfone compounds have a high boiling and melting point; however, some compounds we examined have a low melting point and high boiling point. Electrolytes that have high solubility in a linear-structure sulfone were studied, and SBP-

BF4 was found to be the optimum. Some of the electrolytic solutions obtained by dissolving SBP-BF4 in a linear sulfone were still usable at -30°C while exhibiting very high withstanding voltages of 3.3 V or more, suggesting that the application of linear-structure sulfone compounds to electrolytic solutions for the fabrication of EDLCs is promising. Acknowledgments Part of this study has been made possible by JIRITSU, a research grant program offered by Tokyo University of Agriculture and Technology.

11:15 AM U15.5

Facile Fabrication of Multifunctional Nanostructured Materials. Da Deng and Jim Yang Lee; Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore.

Our lab has been working for several years on the chemical methods of synthesis of various (0-, 1-, 2- to 3-dimensional) nanostructured nanomaterials, emphasizing in particular on the low environmental impact and scalability of the method for volume production. In general we have found a combination of solvothermal synthesis and chemical vapor deposition to be most suitable for such purposes. In this presentation we will demonstrate the use of a simple scalable self-assembly technique to fabricate a new, double-rough chestnut-like Sn@C composite on a copper foil directly. The coated copper foil could be used as a ready anode for lithium ion batteries without any further processing. The performance in terms of rate capability and cyclability were good. In addition the unique double-rough morphology of nanohairs on mesospheres of nanoparticle aggregates also imparted lotus-leave like behavior and the surface was therefore superhydrophobic. Another example is the fabrication of a family of 1-D C-curved nanoarches on a Si wafer for surface wettability control. The nanoarches could be made from single-crystalline Sn nanorods encapsulated in carbon nanotubes (CNTs), CNTs or SnO₂ nanotubes. All of these syntheses are relatively easy to perform and a substantial amount of the product in high purity can be produced per batch.



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