

Wednesday Afternoon, November 12, 2014

Electronic Materials and Processing
Room: 311 - Session EM+EN+TF-WeA

Thin Films and Materials for Energy Storage

Moderator: Christopher Hinkle, University of Texas at Dallas

2:20pm **EM+EN+TF-WeA1 Investigation of Composite Dielectric Materials for Energy Storage, Kimberly Cook-Chennault, U. Sundar, W. Du,** Rutgers, the State University of New Jersey

Electrical energy storage plays a key role in electronics, stationary power systems, hybrid electric vehicles and pulse power applications. Traditionally, bulk ceramic dielectric oxides are used for these applications, though they suffer from inherently low breakdown field strength, which limits the available energy density and increases the dielectric loss. On the other hand, polymers have high break down field strengths, low dielectric losses and can be readily processed into thin films, but suffer from relatively low dielectric permittivity, and thus low energy densities. As a result, contemporary materials have become a limiting factor to the realization of miniaturized devices, due to Moore's Second law, in terms of size, cost and parasitic impedances. Realization of micrometer to sub-micrometer scale commercial and industrial devices such as, high density DRAM (dynamic access memory), non-volatile memory (NRAM) and capacitors, require advanced materials that can both accumulate and deliver vast amounts of energy nearly instantaneously with minimal dielectric losses. This work focuses on examination of piezoelectric-epoxy based composites for dielectric materials, and explores the interrelationship processing plays on realized electrical and dielectric properties. Materials under investigation include lead-zirconate-titanate, and barium titanate – epoxy composites.

2:40pm **EM+EN+TF-WeA2 Preparation and Characterization of ZnO Nano Rods, P. Thamaraiselvan,** Selvam Arts and Science College, India, **M. Saroja, M. Venkatchalam, P. Gowthaman,** Erode Arts and Science College, India, **S. Ravikumar,** Sengunthar Arts and Science College, India, **S. Shankar,** Erode Arts and Science College, India

ZnO nano rods were prepared using chemical bath deposition technique. ZnO seed layer thin films were deposited on glass substrates by dip coating method. Subsequently, ZnO seed-coated glass substrates were immersed in aqueous solution of zinc nitrate and hexamethylenetetramine (HMT) at three different growth time of 3, 4 and 5 hours at low temperature of 90°C. 0.02 mol of Zinc nitrate and 0.2 mol of Hexamethylenetetramine (HMT) on 1:10 molar concentration were used for the growth of Zinc oxide nano rods. The structure and surface morphology of the ZnO nano rod were studied using X-ray diffraction Scanning Electron Microscopy (SEM), respectively.

3:00pm **EM+EN+TF-WeA3 Rational Design of Energy Storage Materials from Earth Abundant Elements, Kyeongjae Cho,** UT Dallas
INVITED

As a part of global scale renewable energy technology solutions, large scale energy storage system (ESS) would be critical in mediating the gaps between cycles of energy demands and intermittent solar and wind energy generations. Furthermore, electric vehicles (EV) require significantly larger energy storage capacity compared to the batteries used electronic device applications. There are significant challenges in extending the current Li ion battery (LIB) technology (based on graphite anode, organic liquid electrolyte, and Co oxide cathode) to EV and ESS applications. Many different approaches are currently investigated to overcome the capacity, safety and cost issues of LIB in EV and ESS applications, and new battery technology researches include Si anode, Na and Mg batteries, metal-air batteries, over-lithiated-oxide (OLO) [1] and silicate cathodes [2] for LIB. OLO and silicate cathode materials provide two times larger charge storage capacity (~300 mAh/g) compare to current commercial LiCoO₂ (LCO) or Li(Ni,Co,Mn)O₂ (NCM) cathodes. Both Li₂MnO₃ and Li₂FeSiO₄ are based on earth abundant transition metals of Mn and Fe so that a successful development of these cathode materials would improve cathode capacity and cost problems. In order to achieve the short term goal of OLO and silicate cathode development and the long term goal of EV and ESS material development, we have applied the rational material design and development framework developed for pollution control technology in which Pt catalysts are replaced by PdAu alloy and Mn-mullite catalysts. [3-5] In this talk, we will discuss the current status of OLO and silicate cathode material research based on the integrated material design-synthesis-characterization framework.

This work was supported by Samsung GRO project.

1. R. C. Longo et al., "Phase stability of Li-Mn-O oxides as cathode materials for Li-ion Batteries: insights from ab initio calculations" (submitted)

2. R. C. Longo, K. Xiong and K. Cho, "Multicomponent Silicate Cathode Materials for Rechargeable Li-ion Batteries: An ab initio study," Journal of the Electrochemical Society 160, A60 (2013).

3. X. Hao et al., "Experimental and Theoretical Study of CO Oxidation on PdAu Catalysts with NO Pulse Effects," Top. Catal. 52, 1946 (2009).

4. B. Shan et al., "First-principles-based embedded atom method for PdAu nanoparticles," Phys. Rev. B 80, 035404 (2009).

5. W. Wang, G. McCool, N. Kapur, G. Yuan, B. Shan, M. Nguyen, U. M. Graham, B. H. Davis, G. Jacobs, K. Cho, X. Hao, "Mixed-Phase Oxide Catalyst Based on Mn-Mullite (Sm, Gd)Mn₂O₅ for NO Oxidation in Diesel Exhaust," Science 337, 832-835 (2012).

4:20pm **EM+EN+TF-WeA7 Transferring Environmentally Sensitive Battery Materials between GloveBox and UHV Surface Analysis Chamber: Composition Study of Model Battery Interfaces and their Controlled Oxidation, Hugo Celio,** University of Texas at Austin

Environmentally sensitive battery materials prepared in an inert environment (e.g., Argon filled glovebox containing trace levels of water and oxygen at ~1 part-per-million) are often difficult to transfer to an ultra-high vacuum (UHV) chamber for surface analysis. While minimizing additional oxidant(s) exposure, three challenging factors arise from transferring environmentally sensitive materials: 1) Engineering a pump-down load-lock to transition from atmospheric pressure to UHV regime, 2) developing a method to generate a set of figures of merit (FOMs) that allows a user to evaluate transfer reliability, and 3) evaluating of the amount of material that subsequently undergoes, due to reaction with trace ppm levels of oxidants in the Argon gas, oxidation during transfer. To target these issues a novel transfer load-lock/capsule was built and directly coupled to a UHV surface analysis chamber, equipped with X-ray photoelectron spectrometer (XPS). This new load-lock/capsule has lead to a new capability to study the composition of model battery materials (e.g., silicon anode and metal oxide cathode) at the solid electrolyte interfacial (SEI) layer, including their controlled oxidation post-transfer.

4:40pm **EM+EN+TF-WeA8 Development of Thin Film Si-C Based High Temperature Microsupercapacitor Devices, J.P. Alper, C.-H. Chang, C. Carraro, Roya Maboudian,** University of California at Berkeley

On-chip integrated energy storage and delivery at high power is an important aspect in realizing the full potential of microsystems technology such as remote mobile sensor platforms. One promising high power device which has garnered much attention is the supercapacitor. Energy is stored in SC's at the electrode-electrolyte interface, making the high specific surface area of thin films of 1-d materials particularly attractive for application to these devices. However many operations such as in the chemical process industries which could benefit from remote sensor deployment reach temperatures beyond current electrode and electrolyte material constraints. Here we report on the use of bottom-up chemical vapor deposition based silicon carbide (SiC) nanowires and top-down chemically etched SiNWs passivated with an ultrathin carbon sheath as thin film micro-SC electrodes. The electrochemical performance of the two nanowire types in high temperature compatible electrolytes such as ionic liquids and yttria stabilized zirconia (YSZ) are presented. The materials are stable during cycling and achieve specific capacitance values comparable to or better than previously reported carbon electrodes. Operation at temperatures above those attainable with standard electrode-electrolyte systems is also demonstrated. Current challenges for the methods presented and strategies for overcoming them are discussed.

5:00pm **EM+EN+TF-WeA9 Rate Capability of Silicon Carbon Nanotube Anodes for Lithium Ion Batteries, Lawrence Barrett, R. Fan, R.C. Davis, K. Hinton, R.R. Vanfleet,** Brigham Young University

Research has shown stable high capacity lithium ion battery anodes can be made from silicon deposited on carbon nanotubes (CNTs). However, rate capability remains a challenge. We have explored two potential limiting factors: diffusion from the top of the forest down and diffusion into the silicon coating. To probe top down diffusion, we compared a uniform CNT forest to a forest with an array 10 um holes spaced 10 um apart to allow channels for faster top down diffusion and found rate capability was unaffected, indicating top down diffusion is not a limiting factor. We also probed diffusion through the silicon coating by changing the thickness and morphology of the coating.

5:20pm **EM+EN+TF-WeA10 Characterization and Optimization of Interface Engineering on Li Metal Anode Using Atomic Layer Deposition and *In Situ* Electrochemical AFM.** *Chuan-Fu Lin, A.C. Kozen, A.J. Pearse, M. Noked, M.A. Schroeder, S.B. Lee, G.W. Rubloff,* University of Maryland, College Park

Rechargeable Li-metal anode batteries could be considered the holy grail of energy storage systems because Li offers extremely high theoretical specific capacity (3860 mAh/g), low density (0.59 g/cm³), and the lowest negative electrochemical potential (-3.040 V vs. standard hydrogen electrode). However, Li is thermodynamically unstable with organic solvents, inviting serious capacity degradation as well as safety concerns such as Li dendrite growth. The prognosis for Li anodes would be profoundly enhanced for next generation batteries if suitable passivation schemes could be developed to protect Li anodes without significantly reducing ion transport between Li and electrolyte.

In our laboratory, we use atomic layer deposition (ALD) to precisely deposit very thin layer of aluminum oxide (Al₂O₃) on Li foils, using glove box and UHV environments to avoid air exposure while depositing passivation layers on the Li metal surface. We then characterize the surface morphology of the passivated Li by AFM at varying stages of electrochemical reaction and as a function of time and film thickness. We observed the growth of defects on ALD-passivated Li metal surface, decorated by AFM structures indicative of localized electrochemical reactions. The resulting defect density decreased as the film thickness increased.

For thinner ALD protection layers, EC-AFM showed bubble-like structures decorating the steps and boundaries of ALD/Li metal surface in electrochemical system, suggesting mechanisms associated with volatile products. While thin ALD layers suppress charge transfer processes which lead to electrolyte decomposition and formation of solid electrolyte interphase (SEI) [1-2], defects in the ALD passivation layer may cause localized SEI formation, which in turn involves volatile products (e.g., C₂H₄, CO). Alternatively, trace H₂O in the propylene carbonate electrolyte may react with Li metal through pinholes in the ALD layer, leading to LiOH and volatile H₂ products. We are working to differentiate between these by applying in-situ mass spectroscopy to monitor the gas formation in the cell as a function of controlled water content and ALD film thickness. The identification of passivation layer degradation mechanisms and the development of robust approaches to metal anode protection have profound benefit to a variety of beyond-Li-ion batteries.

References:

1. Kevin Leung, *J. Phys. Chem. C*, 2012, 117, 1539-1547.
2. Kevin Leung et al., *JACS*, 2011, 133, 14741-14754.

5:40pm **EM+EN+TF-WeA11 The Road to Next-Generation Energy Storage is Paved with Zinc.** *Joseph Parker, C.N. Chervin,* Naval Research Laboratory, *I.R. Pala,* National Research Council postdoc working at Naval Research Laboratory, *E.S. Nelson,* Pathways Student working at Naval Research Laboratory, *J.W. Long, D.R. Rolison,* Naval Research Laboratory
While Li-ion batteries presently dominate the energy-storage landscape, zinc-based batteries offer a compelling alternative due to the earth-abundance of zinc, innate safety and cost advantages that arise from using aqueous electrolytes, and device-realized specific energy that is comparable to or higher than Li-ion. Yet the performance of present-day Zn-based batteries is hindered by suboptimal Zn utilization (typically <60% of theoretical capacity) and poor rechargeability—a consequence of the complex dissolution/precipitation processes that accompany Zn/Zn²⁺ cycling and the ad hoc construction of conventional powdered-bed Zn anodes. We address these limitations by designing and fabricating highly conductive, porous, and 3D-wired Zn “sponge” electrodes from emulsion-cast, consolidated Zn powders that are thermally treated to produce rugged monolithic forms. With this 3D Zn architecture, we achieve >90% Zn utilization when discharged in primary Zn–air cells with retention of the 3D framework of the Zn sponge and uniform deposition of charge/discharge products at the surfaces of the Zn sponge, as verified by scanning electron microscopy and impedance spectroscopy. We further show that the structural characteristics of the Zn sponge promote greater rechargeability when cycled in prototype Ag–Zn and Ni–Zn cells. Our results demonstrate that all Zn-based chemistries can now be reformulated for next-generation rechargeable batteries.

Authors Index

Bold page numbers indicate the presenter

— A —

Alper, J.P.: EM+EN+TF-WeA8, 1

— B —

Barrett, L.: EM+EN+TF-WeA9, **1**

— C —

Carraro, C.: EM+EN+TF-WeA8, 1

Celio, H.C.: EM+EN+TF-WeA7, **1**

Chang, C.-H.: EM+EN+TF-WeA8, 1

Chervin, C.N.: EM+EN+TF-WeA11, 2

Cho, K.J.: EM+EN+TF-WeA3, **1**

Cook-Chennault, K.: EM+EN+TF-WeA1, **1**

— D —

Davis, R.C.: EM+EN+TF-WeA9, 1

Du, W.: EM+EN+TF-WeA1, 1

— F —

Fan, R.: EM+EN+TF-WeA9, 1

— G —

Gowthaman, P.: EM+EN+TF-WeA2, 1

— H —

Hinton, K.: EM+EN+TF-WeA9, 1

— K —

Kozen, A.C.: EM+EN+TF-WeA10, 2

— L —

Lee, S.B.: EM+EN+TF-WeA10, 2

Lin, C.F.: EM+EN+TF-WeA10, **2**

Long, J.W.: EM+EN+TF-WeA11, 2

— M —

Maboudian, R.: EM+EN+TF-WeA8, **1**

— N —

Nelson, E.S.: EM+EN+TF-WeA11, 2

Noked, M.: EM+EN+TF-WeA10, 2

— P —

Pala, I.R.: EM+EN+TF-WeA11, 2

Parker, J.F.: EM+EN+TF-WeA11, **2**

Pearse, A.J.: EM+EN+TF-WeA10, 2

— R —

Ravikumar, S.: EM+EN+TF-WeA2, 1

Rollison, D.R.: EM+EN+TF-WeA11, 2

Rubloff, G.W.: EM+EN+TF-WeA10, 2

— S —

Saroja, M.: EM+EN+TF-WeA2, **1**

Schroeder, M.A.: EM+EN+TF-WeA10, 2

Shankar, S.: EM+EN+TF-WeA2, 1

Sundar, U.: EM+EN+TF-WeA1, 1

— T —

Thamaraiselvan, P.: EM+EN+TF-WeA2, 1

— V —

Vanfleet, R.R.: EM+EN+TF-WeA9, 1

Venkatachalam, M.: EM+EN+TF-WeA2, 1