

FINAL REPORT FOR GRANT DE-FG02-93ER14385

Title from 1993-2000:

“Solid Electrolyte/Electrode Interfaces: Atomistic Behavior Analyzed Via UHV-AFM, Surface Spectroscopies, and Computer Simulations”

Title from 2000-2004

“Computational and Experimental Studies of the Cathode/Electrolyte Interface in Oxide Thin Film Batteries”

Title from 2005-2006

“Atomistic-Level Studies of Oxygen Transport Along and Across Grain Boundaries in Yttria-Stabilized Zirconia Electrolytes for SOFCs”

The goals of the research were to understand the structural, dynamic, and chemical properties of solid electrolyte surfaces and the cathode/electrolyte interface at an atomistic and nanometer level using both computational and experimental techniques. Titles changed based on modification of effort.

UHV-SPM (ultra-high vacuum - scanning probe microscopy, which includes STM, scanning tunneling microscopy, and SFM, scanning force microscopy), XPS (x-ray photoelectron spectroscopy), and molecular dynamics (MD) computer simulations were used in this program. Experimental samples included in-situ deposited thin film oxide batteries, made up of a Li-source anode, thin (30-100nm thicknesses) lithium phosphorous oxide electrolyte, and thin (30nm) vanadia cathodes. These samples were studied using UHV-SPM which included both UHV-STM and UHV-AFM (one of the first in the world that enabled both methods in the same UHV system to be used on the same sample) and was built under the previous DOE grants URIP DE-FG05-8975521 and DE-FG05-88ER-45368. Computationally, we used MD simulations of lithium silicate glass electrolytes in contact with tungsten oxide and vanadia cathodes. Both simulations and experimental studies of the structure and Li ion diffusion into layered nanocrystalline vanadia were also performed. *The work developed one of the first UHV-SPM's, provided the first unambiguous data on the orientation of the layered cathode at the interface of the solid electrolyte surface, the effect of this orientation on Li transport into the cathode, and a unique solution to overcoming this transport barrier through the use of an amorphous film around nanoparticles of the layered cathode.*

Major results include:

- (a) Direct observation of Li ion migration during *in-situ* deposition of electrolyte and cathode oxide layers in solid-state thin film batteries, inherently causing compositional gradients during processing.
- (b) Development of a ‘nanobattery’ using an STM tip to complete the circuit of *in-situ* deposited battery layers in our UHV-STM/AFM, providing nanometer resolution of conductance variations in these thin film devices.
- (c) Experimental verification of a variation in conductance of a factor of 5 at locations separated by 20nm on a thin film solid state battery using *in-situ* UHV-STM/AFM.
- (d) Verification of the structure of the vanadia cathode at the cathode/electrolyte interface, showing unit-cell resolution and preferential order using *in-situ* UHV-STM/AFM.
- (e) Development of interatomic potentials for the MD simulations that accurately reproduced vanadia and γ -Li-vanadate, with variable charge on the V ions, as well as reproducing the correct phase transition that occurs upon intercalation of Li into vanadia.

- (f) The effect of vanadia crystal orientation on Li intercalation into the layered vanadia, with a significant anisotropy in activation energies for Li diffusion.
- (g) Role of the amorphous vanadia film that exists between vanadia nanocrystals on Li ion transport in the cathode. **This provides a mechanism for the development of rapid Li-ion transport paths in solid-state oxide thin-film batteries using nanocrystalline layered cathodes in contact with an amorphous cathode film.**
- (h) Activation energies of Li diffusion in silicate glasses and the effect of the Al/Li ratio consistent with experimental data (within 0.02eV).

Our results were the first such atomistic and interfacial results on these thin film battery systems.

Item (b) was subsequently reproduced on the micron-scale (vs our nano-scale) at LBNL and such an approach is currently being used by a group at BNL in the NECCES EFRC.

Item (d) was the first time that a deposited vanadia surface was imaged via SPM which would be relevant to real working cathodes (all previous work used reduced single crystal surfaces, not deposited nanocrystalline material as occurs in commercially viable systems).

Item (e) required a new methodology to develop a reasonable interatomic potential for allowing charges on ions to change.

Item (f) is significant because it showed, in combination with the experimental verification of the layered crystal orientation on the solid electrolyte, the significantly different activation barriers to Li diffusion into the cathode and led to the concept shown in item (g).

Item (g) has important implications on the method to enhance Li ion transport into layered cathodes that have highly anisotropic Li transport barriers because of the crystal structure; have nanoparticles of the layered cathode in contact with an amorphous cathode film that enables rapid Li transport along the film, then into the rapid transport direction in the layered nanocrystalline cathode, enabling fast transport and high capacity. We believe this concept has been applied in a new commercial battery system.

STUDENTS AND POST-DOCTORAL CANDIDATES SUPPORTED:

M. Garcia, D. Hensley, D. Kulp, W. Li, A. Semenov, P. Shadwell

RELEVANCE TO INDUSTRIAL APPLICATIONS:

Our development and application of UHV-SPM and the MD simulations, as well as our use of XPS, enabled additional studies of similar materials used by the newly formed company, SAGE (Sun Activated Glass Electrochromics) Inc. that now has manufacturing facilities in Minnesota making coatings on window for electrochromics.

PUBLICATIONS IN GRANT PERIOD:

1. "Molecular Simulations of Li Insertion in a Nanocrystalline V_2O_5 Thin Film Cathode", W. Li and S. H. Garofalini, J. Electrochem. Soc. 152 (2005) A364-A369.
2. "Molecular Dynamics Simulation Of Lithium Diffusion $Li_2O-Al_2O_3-SiO_2$ Glasses", W. Li and S. H. Garofalini, Sol. St. Ionics, 166, (2004) 365-373.
3. "Molecular Dynamics Simulations of Li Transport Between Cathode Crystals", S. H. Garofalini, J. Power Socs. 110 (2002) 412-415.
4. "in-situ Deposition and UHV STM/AFM study of V_2O_5/Li_3PO_4 Rechargeable Lithium Ion Battery", A. E. Semenov, I. N. Borodina, and S. H. Garofalini, J. Electrochem. Soc., 148(2001) A1239-A1246.

5. "Molecular Dynamics Simulations of Cathode/Glass Interface Behavior: Effect of Orientation on Phase Transformation, Li Migration, and Interface Relaxation" , S. H. Garofalini and P. Shadwell, J. Pwr. Sources, 89 (2000) 190-200.
6. "Molecular Dynamics Simulation of the Effect of Crystal Orientation on Lithium Ion Diffusion at the V_2O_5/Li_2SiO_3 Interface", M. E. Garcia and S. H. Garofalini, J. Electrochem. Soc. 146 (1999) 840-849.
7. "Scanning Force Microscopy Investigation of Surface Forces at the Tungsten Oxide/Lithium Borate Interface", D. A. Hensley and S. H. Garofalini, J. Electrochem. Soc. 145 (1998) 669-675.
8. "Molecular Dynamics Simulation of V_2O_5/Li_2SiO_3 Interface", M. Garcia, E. Webb, and S. H. Garofalini, J. Electrochem. Soc. 145 (1998) 2155-2164.
9. "Molecular Dynamics Studies of Lithium Injection in Model Electrode/Electrolyte Systems", D.T. Kulp and S.H. Garofalini, J. Electrochem. Soc. 143 (1996) 2211-2219.
10. "Molecular Dynamics Simulation of Elevated Temperature Interfacial Behavior between Silica Glass and a Model Crystal", E. B. Webb III and S. H. Garofalini, J. Chem. Phys. 105 (1996) 792-801.
11. "In situ Deposition and XPS Characterization of Lithium Based Solid Electrolyte/Vanadia Interfaces: Observation of Lithium Migration", D. A. Hensley and S. H. Garofalini, Solid State Ionics 82 (1995) 67-73.
12. "XPS Investigation of Lithium Borate Glass and the Li/LiBO₂ Interface", D. A. Hensley and S. H. Garofalini, Appl. Surf. Sci. 81 (1994) 331-339.

INVITED PRESENTATIONS RELEVANT TO THIS GRANT

Princeton University, 2004
 Cornell University, 2004
 Electrochemical Society, Orlando, FL, 2003
 International Conference on Composites Engineering, ICCE/9, San Diego, CA, 2002
 Johns Hopkins University, Earth and Planetary Sci., Baltimore MD, 2002
 Laboratory for Surface Modification, Rutgers University, Piscataway, NJ, 2002
 Workshop on "Development of Advanced Battery Engineering Models", Arlington, VA, 2001
 University of Missouri, Kansas City, MO, 2001
 Mardi Gras Physics Conference, Louisiana State University, Baton Rouge, LA, 2001
 Materials Research Society, Fall Meeting, Boston, 2000
 Advanced Li Solid State Battery Workshop, Towson MD, 1999
 Oak Ridge National Laboratory, Oak Ridge, TN, 1999
 DOE Advanced Non-Aqueous Battery Technology Workshop, Hunt Valley, MD, 1997
 American Chemical Soc. MARM'97, Molecular Modeling session, 1997
 Molecular Simulations' International Materials Science Symposia, Philadelphia, PA, 1995
 DOE Workshop on Solid Electrolytes for Battery Applications, Colorado Springs, CO, 1995
 STM/AFM Symposium, U. S. Army Natick Research Center, 1994

Plus additional non-invited talks at MRS and Am. Ceram. Soc. Meetings.