

1. Lithographically Patterned Gold/Manganese Dioxide Core/Shell Nanowires for High Power Supercapacitors – Electrochemical and Raman Spectroscopic Characterization

Girija Thesma Chandran, Wenbo Yan, Mya Le Thai and Reginald M. Penner

Department of Chemistry, University of California, Irvine

MnO₂ is the most investigated transition metal oxide electrode material for supercapacitor applications because of its intriguing features including natural abundance, low cost, and high theoretical specific capacitance (1370 F g⁻¹). The theoretical specific capacitance has rarely been achieved in bulk MnO₂ limited by the poor electrical conductivity and limited surface area. Hence there is a rapidly growing interest in developing nanosized MnO₂ electrode materials to increase the surface area. In this project, a symmetrical MnO₂ based hybrid capacitor consisting of interdigitated, horizontal nanowires is fabricated. The nanowires within the capacitor consists of a gold nanowire core encapsulated within a hemicylindrical shell of δ -phase MnO₂. These Au@ δ -MnO₂ nanowires are patterned onto a planar glass surface using lithographically patterned nanowire electrodeposition (LPNE). A power density of 165 kW/kg and energy density of 24 Wh/kg were obtained for a typical nanowire array in which the MnO₂ shell thickness was 68 ± 8 nm. Capacitors incorporating these ultralong nanowires lost ≈10% of their capacity rapidly, during the first 20 discharge cycles, and then retained 90% of their maximum capacity for the ensuing 6000 cycles. It has been demonstrated that ultralong Au@ δ -MnO₂ nanowires can simultaneously deliver high power and high capacity with acceptable cycle life.

2. Binding of Alkali Metals to Pore Walls in Nanopores Modulates Transmembrane Ion Current and Ionic Rectification

Trevor Gamble, Z. Siwy

Department of Physics, University of California, Irvine

Functioning of nanoforest architectures, such as those prevalent in EFRC, is dependent on the ionic distributions inside the nano-constrictions. These distributions are determined by the access of ions to the nanoconstrictions of the forest as well as interactions of the ions with surfaces of varying electrochemical potential. A model system of single conically shaped nanopores provided insight into which interactions of ions with surfaces are important for ionic transport at the nanoscale. Current rectification is the probe used to elucidate ion distributions and transport inside and through nano-confinements. Rectifying nanopores feature ion currents that are higher for voltages of one polarity compared to the currents recorded for corresponding voltages of the opposite polarity. Rectification of nanopores has been found to depend on the pore opening diameter, distribution of surface charges of the pore walls as well as pore geometry. Very little is however known on the dependence of ionic rectification on the type of transported ions. We recorded current-voltage curves in three electrolytes: LiCl, NaCl and KCl. Rectification degree of the pores, quantified as the ratio of currents recorded for voltages of opposite polarities, was the highest for KCl, and the lowest for LiCl. The currents recorded in LiCl as the bulk electrolyte were also several times lower than predicted from relative bulk conductivities of KCl and LiCl. The experimental observations could not be explained by a continuum modeling based on the Poisson-Nernst-Planck equations. All-atom molecular dynamics simulations revealed differential binding between Li⁺, Na⁺, and K⁺ ions and carboxylate residues on the pore wall, resulting in changes to both the effective surface charge of the nanopore and cation mobility within the pore. Differences in ionic current rectification follow from these factors.

3. HIERARCHICAL ARCHITECTURES FOR ENERGY STORAGE DEVICES USING VIRAL NANOTEMPLATES

Konstantinos Gerasopoulos*, Markus Gnerlich*, Sangwook Chu*,
Ekaterina Pomerantseva**, James N. Culver*, and Reza Ghodssi*

* University of Maryland College Park, USA

**Drexel University, USA

We present microfabricated energy storage devices incorporating hierarchical architectures with *Tobacco mosaic virus* (TMV) as nanotemplates. The TMV is a high aspect ratio biomaterial genetically modified to include cysteine groups surrounding its rod-like structure. The self-assembly of the TMV and its fabrication compatibility enable its application as a nano-scaffold for mesoscale architectures.

Three dimensional hierarchical electrodes for lithium ion batteries were demonstrated. Gold micropillars were electroplated followed by TMV assembly and metallization. Finally, a V_2O_5 layer was uniformly deposited with ALD on top of the Ni current collector. A 3-fold increase in V_2O_5 mass loading was confirmed for the hierarchical electrode compared to the nanostructure-only electrode, while a more than 20-fold increase was observed compared to flat electrodes. The charge/discharge curves showed a 3-fold difference in the capacity, in excellent agreement with the theoretical expectation and the electrode material mass comparison results.

This process has also been applied for flexible solid state RuO_2 supercapacitors using Nafion electrolyte. A polyimide layer was spin-coated on a silicon wafer followed by patterning of Ti/Au current collectors. After the TMV self-assembly process, TiN as a barrier was deposited by ALD. Finally, RuO_2 active electrode material was deposited by ALD. Nafion was spin coated over the electrode to a thickness of $20\mu m$.

Cyclic voltammograms indicated that the charge storage is a mix of Faradaic and non-Faradaic mechanisms. A maximum specific capacitance of $5.8F/g$ ($578\mu F/cm^2$ areal capacitance) was achieved at $2mV/s$ with 80% relative humidity. The device cycle stability was tested in two different relative humidity (RH) levels (ambient and 100%RH). At 30%RH, the supercapacitor retained 80% of charge/discharge efficiency after 25000 cycles.

4. 3D Aluminum Oxide: Fabrication, Characterization and Applications as Templates for 3D Structured Electrodes

Eleanor Gillette, Sang Bok Lee

University of Maryland College Park, USA

Well-ordered anodized aluminum oxide (AAO) is a widely known porous material which has been used in a variety of applications. One of the advantages of AAO is its tunable pore diameter and length, which are controlled by the anodizing conditions. Additionally, more complex structures can be produced by modifying the anodization and etching conditions. Here we present a technique for introducing branch points into the pores which allows for controllable branching in sections of the pores while maintaining straight, hexagonally arrayed, regular structures throughout the rest of the alumina membrane. These branched membranes can then be used as templates for a variety of materials, allowing us to investigate their electrochemical performance while controllably modifying the structure. This gives a unique opportunity to compare identical active materials with systematically varied structures, without the need for binders or conductive additives.

5. Scanning Probe Microscopy of Low-Dimensional MnO_2 /Carbon Composite Electrodes

Nathan T. Hahn, Kevin R. Zavadil

Sandia National laboratory – New Mexico

Understanding the fundamental activity of metal-oxide particles attached to a carbon support is critical to electrochemical energy storage applications such as batteries and supercapacitors. The origin and subsequent evolution of the particle-carbon interface during device operation influences charge transfer performance across this interface and ultimately, ensemble electrode performance. In order to better understand the fundamental characteristics of these systems we have generated low-dimensional composite electrodes based on a metal-oxide

nanoparticle deposition scheme that takes advantage of our ability to tune the functionality of a graphitic (HOPG) surface in UHV. By engineering this functionality and, consequently, the surface mobility of manganese-oxygen adatom clusters we are able to control the nucleation, structure, and length-scale of β - MnO_2 particles. Manipulating the particle deposition conditions (e.g. by changing the reactive gas from molecular O_2 to atomic O or by pre-irradiating the substrate with low energy O_2^+) leads to samples possessing distinct particle populations due to their nucleation at graphite step-edges, induced terrace defects, or intrinsic terrace defects. This differentiation enables us to correlate the chemical origin of a particle-carbon interface with the particle's physical and electrochemical properties. We have employed SPM techniques such as in operando AFM and conductive AFM to study the structural and electronic property changes of these nanostructures during potential-controlled lithium-ion insertion/extraction in order to assess individual particle activity, which depends upon its degree of electronic connectivity to the graphite support. These techniques were used in conjunction with ex situ characterization tools to form a more complete picture of the β - MnO_2 particle-carbon system. In principle these particle deposition and characterization schemes could be easily applied to other metal-oxide energy storage materials of interest.

6. *In Situ* Observation of Volumetric Expansion in Nanostructured MnO_2

Brad Corso, Tetyana Ignatova, Deng Pan, O. Tolga Gul, and Philip G. Collins

Department of Physics and Astronomy, University of California at Irvine

By combining in-liquid atomic force microscopy (AFM) with 3-terminal electrochemical cycling, we have studied the volumetric changes that accompany charge storage in nanoscale deposits of MnO_2 . Typical samples consisted of thin films (100 to 500 nm) of porous, nanostructured MnO_2 deposited onto 1 μm electrodes and then cycled in aqueous LiClO_4 electrolyte. Simultaneous, *in situ* measurements observed film expansions of 3% per nC of charge insertion over a wide range of scan rates and voltage windows. The 3%/nC proportionality persisted from 500 mV/s, where the capacitance is entirely double-layer charging, down to the slow limit of 15 mV/s, where the majority of charge is stored within "bulk" redox pseudocapacitances. Volume expansion is generally attributed to bulk charging rather than surface processes, so the invariance of our proportionality was highly unexpected. Further investigation is necessary to understand the practical consequences for bulk nanostructured materials and nanoarchitectures.

7. *IN-SITU*, REAL-TIME MONITORING OF MICROSTRUCTURAL AND MECHANICAL PROPERTY CHANGES IN A V_2O_5 BATTERY ELECTRODE USING A MEMS OPTICAL SENSOR

Hyun Jung¹, Konstantinos Gerasopoulos¹, Markus Gnerlich¹, Alec Talin², and Reza Ghodssi¹

¹ *University of Maryland, College Park, MD, USA*

² *Sandia National Laboratories, Livermore, CA, USA*

This work presents the first demonstration of a MEMS optical sensor for *in-situ*, real-time monitoring of simultaneous microstructural and mechanical property changes in a V_2O_5 lithium-ion battery (LIB) cathode during cycling. Previously, a MEMS platform was used to monitor the volume change in a silicon anode. Here, we report the next-generation device with important additional metrology functionalities as an *in-situ*, multi-modal sensing tool, using V_2O_5 as a model system.

The MEMS sensor consists of a reflective membrane which forms one side of a Fabry-Perot (FP) interferometer, while the other side is coated with V_2O_5 and exposed to electrolyte in a half-cell LIB. The sensor is packaged in a modified coin cell, connected to a potentiostat, and placed under a Raman microscope with two laser sources. A red laser illuminates the FP cavity to produce a fringe pattern, while the Raman laser records the back-scattered spectra from the electrode.

Upon lithium insertion, V_2O_5 expands and the membrane deflects towards the Pyrex causing an increase in fringe radius. During lithium extraction, the electrode contracts, the membrane deflects away from the Pyrex and the fringe radius returns close to its original position. Rapid increases and decreases in fringe radius were observed during this process, and are attributed to the phase transition-induced volume changes in V_2O_5 with varying lithium content. Simultaneously, the *in-situ* Raman spectra were collected and representative data at various points along the discharge/charge curve. The Raman intensity change at 145 cm^{-1} (V_2O_5 layer order/disorder peak) shows that the level of disorder increases (peak vanishes) during lithium insertion and progressively recovers the V_2O_5 lattice during lithium extraction (peak reappears).

This MEMS platform facilitates simultaneous *in-situ* investigations of electrochemically-driven microstructural and

mechanical changes in LIB electrodes. This unique capability enables study of coupled evolutions for a wide variety of thin-film LIB electrode materials.

8. Atomic Layer Deposition of Lithium Solid Electrolytes

Alex Kozen, Alex Pearse, Marshall Schroder, Malakhi Noked, Chanyuan Liu, Chuan-Fu Lin, Sang-Bok Lee, and Gary Rubloff

University of Maryland, College Park

Solid electrolytes are safer and more robust than their liquid counterparts, and so are attractive for use in next-generation lithium-based electrochemical storage devices. However, current fabrication techniques for solid electrolytes are limited to much thicker layers (> 100 nm), and limited aspect ratio substrates. In order to maximize power density these solid electrolytes should be as thin as possible, and to maximize energy density they should be able to coat high-aspect ratio active materials.

Atomic layer deposition (ALD) is ideally suited to fabrication of solid electrolytes due to its highly conformal nature, ability to deposit thin pinhole-free films, and extreme process tunability allowed by the multicomponent reaction chemistry. Thin ALD solid electrolytes can be used for stabilization of traditional anode and cathode materials, however ALD is ideally suited to enable the fabrication of fully solid-state nanoscale electrochemical devices.

We have successfully developed a number of Lithium-containing ALD chemistries including Li_2O , LiOH , Li_2CO_3 , Li_3PO_4 , and LiPON . We demonstrate our ability to tune the chemistry of the resulting films, and we deconvolute the ALD reaction mechanisms and subsequent air reactivity of Li_2O and LiOH thin films via *in-situ* XPS and ellipsometric characterization. We demonstrate the application of the ALD Li_2O process via the fabrication of high-aspect ratio Li-O_2 cathodes with controlled Li_2O mass loading to understand the Li-O_2 charging chemistry. We show that ALD solid electrolytes can conformally coat high aspect ratio structures, paving the way for fully solid-state nanobatteries.

Lastly, we have successfully tuned ALD processes for deposition of pinhole-free films directly onto lithium metal anodes. We will show preliminary results indicating passivation both from atmospheric tarnishing of the lithium metal and from reaction with organic electrolytes. Electrochemical cycling data using passivated lithium metal anodes in the Li-S system indicates that these thin ALD passivation layers do not impede device performance.

9. Ethylene Carbonate Decomposition on LiMn_2O_4 (111) Surface

Nitin Kumar^{1,2}, Kevin Leung², D. J. Siegel¹

⁽¹⁾ Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109-2125, USA

⁽²⁾ Sandia National Laboratories MS 1415, Albuquerque, NM 87185

LiMn_2O_4 (LMO) spinel is a promising cathode material for rechargeable Li-ion battery applications^[1] due to factors like high abundance of manganese (Mn), low cost, and the environmentally friendly nature of the material. The (111) facet of LMO has been experimentally found to be most stable^[2]. Recently, theoretical work by Karim et al.^[3] showed that by choosing proper reconstruction, it is possible to obtain the (111) surface as the most stable facet of LMO. We have studied the decomposition of ethylene Carbonate (EC), a main component of Li-ion battery electrolytes, on Karim et al.'s^[3] prescribed (111) LMO surface. The static calculations show that the EC adsorbs molecularly on this surface and the EC decomposition reactions on this LMO (111) surfaces are endothermic. Karim et al.'s^[3] prescribed (111) LMO surface has no exposed Mn. However, it is well known that Mn dissolves in the electrolyte. In this context, we propose a new reconstruction (Fig. 1) where 5-coordinated Mn is exposed on the (111) surface. This surface is slightly higher in energy than Karim et al.'s surface^[3] but it is still more stable than the (100) facet. Interestingly, we find that EC reacts exothermally with the newly proposed reconstruction. Moreover, some EC decomposition intermediates predicted for our LMO (111) surface are similar to those on (100)^[4]. We will be discussing the reaction barriers for the EC decomposition on the newly proposed LMO (111) surface.^[5] A synergistic study is done on Li-O_2 batteries, which is a promising alternative to Li-ion batteries.

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10. Probing the Li/Si(111) Interface with a CNT-Terminated Tip: Li Nanopipetting and Surface Diffusion

Jonathan Larson¹, Satyaveda C. Bharath², William G. Cullen¹, and Janice E. Reutt-Robey²

¹Department of Physics, University of Maryland, College Park MD, 20742

²Department of Chemistry and Biochemistry, University of Maryland, College Park MD, 20742

Recently our laboratory undertook the study of a model system: a multi-walled carbon nanotube (MWCNT) affixed at the terminus of a conductive scanning probe microscope cantilever, interfaced with a thin film of vapor-deposited lithium atop a silicon (111) substrate under ultra-high vacuum conditions. The study of this system resulted in the development of a dual-purpose technology in which the MWCNT could act as both a lithium nanopipette and probe (LNPP) for non-contact atomic force microscopy (NC-AFM) measurements. With the application of appropriate bias, separation distance, and contact time the LNPP could site-selectively extract (expel) attograms of lithium from (to) the sample surface. Depressions, mounds, and spikes were generated on the surface in this way and were azimuthally symmetric about the selected point of pipetting. Post mass transfer the MWCNT pipette-induced features were sequentially imaged with NC-AFM using the MWCNT as the probe. Monitoring the morphological evolution of the induced surface features in this way revealed a diffusion-limited decay process. The observed surface diffusion motivated the creation of a model describing the system and the surface diffusion coefficient was evaluated: $D=7.5 (\pm 1.3) \times 10^{-15} \text{ cm}^2/\text{s}$. This LNPP technique should support a broad range of time-dependent ion and nanoelectrode characterization studies of fundamental importance to energy storage research.

11. Imaging dynamic Li electrode processes via an *in-situ* TEM liquid cell

Andrew J. Leenheer, John P. Sullivan, Katherine L. Jungjohann,
Kevin R. Zavadil, and C. Thomas Harris

Sandia National Laboratories, New Mexico

The electrode/electrolyte interface in electrochemical devices is largely studied by indirect methods, but advances in microfabrication allow the design of a miniature electrochemical cell to be used in a transmission electron microscope (TEM). We have developed a TEM liquid cell specifically designed for imaging nanoscale electrochemistry that incorporates quantitative electrochemical control, multiple electrodes spaced for easy nanoparticle assembly, and sealable fluid fill ports for operation with air-sensitive materials. In the study of battery materials, we have focused on the electrode/electrolyte interactions on anode materials in lithium-ion batteries such as the formation, growth, and dynamics of the solid-electrolyte interphase (SEI). Filling the liquid cell with aprotic battery electrolyte containing LiPF₆ salt, lithium was clearly and controllably electroplated on nanoscale titanium electrodes under galvanostatic control, and a formation of natural and/or beam-induced SEI was visible on the lithium deposits under scanning mode (STEM) with minimal beam dose. Stripping the lithium showed direct evidence of stranded Li and SEI upon cycling such as might occur in secondary lithium batteries (e.g., Li-S or Li-air). The TEM can provide new, direct information about the structure and dynamics of battery materials and interfaces in the *in-situ* liquid environment.

12. Ion Transport in Nanochannels

Xin Li, Weihua Guan, Mark Reed

Yale University

Ion transport in nanochannels is a burgeoning area of research with a broad range of potential applications including ionic control, filtration, and energy storage and conversion. In our previous study of gated nanochannels, a field effect reconfigurable nanofluidic diode is demonstrated and a solid-state proto cell is investigated with modulating membrane potentials. Currently, we are focusing on divalent ion transport in nanochannels. Using open potential measurement, charge inversion is observed when the bulk ionic strength reaches a critical point. The conductance measurement of MgCl₂ reveals intriguing phenomenon about ion-ion correlation in the high concentration regime of multi-valence ions.

13. All-in-one Nanopore Battery

Chanyuan Liu^{i,ii}, Xinyi Chen^{i,ii,s,†}, Eleanor I. Gillette^{iii†}, Alexander J. Pearse^{i,ii}, Alexander C. Kozen^{i,ii}, Marshall A. Schroeder^{i,ii}, Keith E. Gregorczyk^{i,ii,‡}, Sang Bok Lee^{i,iii*}, and Gary W. Rubloff^{i,ii*}

¹ Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA,

¹ Institute for Systems Research, University of Maryland, College Park, Maryland 20742, USA,

¹ Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA,

^s Lam Research Corporation, Tualatin, Oregon 97062, USA,

[‡] CIC nanoGUNE, 20012 Donostia, Gipuzkoa, Spain

[†] These authors contributed equally to this work.

*e-mail: slee@umd.edu; rubloff@umd.edu

A conformal single nanopore structure that embeds all components of an electrochemical storage device could bring about the ultimate miniaturization of energy storage. At the same time, it provides a testbed for examining the ion transport limits in nanostructured storage. Here, we report a nanobattery comprised of nanotubular electrodes and electrolyte confined within an anodic aluminum oxide nanopore as an “all-in-one” nanopore device. The nanoelectrodes include Ru nanotube current collectors with V₂O₅ storage material on top of the Ru to form a symmetric full storage cell, with anode and cathode separated by an electrolyte region. The V₂O₅ is prelithiated at one end to serve as anode while pristine V₂O₅ at the other end serves as cathode, so that the battery can be asymmetrically cycling between 0.2V and 1.8V. Capacity retention of this full cell at high power (relative to 1C values) is 95% at 5C and 46% at 150C. At 5C rate (12 min charge-discharge cycle), 81.3% capacity remains after 1000 cycles. The all-in-one nanopore battery poses an extreme case of highly confined organic electrolyte environments in ultrasmall batteries and provides a valuable data source for understanding ion transport in dense packed ion storage nanostructures.

14. Controlled Cathode/Catalyst Architectures for Li-O₂ Batteries

Malakhi Noked, Marshall Schroeder, Chanyuan Liu, Alex Pearse, Alex Kozen, Gary Rubloff and Sang-Bok Lee

University of Maryland, College Park

Electrochemical power sources based on anode_{metal}|electrolyte|cathode configuration have the highest specific energy density due to the high energy density of the metal anode (3842mAh/g¹ for Li). Li-O₂ secondary system consumes oxygen from the surrounding environment during discharge to form oxides of lithium on the cathode scaffold with a theoretical reversible potential of ~2.959V and 2.913V (Li₂O₂ and Li₂O respectively). Despite the promising theoretical metrics, a typical Li – O₂ discharge–charge loop will generally present large over-potentials between the oxygen reduction reaction (ORR-discharge) and oxygen evolution reaction (OER-charge), resulting in poor round-trip efficiency and diminished power output.

We present herein the use of a novel Li – O₂ model cathode system to deconvolute the effects of different catalyst systems on the OER/ORR reactions in non-aqueous Li-O₂ cell. We use mesoporous CNT sponge as the main cathode material, and we decorate it with catalyst nano-particle by ALD.

So far we successfully decorated the cathode with various catalysts (Ru, RuO₂, MnO₂, and Pt). We are capable of tuning the loading amount and composition of those catalyst on the cathode by manipulating the ALD conditions. Using homemade Li-O₂ battery, we demonstrated the effect of different catalysts on the voltage of OER and ORR, and on the cycling performances of the cell.

So far we managed to demonstrate LiO₂ cell with more than 15 cycles, at 200 mAg⁻¹ to more than 3000 mAhg⁻¹.

We believe that using a variety of catalysts with similar morphology, and testing these cathodes in the same system will enable us to gain a real comparison and understanding of the role of the different catalyst in the OER and ORR, and to make the right choice of the catalyst for a better Li-O₂ performances.

15. Origins of the enhanced capacity retention in copolymerized sulfur - based nanocomposite cathodes for high-energy density Li-S batteries

Vladimir P. Oleshko,^{†‡} Jenny Kim,[†] Jenny L. Schaefer,[†] Andy Herzing,[†] Jeremy Ticey,[‡] Steven D. Hudson,[†] Christopher L. Soles,[†] John Cumings,[‡] Adam G. Simmonds,[‡] Jared J. Griebel,[‡] Woo Jin Chung,[‡] Jeffrey Pyun^{†‡}

[†]Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD

[‡]Department of Materials Science and Engineering, University of Maryland, College Park, MD

[‡]Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ

Poly(sulfur-random-(1,3-diisopropenylbenzene) (poly(S-*r*-DIB)) copolymers synthesized via inverse vulcanization represent a new class of electrochemically active polymeric materials that exhibit an enhanced capacity retention (1005 mAh/g at 100 cycles) and lifetimes over 500 cycles in cathodes for high-energy density Li-S batteries. As an effective cross-linking agent, DIB enables to confine lithium polysulfides generated during cycling. This can essentially suppress the shuttle effect and therefore extend the long term battery performance. To gain further insights into mechanisms of the enhanced capacity retention, we have investigated the structural architectures, morphology, sulfur and carbon distributions over composite poly(S-*r*-DIB)-conductive carbon cathodes containing various contents of the electroactive poly(S-*r*-DIB) copolymers as well as their transformations under cycling using field-emission scanning electron microscopy, high-resolution analytical electron microscopy and electron tomography. Due to better cohesion between the copolymer and carbon nanoparticles, micron- and submicron-sized particles of poly(S-*r*-DIB) copolymers tend to embed aggregated carbons creating random 3D percolation networks. Disordered onion-like carbon particles of 20 nm to 60 nm in size in such aggregates display local short-range ordering with 0.39 nm inter-shell spacing of outer graphite-type layers and mixed sp²/sp³ carbon-carbon bonding largely responsible for the formation of 3D conductive pathways and creation of large interfacial area electrochemically active interfaces. Furthermore, an increase of the DIB content in the copolymer from 10% wt. up to 50% wt. has dramatically enhanced the molecular level compatibility of the cathode components, thereby significantly improving its homogeneity and mechanical integrity although preserving at the same time meso- and nanoscale porosity.

16. Electrochemical lithiation of manganese dioxide within nanopore structures

Timothy Plett¹, Trevor Gamble¹, Eleanor Gillette², Mya Le Thai³,
Reginald Penner³, Sang Bok Lee², Zuzanna S. Siwy^{1,3}

¹University of California, Irvine, Department of Physics,

²University of Maryland, Department of Chemistry, College Park, Maryland,

³Department of Chemistry, Irvine, California

Understanding and utilizing manganese oxide has been one of the primary thrusts of the EFRC. Major results of the collaboration have shown manganese oxide to have unique capacitance properties at the nanoscale, which are desirable in some electrical applications. Recent work has illuminated the ionic transport properties of the material and has identified its porous structure to have sub 5nm diameter voids. As a result, new areas of inquiry have become available to explore. In this study, we attempted the synthesis of other manganese oxide-based compounds at the nanoscale, in particular lithium manganese dioxide (MnOOLi), a potential candidate for use as cathode material in lithium ion batteries. Multipore samples with opening diameters of 200 nm were coated with a gold layer via sputter deposition and then electrochemically deposited with manganese oxide wires. The gold layer extended inside the pores, in direct contact with the MnO₂ wires, which permitted electrochemical reduction of the wires with a non-aqueous lithium perchlorate solution. Measurements of ionic current through the wires before and after reduction demonstrated a general increase in conductivity, evidence that the material had been successfully altered. Deposition was confirmed by SEM taken after dissolving the multipore membrane. Further confirmation will be sought by analyzing the manganese wires by ICP-MS.

17. Love Thy Neighbor: By Charging Them

Pradeep Ramiah Rajasekaran, Peng Gao, Xiaojian Wu, William Hardy, Charles. R. Martin

Department of Chemistry, University of Florida, Gainesville, FL- 32611

Storing Energy or in layman terms “charging up” entails selective capturing of ions, concentrating them in specific locations and conducting them efficiently. As ions are inherently charged, capturing, concentrating and conducting them require the presence of an opposite or in some cases similar charge in the neighborhood. Our group exploits this fundamental nature of ionic interaction to study the behavior of ions in the vicinity of charged surfaces. Charged surfaces are fabricated by electrical injection of charges and covalent or electrostatic binding of charges to solid substrates. The poster to be presented will briefly explain the various charging techniques employed by our group to capture, concentrate and conduct ions which can lead to a fundamental understanding of the energy transport and storage mechanism apart from opening up various exciting avenues.

Chemically modified crown ether tethered nano pores are employed to capture Pb^{2+} ions with high selectivity. Detection limits as low as 200 ppb is achieved using these membranes. Template prepared voltage charged gold nanotube membrane is used to concentrate ions selectively inside the nanotube. The concentration inside the nanotube is two orders of magnitude higher than the bulk. The concentration of accumulated ions can be modulated by tuning the applied voltage. Similar voltage charged, template prepared carbon mesotube membrane is used to transport molecules via modulating the electroosmotic flow by tuning the applied voltage. Apart from template synthesized membranes, positive or negatively charged solid state planar substrates are also used to increase the ionic conductivity of selective analytes. All the above mentioned techniques can be modified to adapt any system involving ionic transport such as energy storage.

18. Freestanding, Binder-Free, 3D Li-O₂ Battery Cathode

Marshall Schroeder, Malakhi Noked, Alex Pearse, Alex Kozen
Gary W. Rubloff and Sang Bok Lee

University of Maryland, College Park

The capabilities of Li-O₂ battery technology are currently being limited by scientific challenges that must be addressed in each component of the device, but the positive electrode is particularly complicated by its role in OER/ORR, leading to strict requirements for architecture and physicochemical stability for optimal performance. In an effort to satisfy these requirements, we present herein one of the first experimental realizations of a controlled macroscale 3D CNT architecture. Consisting of densely packed vertically aligned carbon nanotubes (VACNT) grown directly on Ni foam with a thin ALD interlayer, this specially tuned hierarchically porous structure can accommodate a substantial amount of reduction product without blocking cathode pore orifices. Practical loading of ~1mg (carbon)/cm² yields significant capacity at high ORR voltages (>2.7V with no catalyst).

19. Electrochemical Insertion/Deinsertion of Mg²⁺ Ions into MnO₂ Nanowires

Jaehee Song, Malakhi Noked, Eleanor Gillette, and Sang Bok Lee

University of Maryland, College Park

We investigated the electrochemical insertion/deinsertion behaviors of Mg²⁺ ions into/from nanostructured MnO₂ by utilizing various spectroscopic and microscopic techniques. We determined the stoichiometry of Mg²⁺ ions and Mn in discharged MnO₂ electrode by directly analyzing the inserted amount of Mg²⁺ ions using inductively coupled plasma – optical emission spectroscopy (ICP-OES). In addition, we studied the effect of small amount of water molecules added to the organic magnesium electrolyte, motivated by the previous studies where positive effect of water molecules in Mg²⁺ insertion behavior into layered structure V₂O₅ was observed. We found that the sluggish Mg²⁺ insertion/deinsertion behaviors into MnO₂ can be suppressed by presence of water molecules in organic electrolytes, presumably due to the preferential solvation of Mg²⁺ ions by water molecules which could “shield” the divalent charges of Mg²⁺ ions reducing the electrostatic force between MnO₂ and Mg²⁺. The cyclic voltammogram

measurements showed that there was no considerable degree of Mg^{2+} insertion/deinsertion reactions in pure magnesium electrolyte whereas distinct peaks that are responsible for Mg^{2+} insertion/deinsertion were observed in water containing electrolytes. In addition, we found that the nanostructured MnO_2 electrode delivered improved Mg^{2+} insertion/deinsertion capabilities compared to the planar MnO_2 electrode due to the shorter ionic diffusion length and high surface area of nanostructure allowing the Mg^{2+} ions to overcome the electrostatic force.

20. Adsorption and Reaction Branching of Molecular Carbonates on Neat and Lithiated C(0001) Substrates

Wentao Song, Satyaveda Bharath and Janice Reutt-Robey

University of Maryland, College Park

The adsorption and interactions of ethylene carbonate (EC) and dimethyl carbonate (DMC) with neat and lithiated graphite substrates were measured by temperature programmed desorption (TPD) and reaction (TPR) methods under UHV conditions. Both EC and DMC interact weakly with the neat C(0001) surface with adsorption energies of 0.60 ± 0.06 eV and 0.64 ± 0.05 eV, respectively. Addition of Li^+ to the C(0001) substrate significantly increases the binding energies of molecular carbonates, and the range of measured values is indicative of EC solvation of lithium ions. EC undergoes complete decomposition on metallic Li films. Organolithium products were quantified by TPRS and the amount of lithium carbonate product was determined by detailed mass balance analysis. Decomposition of 1.5 L of EC resulted in the formation of 0.21 ± 0.02 L lithium ethylene dicarbonate, 0.19 ± 0.02 L lithium ethylene glycol, and 0.89 ± 0.03 L lithium carbonate. This branching indicates that EC decomposition occurs predominantly through two-electron reduction in the monolayer regime.

21. Defect-Tailored Interface Stabilizes Si-C Composite Anodes

Chuan-Fu Sun,¹ Hongli Zhu,² Morihiro Okada,¹ Karen Gaskell,¹ Yoku Inoue,³
Liangbing Hu,² YuHuang Wang^{1*}

¹ Department of Chemistry and Biochemistry, University of Maryland

² Department of Materials Science and Engineering, University of Maryland.

³ Department of Electrical and Electronic Engineering, Shizuoka University, Japan

Email: cfsun@umd.edu; yhw@umd.edu

The structural instability of high capacity electrode materials such as silicon is a challenging issue that seriously restrains their utilization in ion batteries. Here, we describe a Si-CNT composite anode with robust Si-C bonding that effectively addresses this challenge. By chemically introducing functional groups on carbon nanotubes, the defect-tailored Si-C interface significantly reduces delamination and agglomeration of Si. Electrochemical cycling of half cells shows a nine times increase in cycling stability solely due to the chemically tailored Si-C interface.

22. In Situ Electrical Characterization of MnO_2 Nanowires

Mya Le-Thai, Wenbo Yan, Rajen Dutta, Reg Penner

University of California, Irvine

MnO_2 excels as a hybrid electrical energy storage material that can intercalate lithium ions as a secondary battery electrode and instantaneously store energy as an electrical double layer capacitor. The previous work by our group established a system to study ultra long MnO_2 nanowires in depth, and has shown significant improvement in their energy storage performance. In this work, the design is used to investigate the structural and electrochemical changes on delta-phase MnO_2 nanowires through in situ conductivity measurements performed during the lithium ion insertion process. These effects of the lithium ion insertion are studied on arrays of two hundred MnO_2 nanowires that are 40-60 nm in height, 275-870 nm in width and span a 10 μm gap between two Au contacts. As the lithium

ion doping potential decreases to more negative voltages, the resistance of each MnO₂ nanowire array decreases. The change in resistance also depends on the width of nanowires. After doping at -0.8 V vs. MSE, the resistance decreases by 30% for a 870 nm wide nanowire array and 88% for a 275 nm wide nanowire array, respectively. TEM studies show that the difference in porosity among the different width wires alters this variation in resistance response.

23. Graphene/sulfur and CNT/sulfur nanocomposite heterostructures for ultrafast, long-life, high-energy density lithium-sulfur batteries

Jeremy Ticey,[†] Vladimir Oleshko,^{†‡} Chao Luo,[‡] Chunsheng Wang,[‡] and John Cumings[†]

[†]*Departments of Materials Science and Engineering[†] and Chemical and Biomolecular Engineering[‡], University of Maryland, College Park, MD*

[‡]*Materials Science and Engineering Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD*

The increasing reliance on high capacity energy storage systems is constantly pushing research efforts to finding better performing, low cost electrochemical batteries to power emerging technology applications. The lithium-sulfur (Li-S) battery has been deemed one of the most viable candidates due to its high energy density, light weight, abundant, non-toxic and inexpensive components. However, in order to reach its full potential, sulfur, a classical insulator, should be incorporated into a conductive carbon host structure to ensure its electrical conductivity and cycling performance. It has been reported recently that 1D monoatomic sulfur chains confined in the interior of a single-walled carbon nanotube (SW-CNT) exhibit electrically conducting behavior under ambient conditions. In addition to this unique size-confined transformation, the SW-CNT can prevent volume expansion which causes mechanical stresses and battery degradation.^[1] In the case of graphene, graphene sheets surrounding sulfur particles in the cathode can act as both an efficient current collector, and a separating barrier for the diffusion of soluble lithium polysulfides which lead to the capacity fading through the shuttle process.^[2] Although clear improvements in the capacity retention were recently demonstrated, the precise enhancement mechanisms have yet to be clarified. We intend to explore advanced engineering approaches through the fabrication of binder-free nanocomposite cathodes (sulfur-filled CNTs, graphene-sulfur sandwiches and related hybrid heterostructures) as well as Li-based anodes via direct implanting of Li and lithiation of Si nanowires. The new nanocomposite heterostructures will be utilized to assemble Li-S batteries suitable for electrical cycling in a scanning/transmission electron microscope *in-situ*. From this, we intend to gain a deeper understanding of the fundamental electrochemical reaction mechanisms and kinetics, which would allow for the optimization of the key components for next generation of ultrafast, long-life, high-energy density Li-S batteries.

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