

# Tuesday Afternoon, October 19, 2010

Energy Frontiers Topical Conference  
Room: Mesilla - Session EN+EM-TuA

Electronic Materials for Energy Conversion & Storage  
Moderator: G.W. Rubloff, University of Maryland

2:00pm **EN+EM-TuA1 High-capacity and High-rate Metal Oxide Anodes for Li-ion Batteries**, A.C. Dillon, C. Ban, National Renewable Energy Laboratory, L.A. Riley, A.S. Cavanagh, S.M. George, University of Colorado, Y.S. Jung, Z. Wu, Y. Yan, National Renewable Energy Laboratory, S.-H. Lee, University of Colorado **INVITED**

Significant advances in both energy density and rate capability for Li-ion batteries will be necessary for implementation in next generation electric vehicles. By employing metal oxide nanostructures, it is possible to achieve Li-ion anodes that have significantly higher capacity than the state-of-the-art graphite technology. For example we have demonstrated that thin film MoO<sub>3</sub> nanoparticle electrodes (~2 μm thick) have a stable reversible capacity of ~630 mAh/g when tested at C/2.<sup>1</sup> By fabricating more conventional electrodes (~35 μm) with a conductive additive and binder, an improved reversible capacity of ~1000 mAh/g is achieved.<sup>2</sup> The increased capacity for the MoO<sub>3</sub> coin cell electrode compared to the thin film electrode may be attributed to improved electronic/ionic mobility with the conductive additive and more complete access to the nanostructures. We have also demonstrated that by applying a thin atomic layer deposition coating of Al<sub>2</sub>O<sub>3</sub>, improved rate capability for the high volume expansion MoO<sub>3</sub> is achieved for thick more conventional electrodes.<sup>3</sup>

More recently we have focused our work on iron oxide nanostructures, as iron is an inexpensive, abundant and a non-toxic material. Furthermore, we have synthesized binder-free, high-rate capability electrodes. The electrodes contain Fe<sub>3</sub>O<sub>4</sub> nanorods as the active lithium storage material and carbon single-wall nanotubes (SWNTs) as the conductive additive. The highest reversible capacity is obtained using 5 wt.% SWNTs, reaching 1000 mAh/g (~2000 mAh/cm<sup>2</sup>) at C rate when coupled with a lithium metal electrode, and this high capacity is sustained over 100 cycles. Furthermore, the electrodes exhibit high-rate capability and stable capacities of 800 mAh/g at 5C and ~600 mAh/g at 10C. Scanning electron microscopy indicates that this high-rate capability is achieved because Fe<sub>3</sub>O<sub>4</sub> nanorods are uniformly suspended in a conductive matrix of SWNTs. Raman spectroscopy is employed to understand how the SWNTs function as a highly flexible conductive additive. We expect that this method can be used to achieve other binder-free anodes as well as cathodes with similar high-rate capability.<sup>4</sup>

(1) Lee, S.-H.; Kim, Y.-H.; Deshpande, R.; Parilla, P. A.; Whitney, E.; Gillaspie, D. T.; Jones, K. M.; Mahan, A. H.; Zhang, S. B.; Dillon, A. C. *Adv. Mat.* 2008, 20, 3627-3632.

(2) Riley, L. A.; Lee, S.-H.; Gedvilas, L.; Dillon, A. C. *Journal of Power Sources* 2010, 195, 588-592.

(3) Riley, L. A.; Cavanagh, A. S.; George, S. M.; Jung, Y.-S.; Yan, Y.; Lee, S.-H.; Dillon, A. C. *ChemPhysChem* 2010, *in press*.

(4) Ban, C.; Wu, Z.; Gillaspie, D. T.; Chen, L.; Yan, Y.; Blackburn, J. L.; Dillon, A. C. *Advanced Materials* 2010, *in press*.

2:40pm **EN+EM-TuA3 Engineering Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O Thin Films as a Solid Electrolyte for 3D Microbatteries**, Y.-C. Perng, J. Cho, D. Membreno, B. Dunn, J.P. Chang, UCLA

The development of secondary lithium-ion batteries has been directed primarily at portable electronics applications. However, these batteries also have the potential to function as a power source for micro-systems through engineering of electrodes into 3D architectures based on high aspect ratio pillars. In order to utilize this potential, an ultra-thin and highly conformal solid electrolyte layer is required to coat the 3D electrode array. The solid electrolyte lithium aluminosilicate (LiAlSiO<sub>4</sub>), is a promising candidate for this application due to high ionic conductivity along its c-axis resulting from channels formed by the alternating tetrahedra of aluminum-oxygen (Al-O) and silicon-oxygen (Si-O). The length of c-axis of lithium aluminosilicate can be adjusted by changing the crystallization temperature for desired conductivity characteristics.

Atomic layer deposition (ALD) was employed in this work to synthesize thin film lithium aluminosilicate. The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating suitable in 3D micro-battery applications. The metal precursors used in this work are tetraethyl orthosilicate (TEOS), trimethylaluminum (TMA) and lithium t-butoxide (LTB). We also investigated the use of tri-t-butoxy-

hydroaluminat (LTBA) but found that the metal composition was difficult to control and high carbon contents. Using the three precursors mentioned above with water vapor as the oxidant, we deposited SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O, at deposition rates in the range of 0.8~2 Å/cycle. The overall deposition rate of stoichiometric LiAlSiO<sub>4</sub> was ~5 Å/cycle using a chamber base pressure of 10<sup>-2</sup> Torr and substrate temperature of 300°C. The concentration of each metal element in Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O thin films is found to correlate closely to ALD cycles and the associated incubation times. The crystalline structures as well as the local environment of the Li-conducting channels are also affected by the ALD cycles and sequences, as indicated by ultraviolet photoelectron spectroscopy (UPS), transmission electron microscopy (TEM) imaging and nuclear magnetic resonance (NMR) analyses. The Li-ion conductivities of ALD Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O thin films were determined by impedance measurements using a four-point probe setup with contacts made to the film surface. The films have high ion conductivity and low electronic conductivity, the values of which are strongly influenced by the lithium content and distribution in the synthesized thin films.

3:00pm **EN+EM-TuA4 Laser-Deposition and Characterization of Amorphous Thermoelectric Films**, G.B. Wilks, Air Force Research Laboratory, P.T. Murray, University of Dayton, S.B. Fairchild, N.W. Gothard, J.E. Spowart, Air Force Research Laboratory

From the Efficient Cluster Packing model describing the topology of metallic glasses, it is understood that certain compositions are favored for glass-formability based on the ratio of atomic sizes between constituents. In this regard, the half-Heusler composition Zr<sub>0.5</sub>Hf<sub>0.5</sub>NiSn is nearly ideal. Although the crystallized form of this material has been widely studied because of its high thermoelectric power factor, it has been suggested that partial vitrification may enhance the thermoelectric figure of merit by preserving the favorable aspects of electronic structure while significantly disrupting thermal transport. Capitalizing on the high quench rates possible during pulsed laser deposition, a spectrum of thin films including amorphous and partially-amorphous duplex microstructures has been grown under various conditions. Transport characteristics relevant to the thermoelectric effect are rationalized in light of accompanying microstructure characterization.

4:00pm **EN+EM-TuA7 Probing Charge Transport in Exploratory Nanocrystal-Based Devices**, P. Nagpal, V.I. Klimov, Los Alamos National Laboratory **INVITED**

Colloidally synthesized semiconductor nanocrystals offer the exciting opportunity to exploit unique physical properties, such as size tunable band gap, in low-cost, solution-processed thin film devices. However, charge transport in as-deposited thin films of colloidal nanocrystals is hindered by organic ligands. At the Center for Advanced Solar Photophysics (CASP), a DOE Energy Frontier Research Center, we are investigating the mechanism of charge transport in nanocrystal films by employing them in a range of simple device architectures, with the goal of optimizing them for photovoltaic application. As an example, I will present recent work in nanocrystal-based optical field effect transistors specifically designed to study electron transport and the dynamics of the photogenerated carriers in these semiconductor thin films. These devices offer invaluable information regarding field dependant mobility, optical gating and changes in the Fermi-level at the nanocrystal film interface. I will then discuss other exploratory device efforts at CASP, and how the information generated will be used collectively for the development of solar cells and other energy-related applications.

4:40pm **EN+EM-TuA9 Investigation of GaTIP for Use in Multijunction Photovoltaics**, C. Downs, T. Vandervelde, Tufts University

To achieve the highest possible conversion efficiencies in multijunction photovoltaics, the individual layers of the device must both be lattice-matched and have optimal band-gap spacing. Lattice-matched or strain-compensated epitaxy is required for the growth of junctions thick enough to elicit high quantum efficiency. Ideally, for spectral matching, one would have an infinite number of junctions that are current-matched; however, fabrication of a large number of junctions is neither easy nor desirable because of problems that arise from series resistance. In the end, it becomes a balancing act where the optimal number of junctions for a high efficiency concentrator cell is 3-6 junctions, with the conversion efficiency directly linked to how well spacing of the band gaps of the cell are optimized for absorption of the solar spectrum. Unfortunately, many of the optimal lower band-gaps for these multijunction cells do not occur in the dominant materials system (i.e. Ge and mixtures of In, Ga, Al, As, and P). As such, of late there has been a strong push to characterize new materials in hopes of providing more design options for photovoltaic cells. GaTIP is one such material, theorized to be useful as one of the lower junctions of 3+-junction

cells while still being lattice-matched to GaAs and Ge. In this research, the change in lattice constant and band gap of GaTIP with varying compositions are investigated first by computational simulation and then with physical devices. New efficiency records should be achievable by incorporating these new optimal junction materials into the design for multijunction cells. This development will help solar concentrator cells achieve grid parity, thereby becoming a viable renewable energy choice.

5:00pm **EN+EM-TuA10 Photo Induced Ferroelectric Properties of  $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}$  Thin Films**, *H.V. Nampoori, S. Kotru*, University of Alabama

Thin films of lanthanum doped lead zirconate titanate (PLZT) have gained attention due to the large photostrictive response, and their possible use for contact less actuators and sensors. Variation in composition and doping are known to influence the photostrictive responses as well as ferroelectric behavior of these materials. PLZT is also a potential material for photovoltaic devices due to its high electro-optic coefficient and optical transparency.

In this work, thin films of  $\text{Pb}_{0.95}\text{La}_{0.05}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$  (PLZT) were prepared using Metal-Organic Decomposition technique (MOD). The films are deposited by spin coating. Sputter deposited Pt electrodes serve as top contacts for the films. Thickness of the grown films varied from 70-350 nm and the growth temperature was chosen in the range of 550-700°C. Details of the film growth process including effects of temperature, thickness and annealing, and electrical and optical characterization will be presented. In addition parameters which affect the electrical properties like ferroelectric hysteresis and leakage behavior mechanisms will be discussed. The photo induced effects on the ferroelectric and the leakage properties, giving insight to the photovoltaic properties of ferroelectric thin films would be presented

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