The Science of Electrode Materials for Lithium Batteries

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Progress Report
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from

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Abstract

Basic materials science research on materials for anodes and cathodes in electrochemical cells. The work is a mix of electrochemical measurements and analysis of the materials by transmission electron microscopy and x-ray diffractometry. The emphasis is on the thermodynamics and kinetics of how lithium is intercalated and de-intercalated into anode and cathode materials.

Facilities

Two Arbin cyclers in routine operation
Coin cell fabrication is routine
In-situ x-ray diffraction work through windows in cells
Elevated temperature measurements are routine
Electrochemical impedance spectroscopy is performed as required

Personnel

Prof. Brent Fultz, Caltech
Dr. Rachid Yazami, CNRS Grenoble
Dr. Channing Ahn, Caltech
Dr. Jason Graetz, a materials science graduate student who completed his Ph.D. thesis under this grant (graduation in June, 2003)
Shu Miao (materials science graduate student)
Yvan Reynier (Caltech visitor, Grenoble student)
Yasanori Ozawa (Caltech special student, Grenoble student)
Karen Lam (Caltech part-time graduate student, employee of Quallion LLC, Sylmar CA)
Joanna Dodd (Caltech part-time graduate student, employee of Quallion LLC, Sylmar CA)

Research Results

High-Capacity, Cyclable Nanostructured Anode Materials
We prepared nanostructured anode materials of pure silicon [9] and pure germanium [18], and studied their electrochemical performance in half-cells with lithium metal counter electrodes. The capacity of thin film silicon materials exceeded 2 Ah/g for 50 cycles. The germanium anodes were perhaps more impressive, sustaining 1.6 Ah/g for 60 cycles with essentially no capacity fade. We believe that nanostructured materials are not subject to the mechanical damage typical of bulk anode materials. It is unclear if these thin film materials are practical as anode materials, but they do show potential advantages over conventional materials. A U.S. patent application is in preparation.

Entropy of the Li-C system
The open-circuit voltage and its temperature dependence were measured on half-cells with graphite electrodes in varying states of lithiation. These data were used to determine the entropy and enthalpy of lithium intercalation into graphites having different Li concentrations. The entropy is especially sensitive to the crystalline quality of the graphite, and may prove useful for characterizing different graphite materials [15].

Entropy of the Li-$LiCoO_2$ system
A similar study of open-circuit voltages was performed on the Li intercalation reaction in $LiCoO_2$. Large differences in the entropy of intercalation were found in this material owing to phase transitions, or even for intercalation into a single phase. We are trying to account for the sources of this entropy. A neutron inelastic scattering experiment has shown that the phonon entropy is small. It appears that the configurational entropy is large, but not large enough. In a collaboration with Peter Rez, we seem to be finding that the electronic entropy is remarkably large.

Phases in $LiCoO_2$
A TEM study showed the formation of the cubic spinel $LiCoO_2$ after electrochemical cycling and ageing at elevated temperatures or voltages. It appears that this phase forms with close crystallographic registry with the original layered phase, and causes internal stresses when it forms. This spinel phase seems detrimental to electrochemical performance of cathodes, especially since it forms on the surface of the material [4-6,19,20]. We have also indentified the existence of the previously unobserved H1-3 phase by electron diffraction. This H1-3 phase may be an intermediary in the O3 - spinel transformation. This work involves a collaboration with Heike Gabrisch, recently a postdoctoral fellow working on this program at Caltech, and now an Assistant Professor of Chemistry at the Univ. of New Orleans.

EELS of $Li(Ni,Co)O_2$ Cathodes -- Electronic structure
Using electron energy loss spectrometry in the TEM, we have measured the changes during de-lithiation of $Li(Ni,Co)O_2$ in EELS spectra of the Ni and Co $L_{2,3}$-edges and the O K-edge. With help from Peter Rez of Arizona State University, we have found that the Li electron is accommodated primarily by the O 2p states, not states at the Ni or Co atoms [7,8,11,12].

Mechanisms of self-discharge and capacity loss
This work is led by Rachid Yazami, with his Ph.D. student Y. Ozawa from Grenoble [17,21-23]. Fultz is involved when measurements involve activation energies and thermodynamic of kinetic

properties. Several mechanisms are involved in discharge and in capacity losses, and the story is not a simple one. One new result is an observation of the tendency for Li to re-intercalate into $LiCoO_2$, even when this material is not in an electrochemical cell. It may be true that the reintercalation of Li is responsible for much of the capacity loss that is recoverable after recharge, and we are testing if the activation energies are similar. Spinel phase formation in $LiCoO_2$ appears to be important for irreversible capacity losses.

Distributions of Hydrogen and Strains in $LaNi_5$ and $LaNi_{4.75}Sn_{0.25}$

A long-delayed manuscript was published on our measurements by small-angle neutron scattering of hydrogen distributions and internal strains in binary $LaNi_5$ and $LaNi_{4.75}Sn_{0.25}$ [3]. The study suggests that the more homogeneous deuterium distribution in $LaNi_{4.75}Sn_{0.25}$ suppresses the strain gradients that cause decrepitation of the metal hydride. This was the topic by Fultz for his invited talk at the Gordon Conference this summer on hydrogen-metal systems. It was also included in our invited paper in the MRS Bulletin [2].

Dislocations in $LiCoO_2$

We performed a TEM study to understand the dislocations in $LiCoO_2$. We found perfect dislocations, which had been suggested previously, and determined their character and Burger's vector, a new result. We also discovered Shockley partial dislocations in the layered structure of $LiCoO_2$ [4].

Plans for 2003-4

The tasks fall into two inter-related themes. The first is how the equilibrium voltage and capacity of a cell depend on the electronic structure, microstructure, and entropy of the electrode materials. The second theme is the kinetics of phase stability, which often proves important for understanding cycle life.

The TEM imaging study on defect structures in heavily-cycled $LiCoO_2$ is largely complete, but we intend to do further characterization on materials that have lost capacity under unusual conditions of ageing under high voltages and elevated temperatures.

We will perform TEM EELS spectroscopy work on $Li(Mn,Ni)O_2$ with different states of lithiation. There is evidence for Ni^{4+} upon delithiation, but we will also test the role of the oxygen and the Mn on charge compensation during lithiation.

Temperature-dependence of the open circuit voltage on coin cells will be performed on other anode and cathode materials to measure the entropies of lithium intercalation in different materials. These studies serve two purposes:

- The measurements are easy to perform automatically, and may serve as a practical characterization tool for carbons and other electrode materials.
- We are attempting to account for the different sources of entropy of intercalation, and understand how they depend on the local environments for lithium atoms in the material.

We are undertaking a study of the stability of $LiFePO_4$ at elevated temperatures under different conditions of lithiation.

In-situ x-ray diffractometry work of operating cells for a comparative study of cathode materials in coin cells of $LiCoO_2$ and $Li(Ni,Co)O_2$ cathodes. The purpose of this study is to determine how the internal stresses differ in the Ni-bearing materials.

Publications for 2002—2003

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13. Y. Ozawa, R. Yazami, and B. Fultz, "Self-discharge Study of $LiCoO_2$ Cathode Materials", J. Power Sources **119-121** (2003), p. 918.

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Extended Abstracts

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