Electronic Materials and Photonics
Room 102A - Session EM+SS+TF-ThA

Materials and Interfaces for Energy Storage

Moderators: Michelle Paquette, University of Missouri-Kansas City, Lee Walsh, University of Texas at Dallas

2:20pm **EM+SS+TF-ThA1 Strain Engineering of Ultrathin Metal Oxide Coatings Deposited using Atomic Layer Deposition for Controlled Electrochemical Energy Storage***, **Nitin Muralidharan**, R.E. Carter, A.P. Cohn, L. Oakes, C.L. Pint,* Vanderbilt University

Strain engineering has transformed applications in the semiconductor electronics industry, but has not been widely explored as a tool for electrochemical applications. Here we study the role of strain on the electrochemistry of metal oxide coatings deposited using atomic layer deposition onto super-elastic NiTi alloy surfaces. Specifically, we focus on vanadium pentoxide (V_2O_5) due to its well-known capability to function as a cathode for the intercalation of lithium ions. Exploiting the capability of NiTi to “lock-in” strain in the elastic regime, which extends up to ~ 15% strain, we study the correlation between strain transferred to the V_2O_5 active material and the electrochemical performance during lithium intercalation. Overall, our results indicate that pre-straining the material changes both the kinetics and energetics for intercalation properties. Furthermore, the diffusion coefficient of lithium ions in the V_2O_5 lattice can be effectively doubled through the application of elastic strains as low as ~0.25%. These results provide a route to controllably engineer bulk materials using principles of mechanics to improve battery or other electrochemical application performance.

2:40pm **EM+SS+TF-ThA2 Probing Li-Ion Transport in All-Solid-State Batteries through Electron Transparent Electrodes***, **Alexander Yulaev,*** Center for Nanoscale Science and Technology, NIST, Gaithersburg, MD, USA*; A.A. Talin,* Sandia National Laboratories*; M.S. Leite,* University of Maryland*; A. Kolmakov,* NIST/CNST

All-solid-state batteries demonstrate a high power-to-weight ratio and high energy density, offering prospective opportunities for miniaturized micro-electronics and medical devices. Moreover, solid state batteries reduce the safety risk of thermal runaway that may occur in electrochemical cells with liquid electrolytes. In spite of growing interests, the details of lithium transport in solid electrolytes and their interfaces are not yet well understood due to a scarcity of experimental methods to probe electrochemical processes at the nanoscale. For instance, the factors controlling the rate and reversibility of Li ion intercalation are still an active area of research. Here we apply a combination of optical and scanning electron microscopies to resolve spatially Li-ion transport across a thin LiPON electrolyte. Using lithographically patterned electrodes, we monitor Li-ion transport through optically and electron transparent ultrathin anodes made either of high capacity silicon or carbon. The variation of the probing depth is achieved by altering the energy of the primary electron beam from 1 keV to 15 keV. Analogous to SEM tomography, the sequence of depth dependent 2D images can be employed to reconstruct the 3D diffusion pathways of Li ions in the electrolyte. In addition, we investigate Li plating/intercalation reactions, which occur at the anode-electrolyte interface during charge/discharge cycles. We foresee that this approach will help elucidate the effects of chemical and ion transport inhomogeneity inside the electrolyte and electrodes on the overall performance of the battery.

3:00pm **EM+SS+TF-ThA3 Thin Film Battery Materials for Fundamental Studies and Applications***, **Nancy Dudney**, K. Kercher, M. Veith,* Oak Ridge National Laboratory **INVITED**

Although most commercial rechargeable batteries are prepared by bulk and powder processing methods, vapor deposition of materials has led to important advances for fundamental research, modification of battery materials and interfaces, and also for commercialization of thin film batteries. Each of these areas will be illustrated with our studies of thin film materials for electrolyte, anode, and cathode components of rechargeable lithium and lithium-ion batteries with both planar and 3-dimensional architectures.

Acknowledgement: This work was supported by the U. S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

4:00pm **EM+SS+TF-ThA6 Silicon Compatible Pseudocapacitors Based on Nickel Hydroxide Functionalization of Carbonized Porous Silicon***, **Joshua Fain**, J.W. Mares, S.M. Weiss,* Vanderbilt University

We report on silicon (Si) compatible energy-storage supercapacitors (SCs) that incorporate pseudocapacitive nickel hydroxide [$Ni(OH)_2$] coupled with an electric double layer capacitance (EDLC) contributed by constituent $Ni(OH)_2$ and carbon layers. SCs can charge and discharge their energy much more rapidly than conventional batteries (within a few seconds to minutes), while possessing a higher energy storage capability than traditional capacitors (specific capacitances can reach thousands of F/g). Although SCs have made a commercial impact in regenerative breaking, there remains untapped potential for this technology in on-chip energy storage that could lead to reduced size and weight of microelectronic devices. However, advancements in Si-based on-chip energy storage has been hindered due to the rapid corrosion of Si by most electrolytes necessary for energy storage. Recently, it has been shown that conformal carbonization of high surface area porous silicon (PSi) electrodes protects the Si matrix from corrosion while also contributing to energy-storage EDLC behavior. Here, we show that functionalization of carbonized PSi with pseudocapacitive $Ni(OH)_2$ leads to significantly improved energy-storage capabilities of the SC electrode from a few to over 100F/g (with respect to the mass of the entire electrode), and up to 1400 F/g (with respect to the mass of only the $Ni(OH)_2$ - corrected for EDL contribution of the carbon). The electrodes were fabricated by electrochemical etching of PSi, followed by carbonization using chemical vapor deposition, and finally inclusion of $Ni(OH)_2$ into the matrix via a sol-gel process or electrochemical deposition. Cyclic voltammetry (CV) and charge/discharge experiments were carried out to investigate the energy storage capabilities of composite pseudocapacitive electrodes prepared with varying sol-gel concentrations and different electrochemical deposition parameters. Scan rates of 1-50 mV/s were used. Clear oxidation and reduction peaks were evident in the CV curves along with the EDLC contribution. We observed a tradeoff between specific surface area and $Ni(OH)_2$ quantity: the higher the $Ni(OH)_2$ coverage in the PSi matrix, the lower the accessible surface area. The highest specific capacitance of 1400 F/g was measured on an electrode with a modest concentration of $Ni(OH)_2$ (5 mg/mL nickel acetate tetrahydrate:2-methoxyethanol) at 50 mV/s. The results of these studies suggest that PSi is an excellent high surface area host template for $Ni(OH)_2$ that enables high specific capacitance to be achieved on a Si-compatible platform that could be directly integrated into microelectronic devices.

4:20pm **EM+SS+TF-ThA7 In-situ Raman of Sodium Ion Cointercalation into Highly Crystalline Few-Layered Graphene***, **Adam Cohn**, C.L. Pint,* Vanderbilt University

A maximum sodium capacity of ~ 35 mAh/g has restricted the use of crystalline carbon for sodium ion battery anodes. We demonstrate that a diglyme solvent shell encapsulating a sodium ion acts as a “non-stick” coating to facilitate rapid ion insertion into crystalline few-layer graphene and bypass slow desolvation kinetics. This yields storage capacities above 150 mAh/g, cycling performance with negligible capacity fade over 8000 cycles, and ~ 100 mAh/g capacities maintained at currents of 30 A/g (~ 12 second charge). Raman spectroscopy elucidates the ordered, but non-destructive cointercalation mechanism that differs from desolvated ion intercalation processes. In-situ Raman measurements identify the Na+ staging sequence and isolates Fermi energies for the first and second stage ternary intercalation compounds at ~ 0.8 eV and ~ 1.2 eV.

4:40pm **EM+SS+TF-ThA8 Using X-ray Reflectivity to Measure the Vacuum Ultraviolet Absorption Spectrum in Low-k Dielectrics***, **Faraz Choudhury**, H.M. Nguyen, W. Li,* University of Wisconsin-Madison*; Y. Nishi,* Stanford University*; J.L. Shohet,* University of Wisconsin-Madison

During plasma processing, low-k dielectrics are exposed to high levels of vacuum ultraviolet (VUV) radiation that can cause severe damage to the dielectric material. The degree and nature of VUV-induced damage depends on the VUV photon energies.[1] In this work, we determine the VUV absorption spectrum of low-k organosilicate glass (OSG) using specular X-ray reflectivity (XRR). Low-k SiCOH films were exposed to synchrotron VUV radiation with energies ranging from 7 to 25 eV and the electron density depth profile of the VUV irradiated films were extracted from the fitting of the XRR experimental data using the Parratt method. The results show that the depth of the VUV induced damage layer is sensitive to the photon energy. Between 7 to 11 eV, the depth of the damaged layer decreases sharply from 110 nm to 60 nm and then gradually increases to 85 nm at 21 eV. The maximum VUV absorption in low-k films occurs between 11 and 15 eV. This method is also utilized to investigate the penetration depth of 5 to 25 eV photons in porous SiCOH films with porosities ranging from 15 to 50%. It is seen that the penetration depth of photons increases with porosity. This work shows that XRR electron density depth profiling can be a very effective, non-destructive tool to determine the penetration depth and absorption coefficients of photons and other reactive species from a plasma in various kinds of dielectric films.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359

[1] T. V. Rakhimova et al, J. Phys. D: Appl. Phys. 47 (2014) 025102

5:00pm **EM+SS+TF-ThA9 On-chip [^{18}F]fluoride Concentration for Microfluidic PET Tracer Synthesis***, **Xin Zhang**, J. Buck, M. Nickels, C. Manning, L. Bellan,* Vanderbilt University

Positron emission tomography (PET) is a valuable medical imaging method that relies on radioactive tracers that target specific sites in the body. Development of these tracers is currently hindered by the enormous infrastructure requirements to perform the necessary radioisotope production and subsequent reactions. To overcome this hurdle and facilitate PET tracer development, we are designing simple, modular microfluidic systems that support on-chip radiosynthesis reactions with small volumes of reagents. In this work, [^{18}F]fluoride (a positron emitter widely used in PET imaging due to its convenient half-life of 110 minutes) is concentrated with a miniaturized anion exchange column located in a microfluidic device fabricated in polydimethylsiloxane (PDMS). By employing a microfluidic device, we aim to achieve more controlled diffusion and reactive kinetics. Instead of relying on complicated flow control elements (e.g. valves), in this microfluidic system, a channel containing pillars with a spacing less than the average diameter of the anion exchange beads is used to trap relatively monodispersed, rigid polystyrene/divinyl benzene beads. We characterized the ability of this miniaturized on-chip exchange column to capture and release quantities of [^{18}F]fluoride appropriate for human imaging (a typical dose is 10 mCi).

Our device is composed of a main chamber with larger microchannels (9 mm long) connected to an inlet and outlet. A laser writer (Heidelberg µPG 101) was used to create patterns on a silicon wafer using a 60 µm thick layerof mr-DWL resist; this template was subsequently used to pattern a microfluidic structure in PDMS. The desired quantity (2.9 mL) of anion exchange beads was trapped by a double row of square pillars near the outlet of the chamber, and the beads subsequently activated with 1.0 M of $KHCO_3$. Diluted [^{18}F]fluoride (100 mCi/mL) sourced from a nearby cyclotron was introduced into the system using a syringe pump, flowing at 0.05 mL/min for 10 minutes.

By quantifying the radioactivity of the [^{18}F]fluoride introduced, the radioactivity of the chip, and the radioactivity of the outflow, we could determine trapping and release efficiency. We observed near complete capture of [^{18}F]fluoride (50 mCi)on our chips in a relatively short time. Moreover, elution with a small volume (less than 200 mL) of Kryptofix (K_{222})/K_2CO_3 was able to release nearly all the [^{18}F]fluoride (49 mCi). Thus, this device is capable of simply and efficiently trapping [^{18}F]fluoride and controllably releasing the concentrated radiolabel in small volumes for downstream reaction with desired molecules.

5:40pm **EM+SS+TF-ThA11 The Role of Electron-Beam Deposition Rate in Controlling Properties of the Titanium/Semiconductor Interface***, **Keren Freedy**, A. Giri, B.M. Foley,* University of Virginia*; J. Bogan, R. O'Conner,* Dublin City University, Ireland*; P.E. Hopkins, S. McDonnell,* University of Virginia

Electron beam evaporation under high vacuum is very widely used for contact deposition in electronic device fabrication. Ti has a low work function and is commonly deposited as a contact or adhesion layer for other metals in silicon-based devices and more recently in 2D semiconductors. Previous work on Ti/MoS_2 contacts suggests that electron beam evaporation of Ti under high vacuum results in the formation of TiO_2 at the interface while UHV deposition results in unintentional reactions between metallic Ti and the MoS_2 substrate (McDonnell et al., 10.1021/acsami.6b00275). Since the majority of reports using Ti as a contact metal utilize HV rather than UHV e-beam processes, understanding the role of process conditions on the properties of this contact/semiconductor interface is of the utmost importance. To avoid the large variability observed in metal/MoS_2 contacts, we focus on Si as a case study to investigate the thermal and electronic properties of the Ti/semiconductor interface. The present study examines the effect of deposition rate on the properties of the Ti/Si interface. Electron beam evaporation of Ti onto both hydrogen-terminated and native oxide (001) Si surfaces is performed at varied deposition rates ranging from 0.1 to 5 A/s at pressures of ~10^{-6} Torr. Prior to ex-situ characterization, the samples are capped with Au in the evaporator to prevent further oxidation in air. Photoelectron spectroscopy measurements reveal that oxide composition is inversely proportional to the deposition rate. X-ray diffraction data shows no evidence of metallic Ti at slower deposition rates. Due to an appreciable partial pressure of O_2 at high vacuum, the composition of the deposited material is sensitive to the impingement rate of Ti on the surface. It follows that higher deposition rates should result in a smaller fraction of oxide phases. Electron and phonon transport across the interface will be studied as a function of deposition rate.

6:00pm **EM+SS+TF-ThA12 Single Crystal Study of Layered U_nRhIn_{3n+2} Materials: Case of the Novel U_2RhIn_8 Compound***, **Attila Bartha**, M. Kratochvílová,* Charles University, Czech Republic*; M. Dušek,* Institute of Physics ASCR, Czech Republic*; M. Diviš, J. Custers, V. Sechovský,* Charles University, Czech Republic

Materials of reduced dimensionality appear in many contemporary fields of research and technology, because they encompass a wide variety of interesting electronic phenomena. For instance carbon can be prepared in 3D (diamond), quasi-2D (graphite), 2D (graphene) or 1D (carbon nanotubes). All of these structures have distinct electronics. Diamond is an insulator. Graphene is semimetal. However, when the dimensionality is increased by putting several graphene layers together (eventually making graphite), the resulting band structure moves to that of a more trivial metal. Another example is high temperature superconductors being quasi-2D materials as well.

The role of dimensionality in *f*-electron systems has been mainly discussed in the context of quantum phase transitions and related phenomena. The series $Ce_nT_mIn_{3n+2m}$ (n = 1, 2; m = 0, 1, 2; T = transition metal) of layered compounds has been extensively investigated. $CeIn_3$ is cubic (3D) and orders antiferromagnetically (AFM) at T_N = 10.2 K. Under hydrostatic pressure superconductivity appears with highest T_c = 0.3 K at p = 2.5 GPa. In $CeRhIn_5$, the anisotropic crystal structure leads to a quasi-2D electronic and magnetic structure. The AFM order is reduced (T_N = 3.8 K) while superconductivity is supported, T_c increases to 1.9 K at p = 1.77 GPa.

We report on the properties of the novel U_2RhIn_8 compound studied the single crystal form in the context of parent $URhIn_5$ and UIn_3 systems [1]. The compounds were prepared by In self-flux method. U_2RhIn_8 adopts the Ho_2CoGa_8-type structure with lattice parameters a = 4.6056(6) Å and c = 11.9911(15) Å. The behavior of U_2RhIn_8 strongly resembles features of related $URhIn_5$ and UIn_3 with respect to magnetization, specific heat, and resistivity, except for magnetocrystalline anisotropy developing with lowering dimensionality in the series UIn_3 vs. U_2RhIn_8 and $URhIn_5$. U_2RhIn_8 orders AFM below T_N = 117 K and exhibits slightly enhanced Sommerfeld coefficient γ = 47 mJ.mol^{-1}.K^{-2}. Magnetic field leaves the value of Néel temperature for both $URhIn_5$ and U_2RhIn_8 unaffected up to 9 T. On the other hand, T_N increases with applying hydrostatic pressure up to 3.2 GPa. Results of thermal expansion measurement will be discussed in the framework of Ehrenfest relations. The character of uranium 5*f* electron states of U_2RhIn_8 was studied by first principles calculations based on the density functional theory combined with the Hubbard model. The overall phase diagram of U_2RhIn_8 is discussed in the context of magnetism in related UTX_5 and UX_3 (T = transition metal, X = In, Ga) compounds.

[1] A. Bartha *et al.*, J. Magn. Magn. Mater. 381 (2015) 310-315

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