

Thursday Morning, November 3, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-ThM

Nanostructures for Energy Storage and Fuel Cells I

Moderator: J. Lewis, RTI International

8:00am EN+NS-ThM1 Exploring Intercalation Chemistry of Modified Graphene with Ionic Liquids for Energy Storage Applications, *M. Acik*, The University of Texas at Dallas, *D.R. Dreyer*, *C. Bielawski*, The University of Texas at Austin, *Y.J. Chabal*, The University of Texas at Dallas

One of a real-world application of Electrochemical Double Layer Capacitors (EDLCs) is their use in prototype electric vehicles. An EDLC simply consists of two non-reactive, porous electrodes and an electrolyte separated with a membrane. Activated charcoals are one of a commonly used electrode systems which has drawbacks such as limited energy storage due to their large ion size. Therefore, a replacement electrode system with a higher surface area is necessary for a superior EDLC performance. Modified graphene is one of a promising candidate with its high theoretical surface area (2630 m²/g). EDLC working principle also depends on how effectively it can polarize the electrolyte solution. In principle, ionic liquids are promising electrolyte systems with their high non-volatility, non-flammability, thermal stability and good solvating ability.

This study focuses on the intercalation studies of ionic liquids such as N-methyl-N,N,N-tris(2-hydroxyethyl)ammonium iodide, N-methyl-N,N,N-tris(2-hydroxyethyl)ammonium methyl sulfate, 1-butyl-3-methylimidazolium methyl sulfate and N-octyl-N-methylpiperidinium methyl sulfate. To achieve a high surface area material with modified graphene, it is essential to understand the interfacial interactions upon intercalation of ionic liquids.

We study powder X-Ray Diffraction Analysis to characterize the interlayer distance of modified graphene. For instance, its d-spacing increases by about 4-12 Å after intercalating as-synthesized graphite oxide (GO, ~9Å) with N-methyl-N,N,N-tris(2-hydroxyethyl)ammonium methyl sulfate (IL) at room temperature. Annealing at 300-500°C, (002) orientation of GO disappears as a result of thermal exfoliation. In addition, *in-situ* Infrared Absorption Spectroscopy (IRAS) measurements were performed to explore the intercalation chemistry of modified graphene in the presence of ionic liquids. Therefore, we perform thermal reduction studies in vacuum coupled with IRAS measurements to characterize the chemical interactions during thermal exfoliation of reduced GO. After annealing GO intercalated with this IL, the loss of C-N and C-O containing species is identified at ~1000-1500 cm⁻¹ and 800-1200 cm⁻¹ with contribution from C-OH groups at 3000-3700 cm⁻¹. Complete removal of these species is observed after a ~500°C anneal resulting in a weak infrared absorbance intensity of sp²-hybridized C=C species at ~1580 cm⁻¹. The presence of new formation of sheet-to-sheet linking or bonding motifs was also studied with X-ray Photoelectron Spectroscopy (XPS).

*Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC001951.

8:20am EN+NS-ThM2 Electronic Structure and Chemical Composition of Candidate Conversion Material Iron Oxyfluoride, *R. Thorpe*, *S. Rangan*, *R.A. Bartynski*, *O. Celik*, *N. Pereira*, *G. Amatucci*, Rutgers University

Transition metal fluorides have recently gained interest as possible electrode materials in lithium ion conversion batteries. Owing to their large band gaps, they operate at high voltages and enable high energy densities. However this large band gap inhibits charge conduction and thus impedes efficient charge and discharge. One path to overcome this limitation is the use of metal oxyfluorides, which are characterized by a slightly smaller energy gap and thus a higher electronic conductivity. Currently, little is known about the electronic structure of metal oxyfluorides, particularly the relation between chemical structure, composition, and energy gap. Hence, we have produced model oxyfluoride systems in order to characterize the conversion mechanism using surface science tools.

Of all metal fluorides, iron-based compounds are the most promising to maximize energy density. Ultra-thin FeF₂ films have been synthesized via the fluorination of clean Fe foil exposed to XeF₂, following a self-limited Mott-Cabrera mechanism. The FeF₂ films have then been sequentially exposed to a partial pressure of O₂ of 2x10⁻⁶ Torr at 285°C in order to produce iron oxyfluoride. Using x-ray and ultraviolet photoemission as well as inverse photoemission, we have probed the electronic structure of these

FeO_xF_y samples and characterized the occupied and unoccupied states near the band gap of the material.

It has been found that oxygen insertion into the FeF₂ matrix can be controlled until complete oxidation occurs. As expected for a Mott-Hubbard insulator, the valence band and conduction band of FeF₂ can be interpreted using a simple crystal field approach. In the case of Fe₂O₃, strong charge transfer effects need to be taken into account in order to interpret the band edges. To explore the conversion process, Li has been evaporated onto these iron oxyfluorides *in-situ*. Preliminary results addressing the reactivity of lithium at the surface of these materials will also be presented.

8:40am EN+NS-ThM3 Lithium Ion Batteries: Present and Future Technologies, *K. Amine*, *W. Wu*, *I. Belharouak*, *A. Abouimrane*, *Z. Zhang*, *J. Lu*, Argonne National Laboratory **INVITED**

In its goal of developing more fuel efficient vehicles, the US Department of Energy in collaboration with the US auto industries are focusing on high-power and high energy lithium-ion batteries to meet the energy storage requirements for HEV and PHEV applications. Under these auspices, Argonne National Laboratory is investigating several different lithium ion chemistries in order to address the calendar life, cost and safety of high power and high energy lithium ion batteries for transportation applications

To meet the high-energy requirement that can enable the 40-miles electric drive P-HEVs, It is necessary to develop very high energy cathode or anode that offers 5,000 charge-depleting cycles, 15 years calendar life as well as excellent abuse tolerance. These challenging requirements make it difficult for conventional cathode materials to be adopted in P-HEVs. In this paper, we report on several advanced battery chemistry that could be used to power Hybrid electric vehicles. We also discuss several future high energy battery technologies that can enable 40 miles Plug in Hybrid and long range electric vehicles.

9:20am EN+NS-ThM5 Templating of Porous Materials for Energy Storage and Generation, *A. Stein*, *J. Davidson*, *N. Petkovich*, *Y. Qian*, *S. Rudisill*, *L. Venzton*, *A. Vu*, University of Minnesota **INVITED**

Materials containing pores in size ranges from micropores to macropores offer interesting features for a number applications involving energy storage and conversion, such as batteries, fuel cells, hydrogen storage, and sunlight-to-fuel conversion. Depending on the specific application, they can provide large surface areas for reaction, interfacial transport, or dispersion of active sites; they can provide nanostructured features which enhance reactivity, alter materials properties, or shorten diffusion paths; they can act as host materials to stabilize other active components; or, in the case of porous carbons, they can provide electrically conductive phases as well as intercalation sites. However, the higher reactivity brought about by nanostructured features can also lead to decreased stability, particularly in applications where phase changes may alter the structure of the material or where high temperatures are employed. This talk will focus on two redox systems (lithium-ion batteries and sunlight-to-fuel conversion) in which templated porous materials provide a platform for either electrical energy storage or light-to-chemical energy conversion. In the first system the role of pore architecture in carbon-based electrodes will be discussed. Improved rate capabilities for lithiation/delithiation are observed for hierarchically porous carbon electrodes. In composites with tin or tin oxide for anodes these structures maintain electrical contact between tin-based particles, even when those particles undergo significant volume changes during cycling, and hence the composite anode maintains good capacities over multiple cycles. Composites of hierarchically structured carbon with poorly conducting but otherwise desirable electrode materials (like sulfur or LiFePO₄) can be used to overcome limitations in electrical conductivity of those materials, increasing the choice of useful electrode materials. In the second system, we investigate the role of porosity in ceria-based materials of interest for solar thermal splitting of water or carbon dioxide to produce hydrogen or carbon monoxide fuels, respectively. Dopants for ceria are examined to stabilize the porous structures at the high reaction temperatures. The interplay between composition and morphology of these materials, thermal stability, and conversion efficiencies will be discussed.

11:00am EN+NS-ThM10 Exploration of the Effects of Si Nanowire Length and Doping on Li-ion Battery Anode Performance, *F. Rusli*, *V. Chakrapani*, *M.A. Filler*, *P.A. Kohl*, Georgia Institute of Technology
Silicon nanowires have recently garnered significant attention as a potential candidate to replace graphite as the negative electrode in a lithium-ion battery. Silicon's earth abundance, extensive knowledge base, and its theoretical capacity of 4200 mAh/g make it an attractive material for this purpose. While the high incorporation of lithium presents a problem as silicon undergoes a significant specific volume expansion upon

intercalation (up to 400%), nanowires permit facile radial strain relaxation and allow lithiation without pulverization. In this work, we report on the first systematic study of nanowire length and doping on the cycling performance of NW electrodes. Silicon nanowires were grown on stainless steel substrates via the vapor-liquid-solid technique in a cold-wall low pressure chemical vapor deposition reactor. Growth times ranging from 5-60 minutes and doping concentrations between 10^{18} – 10^{20} atoms cm^{-3} were studied. The half cells were cycled against lithium metal between (1) 0.01 and 2.0 V and (2) 0.07-0.7 V at a C/20 rate for 20 cycles. Cycling performance at different depths of discharge was also studied. Nanowires grown at short and long times both exhibit lower capacities than those grown at intermediate times. We attribute this effect to the loss of nanowire contact at the interface between the stainless steel and nanowire array for long nanowires, while the percolation network formed by short nanowires is not sufficiently robust to prevent loss of electrical connectivity upon wire breakage further from this interface. Nanowires at higher doping concentrations were not found to improve cycling performance drastically, which we attribute to the dopant effects on the growth mechanism of the nanowires and placement of dopant atoms in the silicon matrix that may have inhibited lithium atom insertion. We will present novel electrode fabrication routes that overcome these two challenges.

11:20am **EN+NS-ThM11 In Situ TEM Electrochemistry of Anode Materials in Lithium Ion Batteries, J.Y. Huang**, Sandia National Laboratories **INVITED**

We created the first nano-battery inside a transmission electron microscope (TEM), allowing for real time atomic scale observations of battery charging and discharging processes. Two types of nano battery cells [1], one ionic liquid based, and the other all solid based, were created. The former consists of a single nanowire anode, an ionic liquid (IL) electrolyte and a bulk LiCoO_2 cathode; the latter uses Li_2O as a solid electrolyte and metal Li as anode. Four case studies will be presented: 1) Upon charging of SnO_2 nanowires in an IL cell, a reaction front propagates progressively along the nanowire, causing the nanowire to swell, elongate, and spiral. The reaction front contains high density of dislocations, which are continuously nucleated at the moving front and absorbed from behind. This dislocation cloud indicates large in-plane misfit stresses and is a structural precursor to electrochemically-driven solid-state amorphization. 2) In charging Si nanowires, the nanowires swell rather than elongate. We found the highly anisotropic volume expansion in lithiated Si nanowires, resulting in a dumbbell-shaped cross-section which developed due to plastic flow and necking instability. Driven by progressive charging, the stress concentration at the neck region led to cracking, eventually splitting the single nanowire into sub-wires. 3) Carbon coating not only increases rate performance but also alters the lithiation induced strain of SnO_2 nanowires. The SnO_2 nanowires coated with carbon were charged 10 times faster than the non-coated ones. Intriguingly, the radial expansion of the coated nanowires was completely suppressed, resulting in reduced tensile stress at the reaction front, as evidenced by the lack of formation of dislocations. 4) The lithiation process of individual Si nanoparticles was observed in real time in a TEM. A strong size dependent fracture behavior was discovered, *i.e.*, there exists a critical size with a diameter of ~ 150 nm, below which the particles neither cracked nor fractured upon lithiation, above which the particles first formed cracks and then fractured due to lithiation induced huge volume expansion. For very large particles with size over 900 nm, electrochemical lithiation induced explosion of Si particles was observed. This strong size-dependent fracture behavior is attributed to the competition between the elastic energy and the surface energy of the nanoparticles. These results highlight the importance of in-situ studies in understanding the fundamental sciences of lithium ion batteries.

1. J.Y. Huang *et al.*, **Science** 330, 1515-1520 (2010); **Nano Lett.** (revised); **ACS Nano** (in press).

Authors Index

Bold page numbers indicate the presenter

— A —

Abouimrane, A.: EN+NS-ThM3, 1
Acik, M.: EN+NS-ThM1, 1
Amatucci, G.: EN+NS-ThM2, 1
Amine, K.: EN+NS-ThM3, **1**

— B —

Bartynski, R.A.: EN+NS-ThM2, 1
Belharouak, I.: EN+NS-ThM3, 1
Bielawski, C.: EN+NS-ThM1, 1

— C —

Celik, O.: EN+NS-ThM2, 1
Chabal, Y.J.: EN+NS-ThM1, 1
Chakrapani, V.: EN+NS-ThM10, 1

— D —

Davidson, J.: EN+NS-ThM5, 1
Dreyer, D.R.: EN+NS-ThM1, **1**

— F —

Filler, M.A.: EN+NS-ThM10, 1

— H —

Huang, J.Y.: EN+NS-ThM11, **2**

— K —

Kohl, P.A.: EN+NS-ThM10, 1

— L —

Lu, J.: EN+NS-ThM3, 1

— P —

Pereira, N.: EN+NS-ThM2, 1
Petkovich, N.: EN+NS-ThM5, 1

— Q —

Qian, Y.: EN+NS-ThM5, 1

— R —

Rangan, S.: EN+NS-ThM2, 1
Rudisill, S.: EN+NS-ThM5, 1
Rusli, F.: EN+NS-ThM10, **1**

— S —

Stein, A.: EN+NS-ThM5, **1**

— T —

Thorpe, R.: EN+NS-ThM2, **1**

— V —

Venstrom, L.: EN+NS-ThM5, 1
Vu, A.: EN+NS-ThM5, 1

— W —

Wu, W.: EN+NS-ThM3, 1

— Z —

Zhang, Z.: EN+NS-ThM3, 1