Thursday Afternoon, November 3, 2011

Energy Frontiers Focus Topic
Room: 103 - Session EN+NS-ThA

Nanostructures for Energy Storage and Fuel Cells II
Moderator: J. Lewis, RTI International

2:00pm EN+NS-ThA1 Charge-Storage Processes in Model MnO$_2$-Li-HOPG Systems: UHV-STM Investigations, *S.C. Bharath*, *W. Song, J.E. Reutt-Robey,* University of Maryland, College Park*, K.R. Zavadil*, Sandia National Laboratories

Nanostructured materials have the potential to substantially improve the speed, efficiency, and cyclic lifetime of energy storage systems such as the lithium-ion battery (LIB). Nanometer-scale oxide cathodes elements allow for greater extent of lithium incorporation due to improved strain accommodation relative to conventional cathode structures. Exposed surface facets in structures with high surface/volume ratio will act as gateways to lithium insertion, playing an important kinetic role in charge storage. However, detailed mechanisms of lithium insertion and their dependence on oxide facet orientation and grain size and shape are largely unknown. As a platform for fundamental investigations of charge-transfer processes in nanocrystalline materials, we have developed a MnO$_2$-Li-HOPG model system. This system consists of low-dimensional β-MnO$_2$ and cubic spinel Li$_{1+x}$Mn$_{2-x}$O$_4$ nanocrystallites, synthesized by the reactive co-deposition of elemental Mn and molecular oxygen on native and modified graphite (C(0001)) supports under ultrahigh vacuum conditions. Nanocrystallite phase and composition has been confirmed using single particle electron diffraction, as well as TOF-SIMS and scanning AES. Morphology of individual nanocrystallites, and their registration to the C(0001) support, have been determined with ambient AFM and UHV STM methods. The morphological response of β-MnO$_2$ nanocrystallites to Li$^+$ insertion has been preliminarily explored under solid-state conditions with UHV-STM. The sensitivity of these methods are currently limited by low β-MnO$_2$ – C(0001) electrical conductivity, and efforts to overcome this limitation will be described. Additionally, alkali seeded growth of MnO$_2$ nanocrystals will be presented as a means to guide the formation of alternative MnO$_2$ polymorphs.

2:20pm EN+NS-ThA2 The Influence of Surface Chemistry as a Function of Salt Composition on the Rate Capability of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ Composite Electrodes for Li-ion Rechargeable Batteries as Investigated using XPS, *R.A. Quinlan*, Naval Surface Warfare Center, Carderock Division*, Y.C. Lu,* Massachusetts Institute of Technology*, A.N. Mansour*, Naval Surface Warfare Center, Carderock Division*, Y. Shao-Horn*, Massachusetts Institute of Technology

LiCoO$_2$ is currently the most commonly used cathode material in commercial Li-ion battery technology because of its high working voltage, structural stability and long cycle life. However, cobalt is expensive and there are safety and toxicity concerns. Therefore, there has been a considerable amount of work on developing cheaper alternatives for the positive electrode of large-scale lithium ion batteries. LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (LNMO) has emerged as one of the best options due to its high specific capacity, thermal stability and low material costs. Previous studies have illustrated that decreasing the interlayer mixing can increase the rate capability and that increasing the heat-treatment temperature can also increase the rate capability. Recently, the influence that surface chemistry has on the rate capability of LNMO composite electrodes was investigated and it was shown that an additional annealing treatment after quenching the material during synthesis increased the device performance from 50 mAh/g to 180 mAh/g at 55°C and 8C. Via an inspection using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), it was shown that the annealing treatment did not result in significant changes in the lattice parameters or in the cation distributions of the layered structure. However, the annealing treatment was shown to be responsible for removing surface impurity phases such as lithium carbonate species and Mn^{3+}-containing species, which was associated with the observed increase in performance.

In this study, we further investigate the role that surface chemistry, as developed during the operation of the cell, has on the device performance. LNMO electrodes were constructed using quenched and annealed LNMO starting material. Both the quenched and annealed electrodes were cycled in the range of 2.0 V – 4.6 V in 1M LiPF$_6$/EC:DMC (1:1) or 1M LiClO$_4$/EC:DMC (1:1). The composite electrodes (in the discharged state) were disassembled in an Ar environment glove box and transported to the XPS analysis chamber without exposure to ambient. Cycling performance shows enhanced capacity retention and device performance for annealed electrodes cycled in LiPF$_6$, with the little to no enhancement observed for annealed electrodes when cycled in LiClO$_4$. Our initial analysis indicates the formation of both Ni and Mn fluorides/oxyfluoride species on the surface of electrodes cycled in LiPF$_6$. Additional changes in the surface chemistry and the influence on the rate capability will be discussed.

2:40pm EN+NS-ThA3 Hydrogen Storage in Metal Organic Frameworks (MOFs), *N. Nijem*, University of Texas at Dallas*, L. Kong, H. Wu, Y. Zhao, J. Li, D.C. Langreth,* Rutgers University*, Y.J. Chabal*, University of Texas at Dallas

Hydrogen storage is one of the most challenging problems in hydrogen-based energy technologies. One of the goals of hydrogen storage is the ability to store a high volumetric density of hydrogen at room temperature. As a result, studies exploring molecular hydrogen interaction in storage materials are important to facilitate further development of materials. Metal-organic Frameworks (MOFs) are promising candidates for hydrogen storage because their high surface area and porosity facilitate high hydrogen physisorption on specific sites of the structures and because many options are possible to enhance the interaction of molecular hydrogen with the host.

This work explores the incorporation of hydrogen into MOFs using infrared (IR) absorption spectroscopy to characterize its interaction. IR spectroscopy can distinguish possible H$_2$ binding sites based on the perturbation of the internal H$_2$ stretch mode. IR measurements are performed on saturated metal center MOFs varying the ligand and/or the metal center and on unsaturated metal center MOF-74-M (M=Zn, Mg and Ni). We combine room temperature, high pressure with low temperature (20-100K) measurements and theoretical van der Waals density functional (vdW-DF) calculations to derive quantitative information from IR shifts and dipole moment strengths.

Our results show that, in contrast to the current understanding, IR shifts are independent of binding energies and depend instead on the chemical environment of the molecule, including effects such as H$_2$-H$_2$ interactions. For example, we see little difference in IR shifts between saturated MOFs with low binding energy (~4kJ/mol), and unsaturated MOFs with higher binding energy (~10kJ/mol) sites at room temperature. Furthermore, we show that dipole moments of adsorbed H$_2$ depends greatly on parameters such as geometry of adsorption site and H$_2$-H$_2$ interactions. Measurements performed at low temperatures on MOF-74 show that IR shifts of H$_2$ is greatly red shifted (an additional ~-30 cm^{-1}) due to H$_2$-H$_2$ interactions on close proximity adsorption sites, and that dipole moments of adsorbed H$_2$ can appreciably vary with loading.

Our analysis indicate that the intensity of H$_2$ IR band cannot always be a measure of the amount of adsorbed H$_2$, therefore methods such as variable temperature IR (VTIR) used to deduce binding energies cannot always be implemented.

3:00pm EN+NS-ThA4 Nanostructure Engineering and Modeling of 3D Electrostatic Nanocapacitors, *L.C. Haspert*, *G.W. Rubloff, S.B. Lee*, University of Maryland, College Park

Increasing energy demands require innovative nanofabrication techniques for efficiently storing and supplying available energy. This talk discusses how anodic aluminum oxide (AAO) and atomic layer deposition (ALD) technologies are implemented and designed for creating high performance nanoelectrostatic metal-insulator-metal (MIM) capacitors. The densely porous (~10^{10}pores/cm^2) self-aligned, self-assembled AAO nanostructure serves as a complex nanostructured template in which the self-limiting and conformal ALD process can uniformly coat this complex 3D structure. Thus, combining these two technologies results is a nano-capacitor with high power density and increased energy density, comparable to electrochemical batteries.

AAO template fabrication is a two-step anodization process, in which pores self-order in the first anodization. Then, the oxide is removed, leaving in a pre-patterned scalloped Al surface. Peak asperities are rounded with a barrier anodic alumina (BAA) and the rounded structures are retained during the subsequent anodization. Mild anodization (MA) chemistries provide interpore spacings, D$_{int}$ (in nm), equal to 2.5x the anodization voltage, V$_{anod}$ (in V), whereas hard anodization chemistries provide D$_{int}$~2xV$_{anod}$. In this work, oxalic acid MA results in pores spaced 100nm apart and 40nm in diameter. A final step etches pore sidewalls, increasing pore diameters up to 85nm. MIM layers are deposited by sequentially depositing 10nm of Al-doped ZnO (AZO), 8nm of Al$_2$O$_3$ and ~100nm AZO.

The porous structure increases the available surface area on which charge is stored, thus increasing the energy density since $E=\frac{1}{2}CV^2$. The capacitance increases with increasing depth, where planar, 1µm, 1.5µm and 2µm pore depth have capacitance of ~1, 11, 19 and 26µF/cm², respectively. Introducing the BAA reduces leakage currents to ~10^{-10}A/cm² and breakdown fields are increased to 9.3MV/cm. A model simulates performance of the 3D nanogeometry, distributed resistances and dielectric capacitances, and internal non-linear resistance of the capacitor as a function of voltage. Additionally, trade-offs between pore size vs. layer thickness, AAO template interpore spacings vs. capacitance, pore depth vs. electrode series resistance are considered.

The ability to create scalable nano-structured devices is highly desirable for integrating with energy harvesting technologies. The fully self-aligned, self-assembled and self-limiting MIM nanocapacitors fabricated with ALD deposition in AAO templates demonstrate excellent electrical performance. Simulating device performance will aid in further increasing device performance and energy densities.

3:40pm EN+NS-ThA6 Atomic Scale Engineering for Energy Conversion Efficiency, *F. Prinz, N.P. Dasgupta, C.-C. Chao*, Stanford University **INVITED**
The benefits of utilizing nanoscale materials include high surface to volume ratios, short transport lengths, tunable optical and electronic properties, and the ability to take advantage of quantum mechanical effects in low-dimensional structures. Simple scaling laws indicate how nano scale structures may help improving energy conversion efficiency.

Our group has been focusing on two primary application areas of ALD for energy conversion: fuel cells and photovoltaics. In the area of fuel cells, ALD presents several opportunities for reducing efficiency losses. By fabricating oxide-ion conducting electrolyte materials with thicknesses below 100nm which are pinhole free, we have been able to minimize ohmic losses due to ionic transport, allowing for a reduction in the operating temperature of solid oxide fuel cells (SOFCs)[1]. Furthermore, by fabricating 3-D fuel cell architectures[2] and modifying the surface of the electrolyte with a thin ALD layer[3], we have been able to reduce activation overpotentials in these cells and increase power density.

In the field of solar cells, we have been applying ALD to build quantum confinement structures for bandgap engineering. ALD of PbS thin films was performed, and measurements of the localized density of states (DOS) show the ability to tune the bandgap simply by controlling the number of ALD cycles[4]. We have demonstrated a new technique to directly fabricate quantum dots (QDs) during the initial nucleation cycles of ALD PbS[5]. These QDs were deposited directly on nanowire surfaces, suggesting the ability to combine light trapping in nanostructured templates with quantum confinement effects.

[1] J. H. Shim, C.-C. Chao, H. Huang and F. B. Prinz, *Chem. Mater.* **19**, 3850 (2007).

[2] P.-C. Su, C.-C Chao, J. H. Shim, R. Fasching and F. B. Prinz, *Nano Lett.* **8**, 2289 (2009).

[3] C.-C. Chao, Y. B. Kim and F. B. Prinz, *Nano Lett.* **9**, 3626 (2009).

[4] N. P. Dasgupta, W. Lee and F. B. Prinz, *Chem. Mater.* **21**, 3973 (2009).

[5] N. P. Dasgupta, H. J. Jung, O. Trejo, M. T. McDowell, A. Hryciw, M. Brongersma, R. Sinclair and F. B. Prinz, *Nano Lett.* **11**, 934 (2011).

4:20pm EN+NS-ThA8 Nanoscale Characterization of Water Distributions in PEM Fuel Cell Membrane Electrode Assemblies Measured by Scanning Transmission Soft X-ray Microscopy, *A.P. Hitchcock, V. Berejnov*, McMaster University, Canada, *D. Susac, J. Stumper*, Automotive Fuel Cell Cooperation Co, Canada
Successful water management in proton exchange membrane (PEM) fuel cells requires a delicate balance of fuel, oxidant and water transport through a variety of length scales from ~ 1 mm in fuel channels, through ~10-100 mm in the gas diffusion media, to 1-10 nm in the catalyst layer. The combination of a high degree of porosity in the reaction zone, complex composition, heterogeneous wetting properties, and the presence of water in two phases (gas, liquid) makes optimization of the performance of PEM fuel cell challenging. We are studying water distributions *in situ* in thin sections of membrane electrode assemblies (MEA) equilibrated with water vapor under feed-back controlled relative humidity conditions using scanning transmission X-ray microscopy (STXM). The intrinsic soft X-ray absorbance properties of the constituent materials allows direct *in-situ* visualization of water uptake into MEAs and the differentiation and mapping of the gaseous and liquid/sorbed water. The method provides maps of liquid and gaseous water distributed over the catalyst layer, with coincident maps of the ionomer and carbon support in the catalyst layer, as well as the polymer electrolyte membrane. Condensation at specific sites is observed when the relative humidity at the MEA is higher than ~80%.

4:40pm EN+NS-ThA9 Optimization of the Delta Phase in Bismuth Oxide Thin Films, *P. Silva-Bermudez, O. García-Zarco*, Universidad Nacional Autónoma de México, *E. Camps, L. Escobar-Alarcón*, Instituto Nacional de Investigaciones Nucleares, México, *S.E. Rodil*, Universidad Nacional Autónoma de México
Bismuth oxide Bi_2O_3 has interesting technological applications, which have not been largely used due to the particular polymorphism of the material. Bismuth Oxide has five polymorphic forms: α, β, γ, δ and ω -Bi_2O_3. Among them, the low-temperature α and the high-temperature δ phases are stable and the others are metastable phases, as has been established by bulk solid-state studies. Each polymorph possesses different crystalline structures and various electrical, optical and mechanical properties. The face-centered cubic δ -Bi_2O_3 is stable over a narrow temperature range 729–825 °C (melting point) and it has the peculiarity of being among the few materials presenting high ionic conductivity at moderate temperatures (600-700°C). In this research, we aim to obtain δ -Bi_2O_3 thin films as possible ionic conductors for the development of micro solid state fuel cells. However, the first challenge is to find the deposition conditions of the magnetron sputtering system to ensure the formation of the desired δ -Bi_2O_3, which is only thermodynamically stable at high temperatures. Based on previous results of Fan et al. (Fan 2006), we choose as the deposition variables the substrate temperature (room temperature to 300 °C) and the power (100-200 W). Our target was pure Bi_2O_3, but the first results indicated that it was necessary to compensate oxygen losses; therefore the atmosphere was a mixture of Argon and Oxygen, where the Oxygen flow was 20% of the total. The results from the different characterization techniques suggested that substrate temperatures between 150 and 200°C are appropriate to obtain the δ -Bi_2O_3 phase at a high deposition rate, between 1.5 to 2 nm/s. X-ray diffraction (XRD) as a single technique to identify the film crystalline structure demonstrated to be rather difficult, since there is a large overlapping between the diffraction peaks corresponding to the α, β, γ and δ phases. However, we showed that by combining XRD and Raman spectroscopy, it was possible to clearly prove the presence of the δ-phase. The explanation for the stabilization of the high temperature phase might be related to the 2-dimensional confinement and/or then effect of the small crystalline size. The physical properties of the δ -Bi_2O_3 thin films were further investigated; optical properties by transmission spectroscopy and ellipsometric spectroscopy in the ultraviolet-visible range, surface resistivity by the four-points method, composition by X-ray photoelectron spectroscopy and X-ray energy dispersion.

Fan H. T, et al. Thin Solid Films 513 (2006) 142.

5:00pm EN+NS-ThA10 Probing Physical and Interfacial Confinement Effects on Multilayered Piezoelectric Polymeric Films using Second Harmonic Generation Laser Spectroscopy, *J. Jones*, Fisk University, *H. Park*, Vanderbilt University, *L. Zhu*, Case Western Reserve University, *N.H. Tolk*, Vanderbilt University, *R. Mu*, Fisk University
Piezoelectric materials may arguably be the most functional, versatile and widely used materials with a wide range of applications including mechanical sensors, actuators, energy storage and energy harvesting devices. The well established applications are largely based on inorganic piezoelectric materials. The successful employment of polymeric piezoelectric materials, such as polyvinylidene fluoride (PVDF) and its related co-polymers, although light weight, flexible, optically transparent and cost effective, are limited by relatively low piezoelectric coefficients, thermal stability, and durability. The focus of the group is to develop a multilayered piezoelectric PVDF system for improved energy harvesting and energy storage efficiency. These systems are fabricated using enabling technology in co-extrusion which allows more cost effective and large area device production as opposed to more conventional layer-by-layer techniques. Many efforts have been made by the team to fabricate these micro- and nano-layered systems resulting in much improved device performance. A three-time improvement of capacitive electrical energy density has been demonstrated. The focus of this research is to understand the physics of why these multilayered systems perform better than a single layer by developing a characterization technique using both confocal second harmonic generation (SHG) and electric field induced second harmonic (EFISH) laser spectroscopy. Our results have shown that SHG is a very sensitive, non-destructive and versatile technique that can be used to study the piezoelectric and structural properties of layered systems. When combined with EFISH this technique allows the interrogation of electrical properties within the individual layers and at the interfaces between the layers. Further, the proposed techniques can be readily employed *in-situ*

which can provide information in real time during sample processing with static and time-resolved spectroscopic measurements.

5:20pm **EN+NS-ThA11 Electrical Transport in Ultrathin Ruthenium Films formed by Atomic Layer Deposition**, *K.E. Gregorczyk, P. Banerjee, G.W. Rubloff*, University of Maryland, College Park

Next generation nanostructured devices require ultrathin layers of different materials (e.g. current collectors found in solar cells, batteries, and charge storage and memory devices, etc.). However, in the ultrathin regime, expectations from bulk resistivity can be misleading in designing such nanostructures. Here, we show the example of ultrathin (5-24nm) Ru films produced by atomic layer deposition (ALD), where resistivity is dramatically increased: at 5nm resistivity is ~7X higher (~135 μΩ cm) than at 24nm (~20 μΩ cm) and ~18X higher than bulk Ru (7.4 μΩ cm). The drastic differences seen here are explained through Mayadas-Shatzkes (MS) theory, which defines the increase in resistivity through geometrical constraints (e.g. film thickness and grain boundaries). Using MS theory the grain boundary reflection coefficients were calculated as ~0.32 for an 18nm thick film and ~0.66 for a 5nm film. Furthermore, the electrical transport properties of these films were studied as a function of both temperature (80-340K) and film thickness (5-24 nm). Finally, we show that the ALD Ru films are p-type, in agreement with the theory of compensated metals, and report both the temperature coefficient of resistivity and charge carrier mobility as a function of film thickness.

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