

# Wednesday Morning, October 22, 2008

Energy Science and Technology Focus Topic

Room: 203 - Session EN+AS+EM+TF-WeM

## Electrochemical Storage

**Moderator:** S. Haile, Caltech, K. Thornton, University of Michigan

8:00am **EN+AS+EM+TF-WeM1 Molybdenum Oxide Nanoparticles for Improved Lithium Ion Battery Technologies**, *A.C. Dillon*, National Renewable Energy Lab., *S.-H. Lee*, University of Colorado, *Y.-H. Kim*, National Renewable Energy Lab., *R. Deshpande*, Lam Research, *P.A. Parilla*, *D.T. Gillaspie*, *E. Whitney*, National Renewable Energy Lab., *S.B. Zhang*, Rensselaer Polytechnic Institute, *A.H. Mahan*, National Renewable Energy Lab. **INVITED**

Lithium-ion batteries are current power sources of choice for portable electronics. Further improvement of performance and simultaneous reduction in cost could allow for the deployment in hybrid electric vehicles or plug-in hybrid electric vehicles (PHEVs). The development of PHEVs will enable reduced oil consumption in the transportation sector. Importantly, PHEVs will also enable increased use of intermittent renewable energy resources such as solar and wind. By charging PHEVs during peak solar generation times, the load on the grid is effectively "leveled", and the average output of coal-fired power plants will be decreased. Recent efforts for electric vehicle applications are focused on new anode materials with slightly more positive insertion voltages to minimize any risks of high-surface-area Li plating while charging at high rates, a major safety concern. The state-of-the-art anode is graphite with a reversible capacity of ~ 350 mAh/g and a potential of 0.1 V relative to lithium metal. Metal oxides have long been known as Li-insertion compounds and typically operate at higher potential than graphite. Unfortunately they suffer from poor kinetics and/or capacity fade with cycling, especially at higher rates. Hot-wire chemical vapor deposition has been employed as a scalable method for the deposition of crystalline metal oxide nanoparticles at high density. Under optimal synthesis conditions, only crystalline nanostructures with a smallest dimension of ~ 10 - 40 nm are observed. Anodes fabricated from crystalline MoO<sub>3</sub> nanoparticles display both an unprecedented reversible capacity of ~ 630 mAh/g and durable high rate capability. Porous thin film nanoparticle anodes, deposited by a simple electrophoresis technique, show no degradation in capacity for 150 cycles when cycled at high rate (C/2 corresponding to one discharge in 2 hrs.). Micron sized MoO<sub>3</sub> particles are shown to fail after several cycles, under the same conditions. Both x-ray diffraction and in situ Raman spectroscopy studies reveal that upon Li-ion insertion the crystalline nanoparticles become highly disordered. Density functional theory calculations elucidate the complex Li-ion insertion process and reveal a novel mechanism confirming the nanoscale, high-rate, reversible capacity despite the loss of structural order. The synthesis of these novel nanostructured materials and their potential for improving lithium-ion battery technologies will be discussed in detail.

8:40am **EN+AS+EM+TF-WeM3 Boron Oxynitride: An Emerging Dielectric for High Temperature Capacitor Applications**, *N. Badi*, *S. Vijayaraghavan*, *A. Bensaoula*, University of Houston, *A. Tempez*, *P. Chapon*, Horiba Jobin Yvon, France, *N. Tuccitto*, *A. Licciardello*, University of Catania, Italy

Among the many technical challenges encountered in the development of high temperature electronics, the role of a passive component like capacitor is very important. Dielectric integrity at temperatures greater than 250 °C has however, up till now, been one of the major impediments to bringing out a capacitor with suitable performance characteristics at these high temperatures. In this work, we investigate applicability of boron oxynitride (BO<sub>x</sub>N<sub>1-x</sub>) thin films to fabricate capacitors for high temperature applications. Deposited BO<sub>x</sub>N<sub>1-x</sub> layers by a filamentless ion source assisted physical vapor deposition technique show a high thermal stability up to 400 °C and a very high breakdown voltage (BDV) above 400 V/μm. BO<sub>x</sub>N<sub>1-x</sub> samples of thickness varying from 70nm - 200nm were grown in a high vacuum reactor. Prototype capacitors with boron oxynitride dielectric and titanium metal electrodes have been fabricated on 3" Si wafers followed by electrical and thermal characterization. Preliminary results indicate a very small variation (~3%) of capacitance over the frequency range of 10 KHz - 2 MHz and <10% variation in capacitance for the temperature range of 25 °C-400 °C. The device electrical characteristics studies (capacitance, leakage current, breakdown voltage), as a function of temperature and frequency for (BO<sub>x</sub>N<sub>1-x</sub>) dielectrics with varying oxygen to nitrogen ratio, are currently underway and their results will be presented at the conference.

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9:00am **EN+AS+EM+TF-WeM4 Improving Efficiencies of Electrochemical Systems Through Microstructure Optimization**, *H.Y. Chen*, University of Michigan, *J.R. Wilson*, *P.W. Voorhees*, Northwestern University, *S.B. Adler*, University of Washington, *S.A. Barnett*, Northwestern University, *K. Thornton*, University of Michigan

The properties and performance of a wide range of materials depend on their microstructures. This is especially true in multifunctional, multiphase or composite materials in which different phases perform different functions. Therefore, controlling microstructures in these materials is one of the main routes for materials design to achieve optimal performance. Various simulation methods that can be applied to examine processing, property, and degradation during operation, including the phase-field simulations and finite element modeling, will be discussed. Through coupling of simulations of microstructural evolution and transport that use realistic microstructures, microstructural design for optimized performance is investigated. Specific examples will include microstructures found in solid oxide fuel cell electrodes and those resulting from phase separation.

9:20am **EN+AS+EM+TF-WeM5 Layer-By-Layer Approaches to Electrochemical Energy and Storage**, *P.T. Hammond*, MIT **INVITED**

New advances in multilayer assembly have involved the development of ionically conductive multilayer thin films and the introduction of electrochemical functionality. These systems have allowed the formation of a range of ultrathin electrochemical devices including electrochromic displays, proton exchange membranes in fuel cells, and the use of these multilayers in other power and micropower devices. The use of this water based electrostatic assembly method has enabled the use of simple processing conditions, such as salt content and solution pH, to act as tools for the manipulation of ion and electron transport characteristics in the film, as well as the morphology of these unique nano-assemblies. Examples of this approach include the ability to integrate highly water soluble polymers with large sulfonic acid content into mechanically stable ultrathin films has led to new membranes with ionic conductivity approaching that of Nafion, and methanol permeability two orders lower, thus lowering fuel crossover and leading to large enhancements in methanol fuel cell performance with the application of nanometer thick thin films. On the other hand, the incorporation of both organic and inorganic nanoscale objects using the electrostatic assembly approach has enabled the incorporation of genetically engineering virus biotemplates in collaborations with the Belcher research group that have resulted in new developments in battery electrodes, and the integration of titania and other materials systems for reactive electrodes. Ultimately, the use of layer-by-layer systems have led to a range of organic and inorganic materials systems that have incorporated metal oxide nanoparticles, semiconducting carbon elements, and organic polymers to yield systems of interest for solar cells, capacitor/battery and electrochemical energy electrode and separator applications.

10:40am **EN+AS+EM+TF-WeM9 Material Solutions for Solid State Energy Storage**, *L.F. Nazar*, University of Waterloo, Canada **INVITED**

The increasing demand for energy world-wide and inherent pressing environmental needs, have jump-started efforts to develop energy storage systems that can be coupled to renewable sources, and/or viable energy conversion systems. Traditional electrode materials for lithium-ion storage cells are typically crystalline, single-phase layered structures such as metal oxides, and graphitic carbons. These materials power billions of portable electronic devices in today's society. However, large-scale, high-capacity storage devices capable of powering hybrid electric vehicles (HEV's) or their plug-in versions (PHEV's and EV's) have much more demanding requirements. This in turn, means that demands are on chemists to create novel materials, and address fundamental scientific issues relating to mass (ion) and electron transport at rapid rates. Recently, nanostructured solid state materials comprised of two more compositions, are being increasingly exploited. These can take the form of "surface modified nanocrystallites", or stuffed nanoporous materials. For example, we employ porous frameworks as electrically conductive scaffolds to encapsulate active electrode materials, where both components play a role in controlling the electrochemical performance. This presentation will provide an overview of how the nanostructured approach provides benefit over the bulk, using selected examples from a range of promising new solid state materials with targeted, and tuneable structures.

11:20am EN+AS+EM+TF-WeM11 **Platinum Nanorods as PEM Fuel Cell Electrodes**, *M. Gasda, R. Teki, T.-M. Lu, N. Koratkar, G. Eisman, D. Gall*, Rensselaer Polytechnic Institute

Platinum catalyst layers were deposited by magnetron sputtering from a variable deposition angle  $\alpha$  onto gas diffusion layer (GDL) substrates and were tested as cathode electrodes in polymer electrolyte membrane (PEM) fuel cells. Layers deposited at normal incidence ( $\alpha = 0^\circ$ ) are continuous, and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with  $\alpha = 85^\circ$  and continuously rotating substrates yields highly porous layers consisting of vertical Pt nanorods. At  $0.40 \text{ mg/cm}^2$  total Pt loading, the rods are 100-500 nm long and  $\sim 300$  nm wide, separated by 20-100 nm wide voids. The dramatic difference in microstructure is due to atomic shadowing during GLAD that causes Pt flux from highly oblique angles to preferentially deposit on surface protrusions, leading to nucleation and columnar growth on substrate mounds while surface depressions remain uncoated. Fuel cell testing at  $70^\circ\text{C}$  using Nafion 1135 membranes, Teflon-bonded Pt-black electrodes (TBPBE) at the anode, and atmospheric pressure hydrogen and air reactants shows a monotonic increase in performance of GLAD cathodes from  $0.05$  to  $0.40 \text{ mg/cm}^2$  total Pt loading. Nanorod cells exhibit approximately 2x higher mass activity than continuous layers at  $0.50\text{V}$  (corrected for iR, shorting, and gas crossover); for example, GLAD and continuous layers with approximately the same Pt loading ( $0.18$  and  $0.25 \text{ mg/cm}^2$ , respectively) show  $1.7$  and  $0.8 \text{ A/mg}$ . In contrast, at low current density of  $0.10 \text{ A/cm}^2$ , the continuous layers ( $0.70 \text{ V}$  with  $0.25 \text{ mg/cm}^2$  Pt) outperform GLAD cells even with relatively high Pt loadings ( $0.65 \text{ V}$  with  $0.40 \text{ mg/cm}^2$  Pt). The GLAD cells' higher mass-specific performance at high current densities is due to their high porosity which facilitates reactant transport, while the low-current performance of the continuous layer is attributed to a higher active Pt surface area. The sputter-deposited electrodes exhibit a higher platinum utilization in comparison to TBPBE reference cathodes, with GLAD cells ( $1.7 \text{ A/mg}$ ) performing better than TBPBE ( $0.75 \text{ A/mg}$ ) at high current densities ( $0.50 \text{ V}$ ), while continuous layers ( $0.07 \text{ A/mg}$ ) outperform TBPBE ( $0.035 \text{ A/mg}$ ) at  $0.80 \text{ V}$ . These results indicate the promise of nanoengineering to boost catalyst utilization in PEM fuel cells.

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