

Tuesday Afternoon, October 20, 2015

Energy Frontiers Focus Topic

Room: 211B - Session EN+EM+NS+SE+SS+TF-TuA

Batteries and Supercapacitors

Moderator: Elijah Thimsen, Washington University, St. Louis, Andrew C. Kummel, University of California at San Diego

2:20pm **EN+EM+NS+SE+SS+TF-TuA1 Behavior of Layered Cathode Materials: A Route to Higher Energy Density for Li-Ion Batteries.** *Marca Doeff, F. Lin*, Lawrence Berkeley National Laboratory, *I. Markus*, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

The most promising cathode materials for Li-ion batteries geared towards vehicular applications are the so-called NMCs ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$), based on cost and performance considerations. NMCs exhibit a slightly sloping voltage profile in lithium half-cells, with typical utilizations significantly lower than the theoretical capacity of about 280 mAh/g. An attractive strategy for increasing the energy densities of devices meant for traction applications would be to cycle NMCs to a higher potential than is currently used (usually about 4.3V vs. Li^+/Li) so that more lithium can be extracted and cycled. For this approach to be viable, the cathodes must exhibit excellent structural stability and good reversibility over a wide composition range. Our recent work has been directed towards understanding the high-potential behavior of NMCs, using an array of synchrotron x-ray techniques as well as transmission electron microscopy. These techniques show that surface reconstruction to rock salt and spinel phases occur during high voltage cycling, and result in impedance rises and apparent capacity losses. The degree to which this occurs is a function of how the material is made and its electrochemical history. Partial substitution of Ti for Co in NMCs not only increases the capacities obtained during cycling to 4.7V in lithium half-cells compared to baseline materials, but appears to improve the cycling behavior as well. First principles calculations show that the aliovalent substitution lowers the voltage profile slightly. This allows a greater amount of lithium to be extracted and cycled below 4.7V, resulting in higher practical capacities. The Ti-substitution also delays the formation of rock salt during charging, resulting in better capacity retention. These observations suggest that optimizing the synthesis and judicious substitution can mitigate deleterious structural changes of the NMCs due to high potential operation in Li-ion cells. These strategies should be combined with those designed to prevent side reactions with electrolytic solutions during high potential operation, such as new electrolytic solutions with improved oxidative stability, or atomic layer deposition coatings on electrode surfaces, to further ensure stable cycling.

3:00pm **EN+EM+NS+SE+SS+TF-TuA3 Next-Generation Electrolytes for Lithium-Ion Batteries.** *Sarah Guillot*, University of Wisconsin - Madison, *M. Usrey, A. Pena-Hueso*, Silatronix, Inc., *R.J. Hamers*, University of Wisconsin-Madison and Silatronix, Inc.

Current-generation electrolytes for lithium-ion batteries are limited in electrochemical stability and thermal stability. Over the last several years, researchers at University of Wisconsin and at Silatronix, inc. have developed several new generations of electrolytes based upon incorporation of organosilane groups into the molecular structure. A recently developed class of compounds shows unprecedented enhancements in performance, including the ability to cycle full cells over 400 times at 70 degrees C, and the ability to reduce or eliminate "gassing" at cathode surfaces. In this talk we will discuss the molecular structure of these organosilane-based compounds, quantitative measurements of the decomposition pathways, and the resulting mechanistic insights into the molecular properties that gives rise to their outstanding performance characteristics.

3:20pm **EN+EM+NS+SE+SS+TF-TuA4 Physico-Chemical Properties of Polyamidoamine Dendrimer-Based Binders for Carbon Cathodes in Lithium-Sulfur Batteries.** *Manjula Nandasiri, P. Bhattacharya, A. Schwarz, D. Lu*, Pacific Northwest National Laboratory, *D.A. Tomalia*, NanoSynthons LLC, *W.A. Henderson, J. Xiao*, Pacific Northwest National Laboratory

Lithium-sulfur (Li-S) batteries are one of the most promising energy storage systems, offering up to five-fold increase in energy density as compared with state-of-the-art lithium-ion batteries to meet the growing demand for environmentally benign energy storage devices with high energy density, low cost, and long life time. For practical applications, high sulfur (active material) loading ($> 2 \text{ mg/cm}^2$) within the carbon cathode in Li-S batteries is essential. Most reports on engineered cathode materials for Li-S batteries are based upon low sulfur loadings (typically $\sim 1 \text{ mg/cm}^2$), which are

impractical and often give misleading results. It is unknown how these novel engineered cathodes behave under high sulfur loading conditions. The binder is perhaps the most critical material in achieving a high sulfur loading in carbon cathodes. We have recently used dendrimers with various surface chemistries as functional binders in Li-S cells with SuperP-carbon/S as the cathode material. Even without engineering the cathode, very favorable cycling stability and electrolyte wetting were obtained with these binders. It was attributed to the high density of surface functional groups on the dendrimers, high curvature of the binder and its porosity, and the interactions between the large number of basic nitrogen and oxygen atoms on the dendrimers and lithium polysulfides.

Here, we will discuss the fundamental properties of dendrimers as aqueous binders for Li-S battery cathodes and compare their performance with other aqueous, commonly used linear polymeric binders such as styrene butadiene rubber (SBR) and sodium carboxyl methyl cellulose (CMC). Specifically, generation 4 polyamidoamine (PAMAM) dendrimers with hydroxyl (OH), 3-carbomethoxypropylidone (CMP), and sodium carboxylate (COONa) surface functional groups served as good, electrochemically stable binders at high S loadings ($\sim 3\text{-}5 \text{ mg/cm}^2$) with high initial capacities ($> 1000 \text{ mAh/g}$). In comparison to CMC-SBR binder-based electrodes which failed at high C-rates (0.2C) after 40 cycles, dendrimer-based binders showed a capacity retention of $>85\%$ for more than 100 cycles. It was also observed that acidic groups and all- NH_2 surface groups are poor binders, whereas binders with COO^- and neutral surface groups (OH, CH_3) show better performance. X-ray photoelectron spectroscopy was used to identify different surface functional groups in these dendrimers and understand their interactions with SuperP-carbon/S cathode. In addition, a detailed physico-chemical characterization using IR spectroscopy and XANES/EXAFS will be presented to substantiate the superior dendrimer-carbon/S interactions.

4:20pm **EN+EM+NS+SE+SS+TF-TuA7 The Road beyond Lithium Batteries is Paved — In Three Dimensions — With Rechargeable, Dendrite-Free Zinc.** *Debra Rolison, J.F. Parker, C.N. Chervin, I.R. Pala, M.D. Wattendorf, J.W. Long*, U.S. Naval Research Laboratory **INVITED**

Lithium-ion batteries dominate the energy-storage landscape, but do so with the ever-present threat of thermal runaway and conflagration courtesy of flammable electrolytes and oxygen-releasing electrode materials. Fortunately, Zn-based batteries offer a compelling alternative grounded in the innate safety and cost advantages of aqueous electrolytes augmented by the high earth-abundance of Zn and the high energy density of Zn-based batteries (comparable to Li-ion). Traditional Zn-based batteries provide suboptimal utilization of the zinc (typically $<60\%$ of theoretical capacity) and poor rechargeability—thanks to the complex dissolution/precipitation processes that accompany Zn/Zn^{2+} cycling of conventional powder-bed Zn electrode structures in alkaline electrolyte. We address these limitations by redesigning the zinc anode as a porous, 3D-wired "sponge" architecture. Zinc sponge electrodes achieve $>90\%$ Zn utilization when discharged in primary Zn-air cells, retaining both the 3D framework of the Zn sponge and an impedance characteristic of the metal thanks to an inner metallic core of 3D zinc. When cycled in Ag-Zn and Ni-Zn cells, the Zn sponges retain monolithicity and reveal uniform deposition of charge/discharge products at the external and internal surfaces, even to deep depth-of-discharge of the zinc. These results show that all Zn-based chemistries can now be reformulated for next-generation rechargeable, Li-free batteries

5:00pm **EN+EM+NS+SE+SS+TF-TuA9 Porous Silicon Electrochemical Capacitor Devices for Integrated On-Chip Energy Storage.** *Donald Gardner, C.W. Holzwarth III, Y. Liu, S. Clendinning, W. Jin, B.K. Moon, Z. Chen, E.C. Hannah, T.V. Aldridge*, Intel Corp, *C.P. Wang, C. Chen*, Florida International University, *J.L. Gustafson*, Intel Corp

Integrated on-chip energy storage is increasingly important in the fields of internet of things (IoT), energy harvesting, and sensing. Silicon is already the materials of choice for the integrated circuits found in every IoT device; however, the efforts to integrate electrochemical (EC) capacitors on a silicon die have been limited. Unlike batteries, EC capacitors are electrostatic devices and do not rely on chemical reactions enabling cycle lifetimes of $>1\text{M}$. This is especially important for off-power-grid IoT devices where difficulty associated with regularly replacing the batteries of billions of devices is prohibitive. This work demonstrates electrochemical capacitors fabricated using porous Si nanostructures with extremely high surface-to-volume ratios and an electrolyte. Devices were fabricated with tapered channels sized from 100 nm at the top to 20 nm and with aspect ratios greater than 100:1. Surface coatings were necessary for long-term stability because unpassivated silicon structures react with the electrolytes. To obtain uniform coatings using stop-flow atomic layer deposition (ALD), efficient surface reactions are needed between high volatility, low molecular

weight, small molecular diameter precursors without chemical vapor deposition side reactions. TiCl_4 and NH_3 precursors were found to coat porous Si with TiN uniformly. Measurements of coated P-Si capacitors reveal that an areal capacitance of up to 6 mF/cm^2 can be achieved using $2 \mu\text{m}$ deep pores, and scales linearly with depth with 28 mF/cm^2 measured for $12 \mu\text{m}$ deep pores. Three-terminal CV measurements with EMI- BF_4 ionic electrolyte were used to examine the stability of different pore sizes and TiN coating thicknesses. Pores with an average 50 nm width and 100:1 aspect ratio were stable to $\pm 1.2 \text{ V}$ when cycled at 10 mV/s and stable to $\pm 1.0 \text{ V}$ when cycled at 1 mV/s . Different ionic liquids were studied to determine the ionic liquid best suited to TiN coated porous Si including TEA- BF_4/AN , EMI- BF_4 , EMI-Tf, and a 3M EMI- BF_4 /propylene carbonate (PC) mixture. Using impedance spectroscopy, the time constant for a $2 \mu\text{m}$ deep porous Si EC capacitor with a high conductivity TiN coating was found to be 17.6 ms which is fast enough that this can be used for applications involving AC filtering for AC-DC conversion. Measurements of volumetric energy density versus power density of porous Si devices versus other devices show several orders of magnitude higher energy density than electrolytic capacitors with a similar voltage range. These results are also between one to two orders of magnitude higher than other studies utilizing porous silicon and are comparable to commercial carbon-based EC capacitors.

5:20pm **EN+EM+NS+SE+SS+TF-TuA10 Investigations of Magnesium Stripping and Deposition using *Operando* Ambient Pressure X-ray Photoelectron Spectroscopy**, Yi Yu, Lawrence Berkeley National Laboratory, Q. Liu, Shanghai Tech University, China, B. Eichhorn, University of Maryland, College Park, E.J. Crumlin, Lawrence Berkeley National Laboratory

Since the first demonstration of rechargeable magnesium battery, magnesium metal has been considered as an attractive battery anode due to its high volumetric energy density, high negative reduction potential, natural abundance in the earth crust, and relatively good safety features due to its dendrite-free formation. Although it is well accepted that the dissolution and plating of metal plays an important role in the electrochemical properties related to the discharge and charge of the battery, the nature of metal-electrolyte chemical and electrochemical interaction is still not fully established. In an effort to elucidate the interfacial electrochemical mechanisms, we present the studies of magnesium deposition and stripping using *operando* ambient pressure X-ray photoelectron spectroscopy (AP-XPS). Synchrotron X-rays at the Advanced Light Source, Lawrence Berkeley National Laboratory and our 'tender' X-ray AP-XPS endstation allow for probing the liquid-solid interface at pressures up to 20 Torr. Cyclic voltammetry is employed to examine the reversibility of electrochemical magnesium deposition. This talk will provide details on how *operando* AP-XPS coupled with electrochemistry allows for studying electrochemical processes of magnesium deposition and stripping at the liquid-solid interface and yields chemical information relevant to real-world applications.

5:40pm **EN+EM+NS+SE+SS+TF-TuA11 Atomic Layer Deposition of Solid Electrolytes for Beyond Lithium-Ion Batteries**, Alexander Kozen, G.W. Rubloff, University of Maryland, College Park **INVITED**

Solid Li-based inorganic electrolytes offer profound advantages for energy storage in 3-D solid state batteries: (1) enhanced safety, since they are not flammable like organic liquid electrolytes; and (2) high power and energy density since use of the 3D geometry can maximize the volume of active material per unit area, while keeping the active layer thickness sufficiently small to allow for fast Li diffusion. The quality of thin solid electrolytes is currently a major obstacle to developing these solid state batteries, restricting electrolyte thickness to $>100 \text{ nm}$ to control electronic leakage, consequently slowing ion transport across the electrolyte and impeding 3-D nanostructure designs that offer high power and energy.

Furthermore, the ion-conducting, electron-insulating properties of solid electrolytes are promising for their use as protection layers on metal anodes (e.g., Li, Na, Mg) and on cathodes in proposed "beyond-Li-ion" battery configurations such as Li-NMC, Li- O_2 , and Li-S to prevent electrolyte breakdown.

Atomic layer deposition (ALD) is well suited to the challenge of solid electrolytes, providing ultrathin, high quality films with exceptional 3-D conformality on the nanoscale. We have developed a quaternary ALD processes for the solid electrolyte LiPON, exploiting *in-operando* spectroscopic ellipsometry and *in-situ* XPS surface analysis for process development. ALD LiPON has tunable morphology, and a nitrogen-dependent tunable ionic conductivity as high as $3.5 \times 10^{-7} \text{ s/cm}$.

We explore the potential of ALD solid electrolytes for the fabrication of solid, 3D microbatteries, as well as the use of thin ALD solid electrolyte coatings on metal anodes to improve interfacial stability against organic electrolytes and thus prevent SEI formation. We demonstrate and quantify

protection of lithium metal anodes with low ionic conductivity ALD Al_2O_3 coatings to prevent degradation reactions, and probe the surface chemistry and morphology of these anodes. Finally, we demonstrate that protection of Li metal anodes using ALD protection layers can improve the capacity of Li-S batteries by 60% by preventing anode corrosion by dissolved sulfur species in the electrolyte.

This work has implications beyond the passivation of lithium metal besides its focus and greatest impact on the Li-S battery system, as ALD protection layers could also be applied to other promising metal anode battery systems such as Mg and Na, and other beyond Li-ion technologies such as Li-NMC or Li-Air where similar reactivity issues prevent adoption.

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