

## SYMPOSIUM B

### Next-Generation Batteries, Supercapacitors and Other Storage Materials

November 28 - December 1, 2005

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\* Invited paper

**8:00 AM \*B1.1**

**Fabrication and Properties of Electrode Arrays for 3D Battery Architectures.** Bruce Dunn<sup>1</sup>, Yuting Yeh<sup>1</sup>, Fardad Chamran<sup>2</sup>, Hong-Seok Min<sup>1</sup>, Eduardo Falco<sup>3</sup>, Sarah Tolbert<sup>3</sup>, Chang-Jin Kim<sup>2</sup>, Fred Wudl<sup>3</sup> and Dong Sun<sup>3</sup>; <sup>1</sup>Materials Science and Engineering, UCLA, Los Angeles, California; <sup>2</sup>Mechanical and Aerospace Engineering, UCLA, Los Angeles, California; <sup>3</sup>Chemistry and Biochemistry, UCLA, Los Angeles, California.

Three-dimensional architectures offer an interesting direction for miniaturizing batteries. One characteristic feature of such structures is that transport between electrodes is one-dimensional at the microscopic level, yet the electrodes are arranged in complex, non-planar geometries. Such geometries offer certain advantages, with the most attractive being the prospect of achieving high energy and power density within a small areal footprint. These features are especially important for the powering of MEMS devices where the areal footprint for the power source is limited to millimeter dimensions. The central element in creating these new cell architectures is the fabrication of a 3-D matrix of electrodes which meets the requirements of short transport distances and reasonable energy capacity. The present paper addresses our progress in the fabrication of 3-D electrode arrays. Our approach for 3D electrode fabrication is based on combining silicon micromachining with colloidal processing of electrode powders. Silicon molds with 60 micron diameter through holes are fabricated using DRIE. Electrode materials including vanadium oxide nanorolls (VONR) and carbon (MCM) are dispersed in an appropriate solvent and filled into the mold by filtration methods. The electrodes are released from the molds by immersing in tetraethylammonium hydroxide. A back-side conducting epoxy layer provides structural support and electrical contact to the electrode array. In the study reported here, we show that extending the length of the rod to increase the aspect ratio leads to increasing capacity per unit area. 3-D electrode arrays composed of the VONR electrode material exhibited areal normalized capacities ranging from 0.29 mAh/cm<sup>2</sup> to 2.56 mAh/cm<sup>2</sup> for aspect ratios of 0.5 and 2, respectively. By comparison, the same VONR electrode material prepared on a stainless steel screen current collector exhibits an areal capacity of only 0.17 mAh/cm<sup>2</sup> despite the fact that the gravimetric capacity for this material is in the range of 300 mAh/g. These results underscore the point that 3-D batteries become more attractive with increasing aspect ratio, provided the electrode resistance remains low.

**8:30 AM B1.2**

**Colloidal-Scale Self-Organized Lithium Batteries.**

Yet-Ming Chiang, Ryan Wartena and Young Kyu Cho; Materials Science and Engineering, M.I.T., Cambridge, Massachusetts.

The power density - energy density tradeoff that limits electrochemical power sources is determined not only by the active materials and their properties, but also by device design. In pursuit of alternatives to conventional laminated designs with higher performance potential, we have developed a colloid-based approach whereby repulsive forces between dissimilar materials are used to form in-situ electrochemical junctions in dense particle arrays, while attractive forces between like materials are used to form continuous electronically conductive networks. Using surface forces in our favor, such systems tend towards a "phase separated" thermodynamic ground state producing a bipolar electrochemical device, as opposed to directly fabricated structures which may be far from equilibrium. Results will be presented in which repulsive short-range forces are deliberately introduced between the classical lithium ion battery materials LiCoO<sub>2</sub> and graphite by selection of organic solvents, resulting in the first lithium ion battery that is entirely self-organized. Electrochemical tests demonstrating battery functionality, and challenges for device improvement, will also be discussed. This work was supported by U.S. AFOSR Grant No. F49620-02-1-0406. RW was supported by a DCI Postdoctoral Fellowship.

**8:45 AM B1.3**

**Coating Monolithic Macroporous Carbon Electrodes with Polymeric and Inorganic Electrolytes.** Nicholas S. Ergang<sup>1</sup>,

Justin C. Lytle<sup>1</sup>, Kyu T. Lee<sup>2</sup>, Seung M. Oh<sup>2</sup> and Andreas Stein<sup>1</sup>; <sup>1</sup>Chemistry Department, University of Minnesota, Minneapolis, Minnesota; <sup>2</sup>School of Chemical Engineering, Seoul National University, Seoul, South Korea.

Colloidal crystal templating techniques were used for the synthesis of three-dimensionally ordered macroporous (3DOM) Li ion secondary cathodes and anodes with the intention of improving the rate capability of each electrode. Monodisperse poly(methyl methacrylate)

(PMMA) spheres were sedimented to form a cubic close packed colloidal crystal. Sol-gel precursors were infiltrated into the void spaces and the material was heated to an amorphous or nanocrystalline framework around the template. The spheres were removed during calcination, leaving the solid skeleton around ordered void spaces. The electrode structures were composed of well-interconnected pore and wall networks with wall thicknesses of tens of nanometers that allow for shortened diffusion pathlengths, thereby improving the rate capability. Various electrodes from anodes such as SnO<sub>2</sub> and carbon to cathodes such as V<sub>2</sub>O<sub>5</sub>, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiCoO<sub>2</sub> have been synthesized with this architecture. Rate studies of 3DOM LiCoO<sub>2</sub> and carbon anodes have demonstrated improved rate capability relative to bulk electrodes. Millimeter-sized monolithic carbon pieces prepared with this architecture have a robust nature and interconnected macroporosity that make them good candidates for the foundation of a solid-state three-dimensionally interpenetrating battery. The next step involves deposition of a "pinhole-free" organic or inorganic electrolyte onto the carbon framework. Polymer electrodeposition is believed to be a good method for uniform, thin, pinhole free polymer coatings due to the self-limiting nature of the redox polymerization. Three different polymers, sulfonated poly(phenylene oxide) (sPPO), poly(phenylene oxide) (PPO), and PMMA were electrodeposited galvanostatically on the surface of the carbon monoliths. Both sPPO and PPO are of interest as Li ion electrolytes due to high voltage breakdown properties associated with each polymer. Incomplete decay of the electro-oxidative current was observed in electropolymerizations of PPO and sPPO on 3DOM carbon; however, complete decay was achieved on bulk, non-templated carbon monoliths. In order to further explore the role of the electrode porosity on the uniform electrodeposition of a polymer coating, PMMA was electrodeposited on monoliths prepared with varying amounts of mesoporosity. PMMA also served as a basis for the deposition of an inorganic electrolyte, Li<sub>0.5</sub>La<sub>0.5</sub>TiO<sub>3</sub>. The organic and inorganic coatings were analyzed for coating uniformity and coverage. The pore structure of the modified electrodes was characterized by scanning electron microscopy and nitrogen sorption measurements. Cyclic voltammetry and galvanostatic cycling were used to further characterize the coatings.

**9:00 AM B1.4**

**Three-Dimensional Battery Nanoarchitectures.**

Debra R. Rolison<sup>1</sup>, Christopher P. Rhodes<sup>1</sup>, Justin C. Lytle<sup>1</sup>, Jeffrey W. Long<sup>1</sup>, Katherine A. Pettigrew<sup>1,2</sup> and Rhonda M. Stroud<sup>2</sup>; <sup>1</sup>Surface Chemistry, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Sensors and Materials, Naval Research Laboratory, Washington, District of Columbia.

Electrically conductive mesoporous nanoarchitectures with pores sized on the order of tens of nanometers [1] are platforms in which fully interpenetrating three-dimensional charge-storage devices can be created, once appropriate dielectric and/or ionically conducting coatings are synthesized conformally within the confined spaces of the mesoporous electrode structure [2]. The electrooxidation of phenol and substituted phenols in basic electrolyte at films of rough oxides generates poly(phenylene oxide) films that are tens of nanometers thick, conformal, highly electronically insulating, and exhibit dielectric strengths comparable to those measured for the bulk polymer [3]. Ions are incorporated within the electrodeposited films by either solvent casting methods or electrooxidizing substituted phenols with ionic functionality [3]. After the pinhole-free, ultrathin polymer barrier is formed over the "walls" of the birnessite-type lithium-ion-insertion MnO<sub>2</sub> nanoarchitecture, the remaining free volume must then be filled with a counterelectrode. Anhydrous, nanoscopic RuO<sub>2</sub>, which can function as a lithium-ion-insertion counter electrode, is cryogenically deposited [4] on the polymer-coated MnO<sub>2</sub> nanoarchitecture from a solution of RuO<sub>4</sub> in hexane yielding a controlled deposition of RuO<sub>2</sub> within the pore volume. Transmission electron microscopy demonstrates the genesis of 2-nm RuO<sub>2</sub> particles that adhere to the polymer and self-aggregate, resulting in deposition of RuO<sub>2</sub> throughout the architecture. Solid-state electrical measurements of RuO<sub>2</sub> deposited on PPO-coated ITO in a planar configuration demonstrate that RuO<sub>2</sub> can be deposited without electrically shorting the ultrathin films. The MnO<sub>2</sub>—polymer—RuO<sub>2</sub> nanoarchitecture that results is a solid state, fully integrated in three dimensions, nanoscopic energy storage device. [1] D.R. Rolison, B. Dunn, *J. Mater. Chem.* **11** (2001) 963. [2] J.W. Long, B. Dunn, D.R. Rolison, H.S. White, *Chem. Rev.* **104** (2004) 4463. [3] C.P. Rhodes, J.W. Long, M.S. Doescher, J.J. Fontanella, D.R. Rolison, *J. Phys. Chem. B* **108** (2004) 13079. [4] J.V. Ryan, A.D. Berry, M.L. Anderson, J.W. Long, R.M. Stroud, V.M. Cepak, V.M. Browning, C.I. Merzbacher, D.R. Rolison, *Nature* **406** (2000) 169.

**9:15 AM B1.5**

**Electrophoretic Assembly of Rechargeable Batteries.**

Ryan Wartena, Dong-Wan Kim and Yet-Ming Chiang; Department of Material Science and Engineering, MIT, Cambridge, Massachusetts.

A new Li-ion microbattery approach is presented where both electrodes are assembled in a planar configuration by electrophoretic deposition (EPD) and embedded in a solid polymer electrolyte (SPE). This allows formation of a complete battery assembly in-situ in a small number of steps. Small inter-electrode distances (5-20 microns) which allows for high fields and localized deposition enabling a variety of microbattery structures. In this paper, the fundamental particle charging mechanisms are identified, and various deposition modes ranging from uniform particle deposition to dendrite formation are explained. These characteristics are then controlled in order to create microbatteries of a range of size scales, based on both liquid and solid-polymer electrolytes. Detailed electrochemical tests will be presented, and the performance potential of this class of device will be compared to others such as thin film batteries.

#### 9:30 AM B1.6

**Microstructural Modeling and Design of Three-Dimensional Batteries.** R. Edwin Garcia<sup>1</sup> and Yet-Ming Chiang<sup>2</sup>; <sup>1</sup>Materials Engineering, Purdue University, West Lafayette, Indiana; <sup>2</sup>Materials Science and Engineering, MIT, Cambridge, Massachusetts.

The effective power and energy density delivered by a rechargeable lithium ion battery is determined by the electrochemical and kinetic properties of its constituent materials and underlying microstructure. Furthermore, while the thermodynamic state of a volume element of active material is determined entirely by the local particle-particle electrochemical interactions, one dimensional battery designs fail to fully take advantage of the driving forces that control the intercalation and de-intercalation. In this paper, a method is presented where the details of the electrochemical and stress fields are resolved in an effort to maximize the performance of the device. The advantages and limitations of conventional rocking-chair configurations and novel cutting-edge battery designs, such as hybrid, self-assembled, and patterned columnar structures are discussed.

#### 9:45 AM B1.7

**Li-ion Capacity Enhancement in Composite Blends of LiCoO<sub>2</sub> and Li<sub>2</sub>RuO<sub>3</sub>.** Arnold M. Stux and Karen Swider-Lyons; Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia.

The specific capacity and energy of Li-ion batteries is improved at high rates by blending the LiCoO<sub>2</sub> in the cathodes with Li<sub>2</sub>RuO<sub>3</sub>. LiCoO<sub>2</sub> is a standard active material used in Li-ion batteries, and Li<sub>2</sub>RuO<sub>3</sub> is a highly stable Li-insertion compound with high electronic and Li-ion conductivity. Batteries with LiCoO<sub>2</sub> or Li<sub>2</sub>RuO<sub>3</sub> cathodes are compared to ones with blends of the two active materials by discharging from 4.2 to 2.0 V at C/5 and 2C rates. The Li-ion batteries with a 58:42 w/w LiCoO<sub>2</sub>/Li<sub>2</sub>RuO<sub>3</sub> cathode blend have a disproportionate increase of 25 and 36% in their expected specific capacity and energy, respectively, relative to LiCoO<sub>2</sub> when the batteries are charged and discharged at a 2C rate. X-ray diffraction of the electrodes at a high state of charge confirms that the LiCoO<sub>2</sub> and Li<sub>2</sub>RuO<sub>3</sub> phases remain distinct in the electrodes. Analysis of the discharge curves in combination with electrochemical impedance spectroscopy shows that Li<sub>2</sub>RuO<sub>3</sub> lowers the electrical resistance of the electrodes when combined in parallel to the LiCoO<sub>2</sub>. This simple approach may be used to improve the capacity of Li-ion batteries for high rate applications.

#### 10:30 AM B1.8

**Templated Nanocomposite Electrodes for Rechargeable Lithium Batteries.** Elsa A. Olivetti, Jong Hak Kim, Donald R. Sadoway and Anne M. Mayes; Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

In this work, we investigate the fabrication of high energy density electrode materials for solid-state rechargeable batteries by incorporating continuous, nanoscale phases within one component of self-organizing amphiphilic copolymer systems. The in situ growth of cathodic components in ion-conducting copolymer domains allows for control of morphology and increases the interface-to-volume ratio, thereby increasing the specific electrode area over which faradaic reactions can occur and decreasing ion diffusion distances within the electrode. We begin with templates of microphase-separating rubbery block and graft copolymers that our research group has previously developed as solid-state electrolytes. The template systems include atom transfer radical polymerized poly((oxyethylene)<sub>9</sub> methacrylate)-block-poly(butyl methacrylate), POEM-b-PBMA and free-radically synthesized poly((oxyethylene)<sub>9</sub> methacrylate)-graft-poly(dimethyl siloxane), POEM-g-PDMS. The resulting microphase-separated polymer is a structure of alternating hydrophilic (Li-ion conducting) and hydrophobic regions. Sol-gel chemistry involving vanadium alkoxide precursors enables in situ growth of active vanadium oxide phases within the continuous ion conducting domains of the microphase-separated copolymer. Small angle x-ray scattering (SAXS) and scanning transmission electron

microscopy (STEM) reveal the morphology of the nanocomposite and confirm the spatially-selective incorporation of the inorganic component. Through the use of different alkoxide precursors of vanadium and prehydrolyzing the precursor prior to incorporation, up to 30wt% (13v%) inorganic in varying morphologies can be obtained. The nanoscale, structure-directing property of the microphase separating copolymer system can also be used to incorporate electronically conductive components needed for wiring of the lithium-active vanadium oxide domains.

#### 10:45 AM B1.9

**High capacity 3D-microbatteries with electrochemically deposited composite thin-film cathodes.** Menachem Nathan<sup>1</sup>, Diana Golodnitsky<sup>2</sup>, Vladimir Yufit<sup>1</sup>, Ella Strauss<sup>2</sup>, Kathrin Friedman<sup>2</sup>, Larisa Burstein<sup>3</sup>, Alexander Gladkikh<sup>3</sup> and Emanuel Peled<sup>2</sup>; <sup>1</sup>Department of Physical Electronics, School of EE, Tel Aviv University, Tel Aviv, Israel; <sup>2</sup>School of Chemistry, Tel Aviv University, Tel Aviv, Israel; <sup>3</sup>Wolfson Applied Materials Research Center, Tel Aviv University, Tel Aviv, Israel.

Progressing from 2D to 3D thin-film microbattery (MB) structures represents an important shift in the development of miniaturized electrochemical power sources (M. Nathan et al., MRS Proceedings, vol. 835, K.10.10.1 - K10.10.6, 2004). The development process of a 3D-MB on a perforated substrate has to solve complicated technical barriers, such as deposition and/or insertion of a thin-film sandwich comprising a current collector, a high-capacity thin cathode, an ion-conducting membrane and an anode/current collector filling in long (50 micrometer) and narrow (<50 micrometer) channels. Here we report on electrochemically deposited improved "composite" thin-film molybdenum oxysulfide cathodes that allow an almost doubling of a 3D-MB capacity per given footprint over conventional thin-film cathodes. The "composite" refers to the incorporation of PEGDME and PEO additives of different molecular weights and concentrations in a modified electrolyte bath. Various characterizations were performed to elucidate the source of the improved MB performance. SEM micrographs show that cathode films obtained from the modified electrolyte comprise predominantly plate-like crystallites densely covered by small polymer-like single spheres or assemblages of spheres. XPS and TOF-SIMS tests show the formation of sulfur-rich molybdenum oxysulfide compounds, with the presence of polymer both on the surface and in the bulk. We explain the differences in the morphology and adhesion of the deposits as being due to a more rapid nucleation process taking place in the presence of polymers, as a result of strong specific adsorption of the (-CH<sub>2</sub>-CH<sub>2</sub>-O-) groups on the surface. As a result, the reversible capacity of a 3D Li or Li-ion microbattery with modified cathodes is doubled upon a twofold increase in the current density of cathode deposition. A semi-3D cell with a composite cathode on a glass multichannel plate substrate exhibits a stable cycle life with about 3.5 mAh/(square cm) reversible capacity, up to 30 times that of a planar 2D thin-film cell with the same footprint and about twice that of semi-3D cells with unmodified

#### 11:00 AM B1.10

Abstract Withdrawn

#### 11:15 AM B1.11

**Novel All Carbon Nanotube Battery.** R. Scott Morris<sup>3</sup>, Thomas Gennett<sup>1,2</sup>, Brett M. Gall<sup>3</sup>, Brian Dixon<sup>3</sup>, Chaiwat Engtrakul<sup>2</sup>, Jeffrey Blackburn<sup>2</sup> and Michael J. Heben<sup>2</sup>; <sup>1</sup>Chemistry, Rochester Institute of Technology, Rochester, New York; <sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado; <sup>3</sup>Phoenix Innovation Inc, West Wareham, Massachusetts.

Future portable power applications in the marketplace will demand greater specific energy and power from lithium battery technology. These requirements cannot be met by conventional batteries or through extrapolation of the capabilities of conventional systems. New materials and systems must be developed to meet these stringent future requirements. Nanomaterials offer an exciting alternative to the standard materials traditionally used for fabrication of batteries. The work described herein deals with the use of various carbon nanomaterials in the electrodes of lithium-ion batteries. We have synthesized and chemically modified single- and multi-wall carbon nanotubes and subsequently tested these modified nanotubes as electrodes in lithium batteries of up to 12cm<sup>2</sup> in area. The work described includes electrochemical characterization of the novel electrodes as well as to determination of the specific energy of one-cell batteries containing these novel electrodes. Nanotubes produced via the various synthetic procedures, Arc, CNI-HipCo and Laser were evaluated. The range of results for the various SWNT materials and the dependence of performance on nanotube history will be discussed. The best cell performance to date demonstrates laboratory reversible and cyclable secondary cells with specific energies exceeding 400Wh/kg and pulse power exceeding 3kW/kg

### 11:30 AM **B1.12**

**Electrochemically Active Nanoparticles Made by Flame Spray Pyrolysis.** Frank O. Ernst<sup>1</sup>, Sotiris E. Pratsinis<sup>1</sup>, Joachim Uffheil<sup>2</sup> and Petr Novak<sup>2</sup>; <sup>1</sup>Particle Technology Laboratory, ETH Zuerich, Zuerich, Switzerland; <sup>2</sup>Electrochemistry Laboratory, Paul Scherrer Institut, Villigen, Switzerland.

In modern electrochemical applications, nanoparticles are of growing interest as small dimensions reduce diffusion lengths within particles and increase the number of active sites for surface reactions decreasing the local current density. Thus, when nanoparticles are used as electroactive materials in secondary batteries, the resulting overpotentials are expected to be lower and the charging/discharging rates should be higher. The control of crystallinity, particle size, and morphology as well as both productivity and cost efficiency are important for industrial applications. Flame synthesis is a fast, cost-effective, and versatile process for the production of functional nanoparticles. In particular, flame spray pyrolysis (FSP) allows the production of tailor-made particles with high specific surface area and well defined chemical composition, as recently demonstrated both on a lab scale and pilot-plant scale. In this study, electroactive  $\text{Co}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , and  $\text{LiFe}_3\text{O}_4$  particles with spinel structure (normal, normal distorted, mixed, and mixed inverse) were made by flame spray pyrolysis at production rates of 10 to 20  $\text{g h}^{-1}$ . These materials were characterized by X-ray diffraction and nitrogen adsorption and had a primary crystallite size in the range of 8 to 30 nm and exhibited high temperature stability. The electrochemical properties as measured by slow cyclic voltammetry are reported exemplarily for  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as potential cathode and anode material, respectively, in secondary lithium-ion batteries.

### 11:45 AM **B1.13**

**High rate charge/discharge properties of nanostructured electrodes synthesized through soft solution processes.** Itaru Honma, Huisuk Yun, Takashi Watanabe, Mitsuhiro Hibino and Haoshen Zhou; ETRI, AIST, Tsukuba, Ibaraki, Japan.

For the system in which not only high-energy but also high-power operation is required, such as pure and hybrid electric vehicles, it is crucial to develop auxiliary power sources for rapid discharge and charge. If lithium ion battery is applied to this use, its electrode materials should possess low-price, low-toxicity in terms of widespread diffusion as well as high electrode performance. Many manganese oxides have attracted the attentions as electrode materials of lithium ion battery because they can intercalate lithium and have above natures. With a view to rapid discharge and charge, an active material should be prepared in the form of nanostructured materials and contact preferably with conducting additives, while the nanostructured materials has been successfully prepared by sonochemical method and/or soft solution processing. We have already reported that the synthesis of nanostructured manganese oxides in an aqueous solution provide high power and capacity of 20kW/kg and 320Wh/kg although, without careful removal, residual water degrades cyclability of discharge and charge [1]. In this paper, the application of soft solution processing to synthesize the controlled nanostructure of manganese oxides are reviewed and novel non-aqueous preparation is proposed to obtain improved high rate charge/discharge electrode properties. Mesoporous Titania materials are also prepared via. Evaporation induced self-assembly to possess high surface area and electrical conductivities. High rate anode properties are also demonstrated.

SESSION B2: Phosphate Cathode Materials  
Chairs: Bruce Dunn and Christian Masquelier  
Monday Afternoon, November 28, 2005  
Room 310 (Hynes)

### 1:30 PM **\*B2.1**

**Ab Initio Study of Olivine Cathode Materials.** Dane Morgan<sup>1</sup>, Fei Zhou<sup>2</sup>, Thomas Maxisch<sup>2</sup>, Kisuk Kang<sup>2</sup>, Matteo Cococcioni<sup>2</sup>, Chris A. Marianetti<sup>3</sup> and Gerbrand Ceder<sup>2</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Wisconsin - Madison, Madison, Wisconsin; <sup>2</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>3</sup>Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

Some of the most promising materials for next generation cathodes come from the olivine structural family. This talk gives an overview of ab initio quantum mechanical based approaches to understanding these materials. Key properties that are explored are voltage, ionic and electronic conductivity, and phase stability. The use of so-called LDA+U methods are shown to be necessary for quantitative results for some properties, such as voltage, band gap, and phase stability. The Li and electron mobility are studied and their implications for high rate applications are discussed. We demonstrate that  $\text{Li}_x\text{FePO}_4$

is an insulator with good intrinsic Li mobility, but slow electron conduction through a polaron mechanism.

### 2:00 PM **\*B2.2**

**Studies of Fast Ionic Conductors using  $^6\text{Li}/^7\text{Li}$  Solid-State 2D Exchange NMR.** L. S. Cahill<sup>1,2</sup>, R. P. Chapman<sup>1,2</sup> and Gillian Goward<sup>1,2</sup>; <sup>1</sup>Department of Chemistry, McMaster University, Hamilton, Ontario, Canada; <sup>2</sup>Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada.

Many cathode materials have been explored as alternatives to the classic layered transition metal oxide materials used in rechargeable lithium ion batteries. In particular, recent attention has focused on transition metal phosphates which have open-framework structures, facilitating high ionic conductivity. Here we present multi-dimensional solid-state  $^6\text{Li}/^7\text{Li}$  NMR studies of the monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  material, and several members of the electrochemically cycled materials,  $\text{Li}_{3-y}\text{V}_2(\text{PO}_4)_3$ . We correlate our results with related studies of the parent material, and chemically delithiated members of the  $\text{Li}_{3-y}\text{V}_2(\text{PO}_4)_3$  family.<sup>1</sup> 1D NMR spectra acquired under fast magic angle spinning (25kHz) allows for the resolution of the lithium resonances of interest in such paramagnetic materials. Variable temperature studies (250-400K) provide an estimate of the lithium hopping rates, through analysis of the onset of coalescence between the three lithium resonances. 2D  $^7\text{Li}$  exchange NMR was used to study lithium dynamics among the three lithium sites. For the parent material, structural assignment of the three lithium resonances, as well as measures of hopping rates and activation energies for the lithium transport process are obtained. These results are correlated to internuclear distances determined by X-ray diffraction and macroscopic conductivity measurements obtained by impedance spectroscopy. Solid-state NMR was also used to investigate electrochemically cycled samples during various points of the charge/discharge profile, to obtain a local picture of the structural changes induced during the electrochemical process, as observed through the changing  $^7\text{Li}$  chemical shift as a function of discharge. <sup>1</sup>S.C.Yin et al *J. Am. Chem. Soc.*, **125**, 10402, (2003), and S.C.Yin et al *Chem. Mater.* **16** 1456 (2004).

### 3:30 PM **B2.3**

**The Hydrothermal Synthesis of  $\text{LiFePO}_4$  Revisited.** Jiajun Chen and M. Stanley Whittingham; Chemistry Department, Binghamton University, Binghamton, New York.

$\text{LiFePO}_4$  is a very attractive cathode material due to the low cost of the starting materials and its environmental compatibility. We first reported the hydrothermal preparation of  $\text{LiFePO}_4$  in 2001 (Electrochem. Commun. 3, 505); however, it did not exhibit 100 % utilization due to the presence of ca.7%-8% iron occupancy on the lithium site (Electrochem. Commun. 4, 239). These iron atoms resulted in a much lower reactivity of this material to both lithium insertion and removal, because of the one-dimensional nature of the lithium diffusion. Therefore, hydrothermal synthesis was thought not to be a preferred approach for the synthesis of electrochemically active  $\text{LiFePO}_4$ . However, SudChemie et al at IMLB-Nara in 2004 reported the successful hydrothermal formation of  $\text{LiFePO}_4$ ; however without much detail. This study focuses on optimizing the hydrothermal conditions to obtain structurally sound material with optimum electrochemical behavior. Well-crystalline  $\text{LiFePO}_4$  particles were successfully prepared in the temperature range between 150 and 220 C. The sample and structure purities were determined by powder X-ray diffraction and the lattice parameters determined; less than 1% iron was found on the lithium site. The unit cell parameters and volume of these samples are essentially identical to those samples prepared at high temperatures. The minimization of oxidation to ferric was accomplished by the addition of reducing species such as sugar, ascorbic acid and ammonia. Samples so formed are typically around 1 to 2 micrometers in dimension, and are sometimes found in well-defined crystallites. We will discuss our attempts to coat these materials with electronically conducting layers under the synthesis conditions used, forming  $\text{LiFePO}_4/\text{C}$  composites. We will also describe attempts to dope the lattice to enhance either the ionic or electronic conductivity. The electrochemical behavior of these samples will be compared to those synthesized above 500 C. This work is being supported by the US Department of Energy, Office of FreedomCAR and Vehicle Technologies, through the BATT program at LBNL.

### 3:45 PM **B2.4**

**Effect of dopants on lithium and electron transport in olivine  $\text{LiFePO}_4$ .** Jack Treger, Sharon Dalton-Castor, Karen Thomas-Alyea, Dmitri Novikov and Per Onnerud; TIAX LLC, Cambridge, Massachusetts.

$\text{LiFePO}_4$  is of interest for use as a cathode in lithium-ion batteries because of its good capacity, low cost, and high thermal stability relative to oxide materials. However, its discharge capacity at high rates is limited by both electronic conduction and lithium diffusion.

Morgan et al. [1] have performed quantum mechanical calculations which imply that diffusion is facile only along the b axis of the Pmna space group in LiFePO<sub>4</sub>, and postulated that defects along that 1-D path are responsible for the low experimentally observed diffusivity (on order 10<sup>-17</sup> cm<sup>2</sup>/s). Their study has led some to speculate that dopants on the lithium site would block the 1-D paths, thereby impeding lithium diffusion. We will present experimental results demonstrating the effect of divalent dopants, in the range of 0 to 2%, on the lithium transport resistance. X-ray diffraction was used to verify that the dopant is incorporated into the crystal lattice. In addition, we will discuss our findings on the effect of dopants on the iron site and the lithium site on pressed-pellet conductivity and cathode performance at high rate. Reference [1] D. Morgan, A. Van der Ven, and G. Ceder, *Electrochem. Solid-State Lett.* 7 (2004) A30.

#### 4:00 PM **B2.5**

##### **First Principles study of the phase diagram of Li<sub>x</sub>FePO<sub>4</sub>.**

Fei Zhou and Gerbrand Ceder; MIT, Cambridge, Massachusetts.

Li<sub>x</sub>FeO<sub>4</sub> is a promising rechargeable Li-ion battery cathode material. At room temperature the Li<sub>x</sub>FeO<sub>4</sub> system is well known experimentally to phase separate into FeO<sub>4</sub> and LiFeO<sub>4</sub>. The phase stability of the system is essential for better understanding the underlying lithium insertion/extraction reactions and for attempts to improve its electrochemical performance. Previously we showed that the LDA+U method with self-consistently calculated interaction parameters correctly reproduces the instability of Li<sub>x</sub>FeO<sub>4</sub> at intermediate (0 < x < 1) lithium concentrations [*Phys. Rev B* 69 201101 (2004)]. We have thoroughly studied the Li<sub>x</sub>FeO<sub>4</sub> phase diagram with the LDA+U method. At intermediate lithium concentrations charge ordering of Fe<sup>3+</sup>/Fe<sup>2+</sup> ions occurs, resulting in a lattice distortion. The calculated phase diagram is typical of a two-phase system with a critical temperature of about 700 K, above which a transition into solid solution occurs. The calculated solubility limits of lithium in FePO<sub>4</sub> and vacancy in LiFePO<sub>4</sub> are less than 1% at room temperature. We also calculate the spinodal instability curves and compare them to experimental findings.

#### 4:15 PM **\*B2.6**

##### **Local Chemical Bond Analysis to Predict the Redox Properties of Electrode Materials for Li-Ion Batteries.**

Marie Liesse Doublet, Chemistry, CNRS - LSDSMS, Montpellier Cedex 5, France.

Development of density functional theory (DFT) and computers capacities now allow accurate electronic structure calculations of infinite periodic solids, and predictions of solid state crystallographic structures. Simple concepts of chemical bonding, electron transfer and band structure can also be used to access local bond properties and to correlate these local features to chemical and physical macroscopic properties. This powerful tool is being extensively used to rationalize the electrochemical properties of layered or 3D transition metal oxides and phosphates but seldom to more covalent systems, i.e. low potential materials for anodic applications. Based on chemical bond analysis and band structure first-principle calculations our approach seeks in determining the structural and electronic local magnitudes that rule the redox properties of electrode materials. By means of atomic charges, overlap populations analysis and band theory we established the structural and electronic local features electrode materials should exhibit to accommodate large charge variation (i.e. large lithium insertion) and small volume expansion upon lithiation. We found that systems built on weakly interacting molecular anions should exhibit promising electrochemical properties, provided that the redox centre (i.e. the anion) is characterized by strong covalent M-Pn bonds, hence leading to nearly non-bonding electronic levels of the host at the Fermi level. This method has been applied to early transition metal pnictides Li<sub>x</sub>MPn<sub>4</sub> (M = Ti, V ; Pn = N, P, As) and validated by experiments. These systems are built on nearly isolated MPn<sub>4</sub> tetrahedra statistically distributed in a three-dimensional cubic network. The electrochemical performances of such materials have led to specific capacities as high as 1000 mAh/g (i.e. 10 Lithium per transition metal) and to rather good capacity retentions. Those results have then been extrapolated to middle and late transition metal phosphides and to more suitable binary M<sub>x</sub>P<sub>y</sub> systems.

#### 4:45 PM **B2.7**

##### **Modeling Electrode Processes of Supercapacitors and Lithium Ion Batteries for Energy Storage Applications.**

Evangelos D. Tsagarakis, Materials Science and Engineering, Cornell University, Ithaca, New York.

Recent advances in devices for electrochemical energy storage have shown the increasing potential of supercapacitors and lithium ion batteries for applications where high power and energy densities are required. While batteries are capable to accomplish high energy densities, supercapacitors can store electricity and release it within very short times. This work deals with the fundamental aspects and

the electrode processes that lead to charge storage based on these two mechanisms. It is shown how modeling of the electrode processes may be utilized to extract information on the physicochemical phenomena incorporated. The model is also used to investigate the influence of key variables on the electrochemical cell performance and predict suitable cell design. Depending on the combination of materials and processes involved, supercapacitors and rechargeable batteries may exhibit different output characteristics reflecting to fundamentally different storage mechanisms. References: [1] B. E. Conway in *Electrochemical Supercapacitors*, Kluwer Academic Publ. (1999) [2] Robert A. Huggins, *Solid State Ionics* 134 (2000) 179-195

#### SESSION B3: Layered Cathodes

Chairs: Gillian Goward and M. Stanley Whittingham

Tuesday Morning, November 29, 2005

Room 310 (Hynes)

#### 8:00 AM **\*B3.1**

##### **Li De-intercalation Mechanism in LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> Cathode Material: Electrochemical and Electron Diffraction Studies.**

Yang Shao-Horn<sup>1</sup>, Ying Shirley Meng<sup>1</sup>, Sundeep Kumar<sup>1</sup>, Clare P. Grey<sup>2</sup>, Julien Breger<sup>2</sup> and Gerbrand Ceder<sup>1</sup>; <sup>1</sup>Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>State University of New York at Stony Brook, Stony Brook, New York.

As a new potential cathode material, layered O<sub>3</sub>-LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> has attracted much interest in recent years. Structural changes of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> during the charging process have been extensively studied. However, ambiguities still remain since the removal of Li in the transitional metal layer upon charging, as reported by recent NMR study [1] and first-principles investigation [2], was not considered in many previous analyses using X-ray absorption spectroscopy and synchrotron X-ray diffraction [3, 4]. We apply the electrochemical techniques such as impedance spectroscopy (EIS), potential intermittent titration technique (PITT) etc. to understand the variations in electronic resistance and diffusion coefficient of Li during the lithium de-intercalation process. Single-crystal electron diffraction is used to probe the structural changes of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> after the first charge-discharge process with different cut-off voltages, as well as the structural changes after extended cycling. By combing experimental techniques that probing different properties of the material, we will discuss the Li de-intercalation mechanism and its relation to the attractive electrochemical properties in LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>. References: 1 W. S. Yoon, S. Iannopollo, C. P. Grey, et al., *Electrochemical and Solid State Letters* 7, A167 (2004). 2 A. Van der Ven and G. Ceder, *Electrochemistry Communications* 6, 1045 (2004). 3 Y. Arachi, H. Kobayashi, S. Emura, et al., *Chemistry Letters* 32, 60 (2003). 4 W. S. Yoon, C. P. Grey, M. Balasubramanian, et al., *Chemistry of Materials* 15, 3161 (2003).

#### 8:30 AM **\*B3.2**

##### **Structure and Properties of Overlithiated Li(Li,Ni,Mn,Co)O<sub>2</sub> Materials as Positive Electrode for Lithium-Ion Batteries.**

Laurence Croguennec, Nicolas Tran, Francois Weill, Michel Menetrier and Claude Delmas; Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS) and ENSCPB, PESSAC, France.

Layered Li<sub>1+x</sub>(Ni,Mn,Co)<sub>1-x</sub>O<sub>2</sub> materials demonstrated interesting properties as positive electrode materials for lithium-ion batteries, with especially highly improved thermal stability in the deintercalated state. The structure of these materials will be described in details based on X-ray, neutron and electron diffraction data. A cation ordering occurs between the Li, Ni, Mn and Co ions in the slabs, allowing a stabilization of the structure through a minimisation of the strains between cations very different in size. The relationship between the composition, structure, physical properties and electrochemical behaviour will be discussed in details. As it was previously reported by Dahn and coworkers for Li<sub>1+x</sub>(Ni,Mn)<sub>1-x</sub>O<sub>2</sub> materials, an irreversible plateau is especially observed around 4.5 V / Li upon lithium deintercalation. Its length increases with overlithiation (x) and suggests that further lithium deintercalation from the structure is still possible despite a tetravalent oxidation state for all the transition metal ions. To explain this overcapacity phenomena, some proposed that a simultaneous lithium and oxygen extraction occurs during the plateau while others claimed the additional mechanism of an exchange between Li<sup>+</sup> and H<sup>+</sup> ions, generated for these latter by the electrolyte degradation at high potential. Combination of chemical and redox titrations, X-ray and electron diffraction, magnetic measurements, and Li and H NMR experiments allows us to decide that deintercalation of lithium ions associated to oxygen loss is the main mechanism associated to the plateau. The Li<sup>+</sup>/H<sup>+</sup> exchange reaction is only a side-reaction.

#### 9:00 AM **B3.3**

##### **Processing-Structure-Property Relation in Layered**

**O3-LiNi1/2Mn1/2O2.** Ying Shirley Meng<sup>1</sup>, Sundeep Kumar<sup>1</sup>, Clare P. Grey<sup>2</sup>, Julien Breger<sup>2</sup>, Gerbrand Ceder<sup>1</sup> and Yang Shao-Horn<sup>1</sup>; <sup>1</sup>Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>State University of New York at Stony Brook, Stony Brook, New York.

LiNi1/2Mn1/2O2 has been proposed as a promising cathode material with high reversible capacity and better thermal stability to replace LiCoO2 in advanced Li-ion batteries. It has been shown that the electrochemical properties of the material depends on the synthesis conditions, including the precursors used, heat treatment temperature and time, cooling rate etc [1, 2]. Our earlier structure analysis using single-crystal electron diffraction [3] has shown the existence of long range ordering in this material. First principles study and NMR spectroscopy [4] indicate that the amount of Li in the transition metal layer plays an essential role in determining the long range ordering in this material and is crucial for the electrochemical properties of the compound. In this study, we systematically study the short-range and long-range ordering in LiNi1/2Mn1/2O2 synthesized under different synthesis conditions. The electrochemical performance will be compared among different samples and correlated to the three-dimensional crystal structure of LiNi1/2Mn1/2O2. The knowledge of the processing-structure-property relations is essential for optimizing the performance of the LiNi1/2Mn1/2O2 and its derivatives. References: 1 T. Ohzuku and Y. Makimura, Chemistry Letters, 744 (2001). 2 Z. H. Lu, L. Y. Beaulieu, R. A. Donaberger, et al., Journal of the Electrochemical Society 149, A778 (2002). 3 Y. S. Meng, G. Ceder, C. P. Clare, et al., Electrochemical and Solid State Letters 7, A155 (2004). 4 W. S. Yoon, S. Iannopolo, C. P. Grey, et al., Electrochemical and Solid State Letters 7, A167 (2004).

**9:15 AM B3.4**  
**Synthesis and Characterization of LiNi0.45Mn0.45Co0.1O2 as a Cathode Material for Lithium Ion Batteries.** Jie Xiao, Natasha Chernova and M. Stanley Whittingham; Chemistry, State University of New York at Binghamton, Binghamton, New York.

LiNi0.45Mn0.45Co0.1O2 which combines the advantages of both LiNi0.5Mn0.5O2 and LiCoO2 has been synthesized at different temperatures varying from 700°C to 1000°C by co-precipitation method. XRD, TEM and magnetic studies show the evolution of the layered structure with rising temperature and lithium content; increasing temperature significantly reduces the BET surface area. Both the a and c lattice parameters increase with increasing temperature while the c/3a ratio shows no significant change suggesting that synthesis temperature has little influence on the cation mixing content when the products are cooled slowly. For slow cooled samples, the 800°C prepared sample gives the optimum electrochemical behavior, with the actual capacity depending on the charging voltage. Cyclic voltametry results and differential capacity plot are compared and analyzed to understand the electrochemically active elements in this compound. The capacity and rate capability of LiNi0.45Mn0.45Co0.1O2 will be discussed in terms of synthesis temperature, slow cooling vs quench cooling and lithium content. This work was supported by the US Department of Energy, Office of FreedomCAR and Vehicle Technologies.

**9:30 AM B3.5**  
**Electrochemical Lithium Intercalation in New Nanometric Cu- and Co-Doped Manganese Oxides Prepared by Thermal Decomposition of Carbonates.** Pierre Strobel<sup>1</sup>, Celine Darie<sup>1</sup>, Francois Thierry<sup>1</sup>, Alejandro Ibarra-Palos<sup>1,3</sup>, Olivier Proux<sup>4,1</sup>, Maria Bacia<sup>1</sup> and Jean-Bruno Soupart<sup>2</sup>; <sup>1</sup>Lab. Cristallographie, CNRS, Grenoble cedex 9, France; <sup>2</sup>Erachem-Comilog, Tertre, Belgium; <sup>3</sup>Instituto de Investigaciones en Materiales, UNAM, Mexico, Mexico; <sup>4</sup>Lab. Geophysique Interne, University Joseph Fourier, Grenoble, France.

The thermal decomposition of manganese carbonate gives an X-ray amorphous manganese oxide in a narrow temperature range below 400°C. Using freshly coprecipitated mixed manganese and copper or cobalt carbonates, we were able to obtain new nanometric doped manganese oxides agglomerated in submicronic spheres. These X-ray amorphous materials are characterized by a nanometric grain size, high surface area (100-112 m<sup>2</sup>/g) and a manganese valence close to 3.5. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) show that they are actually not amorphous but nanocrystalline with grain size in the 10 nm range and a spinel substructure. These materials can be successfully cycled in lithium batteries at a potential around 3V vs. Li/Li<sup>+</sup>. Step-potential electrochemical spectroscopy shows that the initial discharge gives rise to a 2-phase transition and is followed by stable, reversible, single-phase cycling. The capacity fade on cycling depends dramatically on doping and, to a lesser extent, on the salt initially used for carbonate coprecipitation. Best results are obtained on a cobalt-doped manganese oxide (Co:Mn molar ratio 1:5), which can sustain more than 100 charge-discharge cycles with a 175 mAh g<sup>-1</sup>

capacity in the 1.8-4.2 V range. XAS spectra were recorded on pristine and electrochemically discharged materials using both manganese and cobalt edges. These measurements show that (1) the variations in local structure around Mn on discharge are much smaller than in long-range ordered compounds such as Li-Mn-O spinels, (2) in the cobalt-doped material, cobalt is divalent and manganese is the only redox-active species.

**10:15 AM \*B3.6**  
**First Principles Investigation of New Cathode Materials for Batteries.** Anton van der Ven, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Ann Arbor, Michigan.

First-principles computational schemes have reached a stage where they can be used to predict a wide range of materials properties with reasonable accuracy. Typically these methods use density functional theory (DFT) to describe the electronic structure and energy of the solid at zero Kelvin and techniques from statistical mechanics to predict temperature dependent thermodynamic and kinetic properties such as phase stability, diffusion and phase transformations. In this talk I will give an overview of first-principles computational methods and illustrate how they can be used to elucidate the properties of new cathode materials, including Ni-hydroxide compounds as well as Li<sub>x</sub>(Ni<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>2</sub>, a new but poorly characterized Li-intercalation compound.

**10:45 AM B3.7**  
**Computational Structure Determination of LiNi1/2Mn1/2O2.** Yoyo Hinuma, Ying Shirley Meng, Kisuk Kang and Gerbrand Ceder; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

As a promising cathode material for advanced lithium rechargeable batteries, layered LiNi1/2Mn1/2O2 is well known for its high reversible capacity and good thermal stability [1, 2]. The performance of this material depends considerably on the synthesis conditions. Recent theoretical and experimental work [3, 4] has indicated that Li, Ni and Mn are not at all randomly distributed in the structure, and hence property variations with synthesis conditions may be related to changes in the local order. Long range ordering has been detected with single crystal diffraction even though the superstructure cannot be detected in powder X-ray and neutron diffraction [5]. NMR [3] has indicated that a significant amount of Li in the transition metal layer and gives evidence that these Li ions have a strong preference to be surrounded by 6 or 5 Mn nearest neighbors. The three-dimensional crystal structure of LiNi1/2Mn1/2O2 is not yet fully understood, though the knowledge of the cation arrangement is crucial for finding the optimal processing conditions. We apply first-principles computation methods to study the stable ordering of Li, Ni and Mn, taking the amount of cation mixing (Li-Ni interlayer mixing) into consideration. A previous structural model<sup>6</sup> (the 'flower' structure) proposed by us predicted 8.33% Li composition in TEM layer. This model agrees well with both NMR and TEM experimental observation. It is believed that the Li in the transition metal layer is a critical aspect of the structure of this compound. In more recent study, we apply the generalized gradient approximation with Hubbard U correction term (GGA+U) to better describe the real crystal structure on the basis of the flower structure model. We also investigated the lithium de-intercalation mechanism through the combination of first-principles computations and experiments. References 1 T. Ohzuku and Y. Makimura, Chemistry Letters, 744 (2001). 2 Z. H. Lu, Z. H. Chen, and J. R. Dahn, Chemistry of Materials 15, 3214 (2003). 3 W. S. Yoon, S. Iannopolo, C. P. Grey, et al., Electrochemical and Solid State Letters 7, A167 (2004). 4 C. G. Meng Y.S., Grey C. P., Yoon W.-S., and Shao-Horn Y., Electrochemical and Solid State Letters 7, A155 (2004). 5 Z. H. Lu, L. Y. Beaulieu, R. A. Donaberger, et al., Journal of the Electrochemical Society 149, A778 (2002). 6 A. Van der Ven and G. Ceder, Electrochemistry Communications 6, 1045 (2004).

**11:00 AM B3.8**  
**First principles study of the factors affecting Li mobility in layered lithium transition metal oxides.** Kisuk Kang and Gerbrand Ceder; Materials Science & Engineering, MIT, Cambridge, Massachusetts.

For large scale applications, such as hybrid electric vehicles (HEV), or power tools, the rate capability of the battery is one of the most important factors in choosing a battery. Especially in rechargeable Li batteries, Li diffusion in the electrode is considered to be critical in supporting the rate capability, since the Li diffusivity in the electrode is usually orders of magnitude lower than in the electrolyte [1-4]. The systematic study of Li diffusion by experiments is often very complicated due to many external factors involved such as the different grain size, morphology, amounts of defects in the structure and so on. In our work we use first principles computations of the

activation barrier for Li motion to understand how different structural aspects affect it. Many researchers have suspected that Li slab space, cation mixing and the different metals in transition metal layer could affect the Li mobility in the layered structure. It is investigated how and to what extent these affect the Li mobility. The dependence of the activation barrier for the Li motion on the lattice parameter, Li slab space, transition metal species, cation mixing, non-transition metal doping and anion species within this structure will be studied quantitatively using first principles calculations and the general rules can be extracted.

#### 11:15 AM B3.9

**Effect of Metal Ions Doping on the Structural and Electrochemical Properties of Layered Li-Ni-Co-O Compound.** Santander Manuel Nieto<sup>1</sup>, Maharaj Tomar<sup>2</sup>, Subhasish B. Majumder<sup>1</sup> and Ram S. Katiyar<sup>1</sup>; <sup>1</sup>Physics, University of Puerto Rico, San Juan, Puerto Rico; <sup>2</sup>Physics, University of Puerto Rico, Mayaguez Campus, Mayaguez, Puerto Rico.

During the past decade, lithium transition-metal oxides, have received a great deal of interest as a cathode material for Li-ion rechargeable batteries. Among them LiCoO<sub>2</sub> is still the only commercialized cathode material due to its excellent electrochemical properties. However, cobalt is relatively expensive and toxic and only 50 % of the theoretical capacity could practically be utilized. Nevertheless, stoichiometric LiNiO<sub>2</sub> is difficult to synthesize, due to difficult oxidation of Ni<sup>2+</sup> to Ni<sup>3+</sup> and the volatility of the lithium compounds, nonstoichiometric oxides are usually obtained and in the charged state migration of Ni ions from the 3b octahedral site to 3a octahedral site (occupied by Li ion) poses high polarization loss and poor reversibility due to the formation of undesired phase. In this work Zr and Mo doped lithium nickel cobalt oxides are prepared and their structure and electrochemical properties were characterized. Compounds were prepared by solid-state route. The charge/discharge tests were carried out using the CR2032 coin-type cell using lithium metal as anode. The discharge capacities of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>, LiNi<sub>0.8</sub>Co<sub>0.15</sub>Mo<sub>0.05</sub>O<sub>2</sub> and LiNi<sub>0.8</sub>Co<sub>0.15</sub>Zr<sub>0.05</sub>O<sub>2</sub> cathodes, measured at constant current-densities 0.48 mAcm<sup>-2</sup>, were 100.05, 155, and 103 mAhg<sup>-1</sup> respectively. Thus better discharge capacities are obtained in M (M=Mo,Zr) doped LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode. After 20th charge-discharge cycles the discharge capacities for LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>, LiNi<sub>0.8</sub>Co<sub>0.15</sub>Mo<sub>0.05</sub>O<sub>2</sub>, and LiNi<sub>0.8</sub>Co<sub>0.15</sub>Zr<sub>0.05</sub>O<sub>2</sub> were 72.47, 138 and 103 mAhg<sup>-1</sup> respectively. Hence the capacity retention of M doped cathodes was also better as compared to LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode. Results of XRD diffraction and Raman spectroscopic studies show that M doping does not change the crystal structure parameters. M doping into lithium nickel cobalt oxides is helpful to the formation of the layered structure and alleviated the degree of the cation mixing.

#### 11:30 AM \*B3.10

**New Cathode Phases in the Lithium Manganese Dioxide System.** William Bowden<sup>1</sup>, Rimma Sirotina<sup>1</sup>, Todd Bofinger<sup>1</sup>, Fan Zhang<sup>1</sup> and Steve Hackney<sup>2</sup>; <sup>1</sup>Gillette Technical Center, Needham, Massachusetts; <sup>2</sup>Michigan Technological University, Houghton, Michigan.

Lithium/manganese dioxide primary batteries use heat treated manganese dioxide (HEMD), a defect pyrolusite structure material as the cathode active material. Partial ion exchange of the structural protons in electrolytic manganese dioxide (EMD) with lithium before heating has been shown to result in a formation of a lithium containing  $\gamma$ -MnO<sub>2</sub>. Heating the lithium substituted MnO<sub>2</sub> to 350-400 C results in a partially ordered HEMD like MnO<sub>2</sub> (LiMD350) phase with higher running voltage and superior discharge kinetics. Continued heating to 450-480 C under oxygen partial pressure results in formation of a mixed phase containing both HEMD and a new MnO<sub>2</sub> phase (LiMD450). More exhaustive replacement of structural protons by lithium results in formation of a  $\gamma$ -MnO<sub>2</sub> phase substantially free of protons and containing about 1.8 % Li. This highly substituted lithium containing MnO<sub>2</sub> discharges between 3.5 and 1.8 V with a capacity of 250 mAh/g. There are two reduction processes, one at 3.25 and the other at 2.9 V. Heating the high lithium MnO<sub>2</sub> to 350-400 C results in formation of the partially ordered LiMD 350 MnO<sub>2</sub> phase as with the previous partially lithium substituted MnO<sub>2</sub>. Additional heating of the highly lithium substituted MnO<sub>2</sub> to 450-480 C under oxygen results in formation of the new LiMD450 phase in substantially pure form. XRD and TEM studies of the new material suggest it has a monoclinic unit cell described by Chabre and Pannetier, consisting of alternating 1x1 and 2x1 tunnels. The proposed structure is also similar to that described by Verbaere and Hill as highly ordered manganese dioxide or HOMD. Discharge of the new HOMD phase shows it has a discharge capacity near 200 mAh/g between 3.4 and 2.4 V vs. lithium in a single, well-defined discharge process. The HOMD demonstrated good cycling against Li with no indication of formation of LiMn<sub>2</sub>O<sub>4</sub> spinel after 100 deep discharge cycles.

SESSION B4: Vanadium Oxide and Other Cathodes  
Chairs: Marie Liesse Doublet and Debra Rolison  
Tuesday Afternoon, November 29, 2005  
Room 310 (Hynes)

#### 1:30 PM \*B4.1

**The Origin of 5 V Electrochemical Activity Observed In Divalent Cations Doped LiM<sub>0.5-x</sub>Mn<sub>1.5+x</sub>O<sub>4</sub> (0<x<0.5)(M=Cu, Ni, Zn & Mg) Cathode Materials.** Yair Ein-Eli, Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel.

The current drive towards greater portability in consumer electronics and the need for more efficient power sources is constantly driving the scientific community to search for improved technologies and materials. LiMn<sub>2</sub>O<sub>4</sub> is still recognized as a prosperous cathode material for next generation of lithium batteries. It has a FCC spinel structure with lithium ions and Mn ions occupying tetrahedral sites and octahedral sites, respectively. The theoretical specific capacity of this material is 148.2 mAh/g, with the characteristic two-step charge and discharge behavior, due to the formation and existence of two cubic structures during the whole charging and discharging processes. It was found that doping the spinel Mn-oxide matrix with low valence state transition metal ions instead of Mn resulting in a general composition of LiM<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> improves the cycle life of the spinel compound. Attempts to substitute Mn with elements such as Co, Mg, Cr, Ni, Fe, Ti and Zn have been reported previously. Initial results on these substitutions reported a lower capacity in the 4 V potential plateau compared with LiMn<sub>2</sub>O<sub>4</sub> spinel. Later studies have shown that some of these mixed oxide spinels possess a higher voltage plateau between 4.5 and 5.0 V as was reported with Cu, Ni, Cr, and Fe. Extraction of Li from LiNi<sub>0.5-x</sub>Mn<sub>1.5+x</sub>O<sub>4</sub> (where, 0<x<0.5) provides an additional potential plateau at 4.6-4.7 V (in addition to the 4.1 V potential plateau). At x=0.0, only the higher potential plateau was obtained, attributed to the oxidation of Ni<sup>2+</sup> to Ni<sup>4+</sup>. Copper, on the other hand having filled d shells, fairly readily lose one or two d electrons to yield ions or complexes in the II and III oxidation states, as was demonstrated in our previous studies with Cu doped LiMn<sub>2</sub>O<sub>4</sub> spinel compounds of the type LiCu<sub>0.5-x</sub>Mn<sub>1.5+x</sub>O<sub>4</sub>. However, this can not be anticipated from zinc, being a member in Group IIB (12) elements. The talk will describe the influence of a reactive Red-Ox cations in a valance state of +2 (Cu and Ni) and non-reactive divalent cations such as Zn and Mg, which can not be further oxidized, on the overall material electrochemistry and crystallographic of doped lithiated Mn spinel compounds. Synchrotron based In-situ XANES and XRD results points that the strong tetrahedral site preference of a divalent non reactive cation, such as Zn and Mg, is forcing Li cation onto octahedral sites in this material, thus causing electroactivity at 5 V from the displaced Li in the 16d sites of the spinel compound.

#### 2:00 PM B4.2

**Acid-treated Layered Materials, Li[LiyMn1-y]O<sub>2</sub>, as Electro-Catalysts for Li-Air Batteries.** Katana Ngala<sup>1</sup>, Arthur Doble<sup>2</sup>, Shaun Alia<sup>1</sup> and Steven L. Suib<sup>1</sup>; <sup>1</sup>Chemistry, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Lithion, Inc., Pawcatuck, Connecticut.

The proton-exchanged compounds of the layered materials, Li[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> and Li-[Li<sub>1/2</sub>Mn<sub>1/2</sub>]O<sub>2</sub>, have indicated suitable properties as potential catalysts for Li-air batteries. Acid treatment of Li[LiyMn1-y]O<sub>2</sub> materials at room temperature leads to a decrease in particle size, as a result of proton exchange with the Li<sup>+</sup> ions [1]. The increase in surface area favors an increase in the number of active sites for possible oxygen reduction. Moreover Li extraction from the main framework leads to defects [1], thus creating other suitable active sites. The acidity of the acid-treated Li[LiyMn1-y]O<sub>2</sub> materials is also expected to impact the catalytic activity. Thus, generally, catalytic activity varies with the extent of proton-exchange of the parent materials. For instance, when the compound Li<sub>0.1</sub>H<sub>0.9</sub>[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> was tested in a Li-air cell it indicated a discharge specific capacity of 2531 mAh/g, representing an increase of about 60% over that of carbon (1555 mAh/g). Thus, this type of materials possess interesting properties for possible application in metal-air batteries and low energy fuel cells. Reference: 1. Y. Paik, C. P. Grey, C. S. Johnson, J.-S. Kim, M. M. Thackeray, Chem. Mater., 14(2000) 5109

#### 2:15 PM B4.3

**Searching for Reversible Copper Extrusion-Insertion Electrode for Rechargeable Li Batteries.** Mathieu Morcrette<sup>1</sup>, Rozier Patrick<sup>2</sup>, Dupont Loic<sup>1</sup>, Swajwaj Olivier<sup>2</sup>, Bodenez Vincent<sup>1</sup>, Murphy Don<sup>1</sup> and Tarascon Jean-Marie<sup>1</sup>; <sup>1</sup>Laboratoire de Reactivite et de Chimie des Solides, Amiens, France; <sup>2</sup>CEMES, Toulouse, France.

The present paper is a continuation in part of our recent work dealing with the fully reversible Li-driven Cu extrusion/injection of Cu in  $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$ . The peculiar electrochemical property of such a compound was ascribed to both structural considerations (presence of anchoring oxygen giving the  $\text{V}_4\text{O}_{11}$  layers a flexibility), and electronic considerations, such as the existence of a delicate balance between the two  $\text{Cu}^{1+}/\text{Cu}^{2+}$  and  $\text{V}^{4+}/\text{V}^{5+}$  redox levels that falls within the same range of energies. Bearing this in mind we have embarked in a well worked out research to find another equivalent to the  $\text{Cu}_{2.33}\text{V}_4\text{O}_{11}$  material. Considering the d-metals ionisation energy diagram, substituting V, a 3d-metal, for a 4d-metal such as Nb in Cu-based compounds, was carried out in the hope of better adjusting the redox value of  $\text{Nb}^{5+}/\text{Nb}^{4+}$  to that of Cu. A survey of numerous (Cu)-Nb-O compounds ( $\text{Cu}_2\text{Nb}_4\text{O}_{11}$ ,  $\text{CuNb}_3\text{O}_8$ ,  $\text{CuNb}_2\text{O}_6$ ) was conducted, and the study extended to some Ag-based compounds. The electrochemical performances of these phases towards Li, some of which show excellent capacity retention, will be reported and the mechanisms by which they react with Li discussed. In light of such findings, the interest to revisit the electrochemical reactivity of old insertion materials such as  $\text{CuTi}_2\text{S}_4$  will be documented as well. 1)M. Morcrette, P. Rozier, L. Dupont, E. Mugnier, L. Sannier, J. Galy, J.M. Tarascon, *Nature Materials*, 2, (2003) 755-761

### 3:30 PM B4.4

**Doped Nanotubes Vanadium Oxide Macrocellular Foams: Positive Electrodes for Lithium Batteries.** Florent Carn<sup>1</sup>, Lahire Biette<sup>1</sup>, Mathieu Morcrette<sup>2</sup>, Christine Surcin<sup>2</sup>, Nathalie Steunou<sup>3</sup>, Jacques Livage<sup>3</sup> and Renal Backov<sup>1</sup>; <sup>1</sup>Centre de Recherche Paul Pascal (UPR-CNRS 8641), Pessac, France; <sup>2</sup>Laboratoire de Reactivite et de Chimie des Solides (UMR-CNRS 6007), Amiens, France; <sup>3</sup>Laboratoire de Chimie de la Matiere Condensee (UMR-CNRS 7574), Paris, France.

Chemistry of shapes is a new field of research where fluid complexes and inorganic chemistry can be associated. In such context, designing new porous monolith-type materials involving hierarchical porosity and tailored macroscale shapes is an emerging area of technological interest toward heterogeneous catalysis, phase separations, artificial bone structure, thermal and/or acoustic insulation, ion-exchange operation, and so forth. Different patterns can be used at the macroscopic length scale as biliquid<sup>[1]</sup> or air-liquid foams.<sup>[2]</sup> Different inorganic polymers can be used toward specific applications mentioned above, among those, extensive interest is focused over vanadium oxides mainly for their structural and textural<sup>[3]</sup> diversity and potential applications in various domains as for instance, heterogeneous catalysis, cathode materials for advanced lithium batteries, visible light photochromism and electro-chromic devices. Present work<sup>[3]</sup> extends the recently reported study<sup>[3]</sup> on the preparation of vanadium oxide foams using air-liquid bubbling process. In this issue, to create new advanced cathode devices dedicated for lithium batteries, carbon nanotubes have been added within the vanadium oxide macrocellular foam walls. Results will be discussed both in terms of interlayer distance parameters and carbon nanotubes percentages associated to the  $\text{V}_2\text{O}_5$ /Carbon nanotube composites. Charge-discharge cycling experiments and induced-capacities will be presented. 1- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, E. Sellier, M. Birot, R. Backov *J.Mater.Chem.*, 2004, 14, 1370. 2- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, C. Sanchez, R. Backov *Adv.Mater.*, 2005, 17, 62. 3- F. Carn, N. Steunou, A. Colin, J. Livage, R. Backov *Chem.Mater.* 2005, 17, 644.

### 3:45 PM B4.5

**Electrospinning of Novel Vanadium Oxide Nanofibers.** Chunmei Ban, Hong Dong and M. Stanley Whittingham; Chemistry and Materials, SUNY at Binghamton, Binghamton, New York.

Here, we report a novel method for preparing vanadium oxide nanofibers with a layered structure by electrospinning PMMA/vanadium oxytriisopropoxide gels; the composite fibers, so formed, are then hydrothermally treated around 160°C for 24 hours. These vanadium oxide nanofibers have cross-sectional dimensions less than 100nm. The fibers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), FT-IR, X-ray diffraction, thermal gravimetric analysis (TGA) and electron diffraction. The results from X-ray diffraction show that the vanadate nanofibers have a layered structure with a largest interlayer spacing of 11.2 Å, with the structure being influenced by the hydrothermal temperature. The FT-IR spectrum of the vanadate nanofibers exhibits the characteristic peaks of the vanadium oxide network at 510, 745 and 1013  $\text{cm}^{-1}$ , corresponding to the V-O vibration bands and  $\text{V}=\text{O}$  bands; these suggest a double sheet structure as in  $\text{MxV}_4\text{O}_{10}$  and the vanadium oxide nanotubes. Electron diffraction patterns suggest that each fiber is a single crystal. TGA shows that the triisopropoxide groups in vanadium compounds have been removed during the hydrothermal process, but the chains of the PMMA still exist in the final nanofibers. The novel properties of these nanostructures will be discussed. This work is supported by NSF-DMR 0313963.

### 4:00 PM \*B4.6

**From vanadium oxide gels to  $\text{Li}_1+\alpha\text{V}_3\text{O}_8/\beta\text{-Li}_1/3\text{V}_2\text{O}_5/\text{C}$  nanocomposites.** Joel Gaubicher<sup>1</sup>, M. Dubarry<sup>1</sup>, P. Moreau<sup>1</sup>, D. Guyomard<sup>1</sup>, O. Durupthy<sup>2</sup>, N. Steunou<sup>2</sup>, J. Livage<sup>2</sup>, N. Dupre<sup>3</sup> and C. P. Grey<sup>3</sup>; <sup>1</sup>IMN, Nantes, France; <sup>2</sup>Laboratoire de Chimie de la Matiere Condensee, Universite Pierre et Marie Curie-Paris VI, Paris, France; <sup>3</sup>SUNY, Stony Brook University, Stony Brook, New York.

$\text{Li}_1+\alpha\text{V}_3\text{O}_8$  ( $\alpha=0.1-0.2$ ) has been extensively studied during the past 20 years for its attractive electrochemical properties in rechargeable lithium batteries. Two main routes have been considered to synthesize this oxide: solid state reactions and heat treatment of a xerogel precursor. Regarding the sol-gel route, the lithium intercalation behavior in  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$  strongly depends on the firing temperature of the xerogel: samples prepared upon heating at 580C exhibit a stable capacity of 180 mAh/g upon cycling, whereas those heated at 350C, exhibit a larger initial capacity (300 mAh/g) that decreases rapidly upon cycling. The purpose of this paper is on one hand to study the reaction mechanisms that occur from the pristine solute species to anhydrous  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$  as well as their consequences regarding the electrochemical behaviors, and on the other hand, to improve capacity retention of low temperature prepared  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$ . Unlike  $\text{V}_2\text{O}_5$  gel, the  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$  gels are biphasic materials made of intimately mixed solid and liquid phases having very close Li/V stoichiometry. At room temperature the solid component contains presumably an hewettite type structure whereas the liquid part crystallizes into lithiated decavanadic acids. A mechanism of formation of the  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$  gel-like precipitate via solubilized vanadic species will be proposed. Formation of anhydrous  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$  from the xerogel has been studied from thermodiffraction and temperature dependant 51V MAS NMR. Completion of dehydration leads to a sample characterized by a bimodal grain size distribution, with each size coming from each component of the xerogel. Specific reactions have been evidenced for each component. It will be shown that the biphasic character of the pristine gel-like precursor influences the electrochemical behavior of anhydrous  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$ . As capacity fading of low temperature prepared  $\text{Li}_1+\alpha\text{V}_3\text{O}_8$  was ascribed to electrolyte/material interfacial reactions, modification of the surface was investigated by thermal carbo-reduction.  $\text{Li}_1+\alpha\text{V}_3\text{O}_8/\beta\text{-Li}_1/3\text{V}_2\text{O}_5/\text{C}$  nanocomposites ( $n \approx 0.3$ ) were obtained upon heat treatment of a carbonated gel using a fast firing technique under argon atmosphere for 1 to 60 minutes. Very promising electrochemical performance were obtained. Key points regarding the improvement of the capacity retention will be discussed.

### 4:30 PM \*B4.7

**Reversible Conversion Metal Fluoride Nanocomposites: New Options for Next Generation High Energy Lithium Batteries.** Fadwa Badway, Mathieu Bervas, Jafar Al-Sharab, Irene Plitz, Frederick Cosandey and Glenn G. Amatucci; ESRG, Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, North Brunswick, New Jersey.

The present day state of the art Li-ion battery technology exhibits an energy density in excess of 150 Wh/kg and 250 Wh/l. Based on electrodes utilizing intercalation processes, the technology has become ubiquitous in the world of portable electronics. In recent years, a revival of effort has been expended on optimizing metal air technologies and fuel cells. However, the energy density of lithium battery technology is far less than half of the theoretical energy densities that could be achieved. The energy density of lithium battery technology is limited by the energy density of the positive and negative electrode materials. Of these, the positive electrode is by far the most limiting especially with respect to the negative electrode of graphite and newer Li metal and Li metal alloy compositions. Intercalation reactions are limited in the amount of Li transferred thereby limiting electron transfer to typically less than 1e- per compound such as  $\text{LiMeO}_2$  where Me is a transition metal. An alternative to intercalation materials is to utilize the concept of conversion and reversible conversion compounds where multiple electrons can be transferred to the active electrode to reduce fully to the metal state plus lithium salt and then subsequently reoxidize back to the original compounds. In theory these reactions can lead to specific capacities in excess of 700mAh/g. In the past few years these reactions have been shown to exist for dichalcogenides (Poizot et al.) and nitrides (Pereira et al.) in the reaction range of 0.5-2V. To increase the potential of such reactions and make attractive for use as positive electrodes, a move to highly ionic halides was necessary. Metal fluorides have been known for well over 30 years as attractive electrode materials, however the higher voltage materials exhibit a high bandgap resulting in insulator properties and very poor electrochemical activity. Recently, for the first time, reversible conversion reactions in metal fluorides have been shown to occur in the metal fluorides in parallel but separate work by Maier et al. with lower voltage macromaterials and our group (Badway et al.) with higher voltage nanocomposites. Our work for the past few years has



been focused on the enablement of a variety of high bandgap, insulating metal fluorides by the use of nanocomposite technology. Although in its early years, a number of systems have been shown to exhibit near theoretical conversion voltages (2-3.2V) and specific capacities from 400 to 700 mAh/g. Systems including fluorides and in some cases oxyfluorides of Fe, Ni, Co, Cr, Bi, and Cu have been investigated in depth. This paper will review our progress to date with discussion of reaction mechanisms and challenges that remain.

SESSION B5: Supercapacitor  
Chairs: Glen Amatucci and Laurence Croguenec  
Wednesday Morning, November 30, 2005  
Room 310 (Hynes)

#### 8:00 AM \*B5.1

##### **Sequestration Effect on Carbon Replica Obtained from Polymer and Biopolymer Interleaved into Layered Double Hydroxide: Nanotexture and Capacitance Properties.**

Fabrice Leroux<sup>1</sup>, Encarnacion Raymundo-Pineiro<sup>2</sup> and Francois Beguin<sup>2</sup>, <sup>1</sup>Materials Chemistry, Universite Blaise Pascal, Aubiere, France; <sup>2</sup>Centre de Recherche sur la Matiere Divisee CRMD, Orleans, France.

Under specific conditions, organic molecules and polymers, when confined into a host structure, may give rise to carbon materials associated to a large microporosity. It is accepted that the collapse of the structure impedes the reaction of cross-linking to occur. It has been illustrated by several examples such as clay materials, but also with 3D host structures such as MCM-48. In this idea, various monomers and polymers have been incorporated between the sheets of layered double hydroxides (LDHs). We will focus on vinylbenzenesulfonate (VBS), and biopolymers, such as sodium alginate and carrageenan. The synthesis of the inorganic - organic hybrid materials will be described, and the interaction between the host structure and the guest molecule will be discussed according to the preparation pathway. For vinyl-based interleaved monomers, the in-situ polymerization reaction will be characterized, and the thermal behavior will be presented. Carbon material is recovered after pyrolysis of the former hybrid materials and the subsequent dissolution of the inorganic part. The nanotextural properties, porosity and specific surface area, and related results obtained by Raman spectroscopy will be discussed according to the mode of preparation. Specific surface area up to 2300 m<sup>2</sup>/g may be reached for samples prepared initially via the monomer intercalation and its subsequent in-situ polymerization. The carbons have been tested as active electrode material of supercapacitors in sulfuric acid medium by means of galvanostatic and potentiodynamic techniques and by complex impedance spectroscopy. Some of the materials present interesting capacitance values ranging from 140 up to more than 200 F/g associated to a good cyclability.

#### 8:30 AM \*B5.2

##### **Active Material/Current Collector Interface: A Key Issue for Performances Improvement in Energy Storage Devices.**

Patrice Simon, CIRIMAT, Universite Paul Sabatier, Toulouse, France.

Electrodes used in most of the electrochemical energy and power sources can be described as a current collector/active material film/electrolyte string. This schematic description highlights the importance of the two interfaces present at the outer and the inner side of the electrodes. At the active material/current collector interface are concentrated all the contacts problem arising from the adherence of the active layer onto the current collector surface. This contact impedance is an important contribution to the whole series resistance of the device. On the other side, the active material/electrolyte interface mainly drives (for a given redox system) the quantity of electricity that will be stored by square cm of electrode. There is then a real challenge to design specific properties at these two interfaces, in the aim to improve the performances of the electrochemical energy and power sources. Results about the active material/current collector interfaces in supercapacitor systems (power) [1] and Li-Ion system [2] (energy) will be presented in this talk. In a first part devoted to supercapacitors systems, specific surface treatments developed to improve both the contact and the surface at the active material film/current collector interface will be described [3] and the results discussed. The second part will be devoted to the elaboration of a new nanostructured Cu current collector for Li-ion batteries, developed in the frame of Alistore, a European Network of excellence headed by Prof. Tarascon. Results presented will demonstrate the real interest of developing a high-surface area at the current collector/active material interface, in terms of power delivery and cycling stability. References: [1] B. E. Conway, *Electrochemical Supercapacitors: Scientific, Fundamentals and Technological Applications*, 377-416 (1999) [2] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont et J.-M. Tarascon *Nature* (407)(6803),

496-499 (2000) [3] C. Portet, P. L. Taberna, P. Simon and C. Laberty-Robert, *Electro. Acta*, 49, Issue 6, March 2004, 905-912.

#### 9:00 AM B5.3

##### **Novel Electrode Materials for Supercapacitors: Amorphous MnO<sub>2</sub>-Single Walled Carbon Nanotube Composites.**

Bingqing Wei and Subramanian Venkatchalam; Electrical and Computer Engineering, Louisiana State University, Baton Rouge, Louisiana.

Supercapacitors (SCs) or electrochemical capacitors form a new category of versatile power sources which lies between the conventional capacitors and batteries. SCs have attracted much attention in recent years, mainly owing to their wide range of applicability such as hybrid power sources, backup power storage, peak power sources, etc. SCs are broadly classified as (i) electrical double layer capacitors (EDLC) exhibiting a non-faradic charge accumulation at the electrode-electrolyte interface and (ii) faradic redox pseudocapacitors. The main advantage of the pseudocapacitor based SCs is the high energy density. On the other hand, various high surface area carbon materials including carbon nanotubes have been investigated for EDLC applications. The main advantage of the EDLC based SCs is their high power density. In recent years, development of a composite electrode material comprising of both carbonaceous and noble/transition metal oxide has greatly intensified because of the combined advantages of both EDLC and pseudocapacitors. In this presentation we will present a simple way of preparation of novel amorphous MnO<sub>2</sub>-single-walled carbon nanotube (a-MnO<sub>2</sub>/SWNT) composites at room temperature and their high rate capability. A simple precipitation technique using ethanol has been employed to prepare the composites starting with potassium permanganate and commercial SWNTs. The composition of SWNTs in the composites was varied so as to optimize the electrochemical properties with best rate capability and high capacitance. The prepared materials were characterized by various analytical techniques such as XRD, SEM, HRTEM, XPS, surface area and electrochemical measurements. The rate capability of the prepared composites was studied at a very high current of 2 A/g between 0 and 1V in a 1M Na<sub>2</sub>SO<sub>4</sub> electrolyte. The dependence of capacity and current capability with respect to the SWNT content has been correlated and will be discussed in detail.

#### 9:15 AM B5.4

##### **A new mesoporous carbon electrode material for its application to electric double layer capacitors (EDLC).**

John Lourdu Kennedy<sup>1,2</sup>, Justin Raj<sup>1,2</sup>, Judith John Vijaya<sup>2,1</sup> and Ganesan Sekaran<sup>1,2</sup>; <sup>1</sup>Environmental Technology, CLRI, Chennai, Tamil Nadu, India; <sup>2</sup>Chemistry, Loyola College, Chennai, India.

A new electrode material for the electric double layer capacitor (EDLC) using mesoporous activated carbon derived from rice husk has been investigated. The activated carbon used in this study was prepared by two stage process: carbonization and chemical activation at temperatures 700, 800 and 900°C. The mesoporous carbon materials were characterized using X-ray diffraction and SEM technique. The performance of activated carbons as EDLC electrode was characterized using cyclic voltammetry and galvanostatic charge/discharge techniques using 1 M H<sub>2</sub>SO<sub>4</sub> as an electrolyte. The BET surface area of the prepared C700, C800 and C900 carbon materials were in the range 345, 379 to 440m<sup>2</sup>/g. The specific capacitance values were linearly related with BET surface area of activated carbon. The cyclic voltagram of the EDLC demonstrated that the electric charges were stored in the electric double layer at the interface between the polarizable electrode and the electrolyte. The specific capacitance of C700, C800 and C900 were 8.3, 24 and 143mF/g respectively. The capacity was maximum of about 143 mF/g for activated carbon containing 69% mesopore concentration. The specific capacitance of the mesoporous activated carbon was majorly dependent on the surface functional groups such as hydroxyl, carbonyl and carboxyl groups determined through FT-IR technique. The stability of the activated carbon capacitors was examined by conducting repeated charge-discharge cycles. The result of 100 cycles demonstrate that the capacitor has stable capacitance with columbic efficiency of about 99.5%.

#### 9:30 AM B5.5

##### **Double Layer Capacitance of Carbide-Derived Carbon in Organic Electrolyte.**

John Chmiola<sup>1</sup>, Gleb Yushin<sup>1</sup>, Cristelle Portet<sup>2</sup>, Pierre Louis Taberna<sup>2</sup>, Patrice Simon<sup>2</sup> and Yury Gogotsi<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; <sup>2</sup>CIRIMAT, UMR CNRS, Toulouse, Haute-Garonne, France.

In this study, we investigated the performance of a new class of nanostructured carbon, Carbide Derived Carbon (CDC), as electric double-layer capacitors in a 1.5 M NEt<sub>4</sub>BF<sub>4</sub>/acetonitrile electrolyte. The pore size distribution, carbon structure and specific surface area of the CDCs were controlled by varying both the starting carbide and

the synthesis temperature between 600C and 1200C. A systematic study using cyclic voltammetry, impedance spectroscopy and galvanostatic cycling was conducted to assess the effect of structure and porosity on both specific capacitance and frequency response behavior. It was shown that increasing the synthesis temperature generally resulted in both wider pores and a more graphitic structure, which lead to faster frequency response. In general, increasing the synthesis temperature had the opposite effect on specific capacitance. CDC showed very promising initial performances, with a specific capacitance in excess of 100 F/g and a series resistance of  $0.5 \Omega \text{ cm}^2$  or less, which shows the ability of CDC to be used in high-power applications.

#### 10:15 AM \*B5.6

**Highly Reversible Nanocrystalline Vanadium Nitride Based Pseudocapacitors.** Prashant Nagesh Kumta<sup>1,2</sup>, Daiwon Choi<sup>1</sup> and George E. Blomgren<sup>1,3</sup>; <sup>1</sup>Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; <sup>2</sup>Biomedical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; <sup>3</sup>Blomgren Consulting Services, Ltd, Cleveland, Ohio.

Electrochemical capacitors classified as electrical double layer (EDL) and pseudocapacitor type are considered as one of the potential energy storage systems in addition to batteries and fuel cells. With the advent of sol-gel methods and other emerging techniques in recent years, materials exhibiting very high surface areas have been realized to date. Consequently, it has been possible to generate high surface area materials exhibiting pseudocapacitance as well as electrical double layer type response. This has given rise to the class of materials known popularly today as supercapacitors. Among the several transition metal oxides and carbon xerogels studied for capacitor response, the only oxide that has been widely researched and known for its superior electrochemical capacitor response to date are the various crystallographic and morphological forms of ruthenium oxide. Unfortunately, the expensive nature of ruthenium has limited the technological viability of this material. Consequently, the field of electrochemical capacitors has not witnessed many advances. In this presentation we report the synthesis and electrochemical response of a new class of chemically synthesized nanocrystalline transition metal nitrides (TMN) based on vanadium nitride. These nitrides deliver a specific capacitance of 1340 F/g when tested at low scan rates of 2mV/s and 554 F/g when tested at high charging rates of 100 mV/s using 1M KOH electrolyte. Such a high capacitance response has never observed before in transition metal nitrides or carbides. The excellent capacitor response exceeding that of RuO<sub>2</sub> is believed to be caused by vanadium undergoing a series of redox reactions resulting in the formation of a reversible hydroxide and oxide on the surface of the nanocrystalline VN. As a result, it is believed that a series of mixed vanadium oxides are generated on the surface of the nitride during cycling with V undergoing a range of different oxidation states while preserving the underlying nitride which maintains the required electronic conductivity. In the literature, transition metal nitrides and carbides synthesized using sol-gel methods have been reported to exhibit capacitance value of 226 F/g. In our study, nanocrystalline VN powders have been generated using a two-step ammonia treatment of the precursors at relatively low temperatures of 400°C. The resultant nanocrystalline nitride powders have been characterized systematically using a variety of analytical techniques. High resolution transmission electron (HRTEM) microscopy results indicate that these nitrides are in the size range of 5nm. The nitride generated at 400°C exhibited a modest specific surface area of 40 m<sup>2</sup>/g. Detailed X-ray diffraction, Rietveld refinement; thermogravimetric and mass spectroscopic analysis combined with HRTEM, X-ray photoelectron spectroscopy (XPS) and electrochemical response analyses have been conducted. Results of these studies will be presented and discussed.

#### 10:45 AM B5.7

**Multifunctional Carbon-Based Hybrid Nanoarchitectures for High-Performance Electrochemical Capacitors.**

Jeffrey Webster Long, Todd M. McEvoy, Christopher P. Rhodes, Michael S. Doescher and Debra R. Rolison; Chemistry Division, NavalResearch Laboratory, Washington, District of Columbia.

Carbon aerogels and related nanoarchitectures are appealing as electrode structures for electrochemical applications due to their high surface areas, through-connected porosity, and high electrical conductivity [1-3]. The synthesis and processing methods for producing these nanoarchitectures are also highly flexible, allowing for tuning of such properties as the density and pore-size distribution. These conductive nanoarchitectures are particularly beneficial for high-rate electrochemical capacitors, where the inherent mesopore/macropore network of the carbon aerogel serves as an effective reservoir and transport path for solvent and ions to interact with the extended electrified interface. However, the overall energy-storage capacities of unmodified carbon aerogels are limited, as they rely primarily on a double-layer capacitance mechanism. To address this issue, we are developing hybrid electrode structures

comprising carbon nanoarchitectures with ultrathin (<50 nm) electroactive coatings. Taking advantage of the conductivity and highly accessible electrified surface area of the porous carbon platform, we use electropolymerization to directly deposit conformal polymer coatings onto the surface of the carbon nanoarchitecture. The critical step in generating controlled, conformal polymer coatings within porous nanoarchitectures is the use of electrodeposition conditions where polymer growth is self-limiting, which for arylamine monomers is achieved by performing the electropolymerization in aqueous electrolytes with pH>1. The resulting ultrathin poly(arylamine) coatings are electrochemically activated by exposure to aqueous acid electrolytes. When incorporated into carbon aerogels, the faradaic pseudocapacitance of the polymer coating enhances the overall gravimetric capacitance by >50% and the volumetric capacitance by >100%, relative to native carbon aerogels, even under high-rate conditions [4]. We have recently extended this approach to generate self-limiting, ultrathin (55 nm) composite polymer-MnO<sub>2</sub> coatings in which the MnO<sub>2</sub> phase exhibits high capacity and electrochemical reversibility when cycled in neutral-pH aqueous electrolytes. Future hybrid electrodes will be designed to exploit the functions of both the electroactive coating and carbon nanoarchitecture components to achieve structures that exhibit both high energy density and high power density when used in electrochemical capacitors. [1] E. Frackowiak and F. Beguin, Carbon, 39, 937 (2001). [2] R.W. Pekala, J.C. Farmer, C.T. Alviso, T.D. Tran, S.T. Mayer, J.M. Miller, and B. Dunn, J. Non-Cryst. Solids, 225, 74 (1998). [3] U. Fischer, R. Saliger, V. Bock, R. Petricevic, and J. Fricke, J. Porous Mater., 4, 281 (1997). [4] J.W. Long, B.M. Dening, C.P. Rhodes, M.S. Doescher, T.M. McEvoy, and D.R. Rolison, J. Non-Cryst. Solids, 350, 97 (2004).

#### 11:00 AM B5.8

**Nano-Structured Oxides of Cobalt, Nickel and Manganese as Electrochemical Supercapacitors: Electrosynthesis and Properties.** Nandakumar Nagarajan, Elizabeth A. McNally, Harith Humadi, Hailun Huang, David S. Wilkinson and Igor Zhitomirsky; Materials Science and Engg, McMaster University, Hamilton, Ontario, Canada.

New electrochemical methods were developed for the fabrication of nano-structured oxides for application in electrochemical supercapacitors. In the proposed methods, cathodic electrosynthesis of nanostructured oxides or hydroxides of Co, Ni and Mn was performed in-situ in a polymer matrix. The new methods were based on the use of polyelectrolytes and polymer-metal ion complexes. The results of thermogravimetric analysis indicated that the deposit composition can be varied by the variation of polymer content in the solutions. Deposition yield has been quantified at various experimental conditions. Sintering resulted in burning out of polymer and formation of nano-structured films. The phase content of the films annealed at different temperatures was studied by X-ray diffraction analysis. The electrochemical performance of the films sintered at different temperatures was studied by cyclic voltammetry, chronopotentiometry and impedance spectroscopy in KOH (NiO and Co<sub>3</sub>O<sub>4</sub>) and Na<sub>2</sub>SO<sub>4</sub> (Mn<sub>3</sub>O<sub>4</sub>) solutions. The films showed excellent pseudocapacitive behavior. The specific capacitance was obtained from the CV data at a scan rate of 10-200 mV/s and compared with results from chronopotentiometry. Obtained films showed specific capacitance in the range of 150-500 F/g. Cycling performance of the films (up to 1000 cycles) has been investigated. The results indicate that the proposed method can be used for fabrication of electrodes for electrochemical supercapacitors.

#### 11:15 AM B5.9

**Computational study of SiO<sub>2</sub> and HfO<sub>2</sub> based polymer-inorganic nano-composites for high energy density and energy storage applications.** Ning Shi and R. Ramprasad; Materials Science & Engineering, Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

Next generation high energy density and energy storage devices will require materials with higher dielectric constant and/or higher breakdown strength than has been possible so far. One option that could help achieve these goals is the use of polymer-inorganic nano-composites, using inorganic species such as nano-composite or nano-platelet SiO<sub>2</sub> (for high dielectric strength) or HfO<sub>2</sub> (for high dielectric constant). Crucial to the use of such nano-composite systems is an understanding of the properties of such systems as the typical size of the particles reaches nano-scale dimensions. For instance, surface/interface properties (at the polymer-inorganic interfaces) such as polarization will be dominant in determining the dielectric properties of such systems. A computational study, based on first principles density functional theory, of alpha-quartz SiO<sub>2</sub> and cubic HfO<sub>2</sub> surfaces, terminated with various relevant species such as H, OH, and small polymer chains, will be presented here. As part of this investigation, a new theoretical framework that helps explore the impact of an external electric field on both the bulk and interface

polarization in confined systems has been developed [R. Ramprasad and N. Shi, to appear in Phys. Rev. B]. This theoretical framework allows for a partitioning of the net field induced polarization in nano-particles into bulk and surface/interface parts, with the bulk part (if large enough) resulting in the bulk dielectric properties, and the surface/interface part indicating the modification due to various types of surface terminations. This framework also allows for the treatment of both the high frequency (when only the electrons are allowed to respond to the external electric field, while the ionic cores are held fixed) and low frequency (when both the electronic and ionic degrees of freedom are allowed to relax) effects. Specifically, for nano-scale SiO<sub>2</sub> and HfO<sub>2</sub> systems, we find that the bulk dielectric properties (both at the high and low frequency limits) as determined using this technique are in excellent agreement with experiments, thereby validating our method. Variations of the surface/interface part of the polarization due to various choices of nano-particle surface terminations follow interesting and unanticipated trends. These results form the groundwork for a computational design of advanced high energy density systems.

#### 11:30 AM B5.10

**New n-Dopable Materials for Advanced Charge Storage Applications.** David Witker, Sean O. Clancy, Adam P. Closson, John D. Stenger-Smith, David J. Irvin and Jennifer A. Irvin; Chemistry and Materials Division, Naval Air Warfare Center, China Lake, California.

As new technologies continue to emerge, the demand for devices capable of storing the considerable energy necessary for these applications is also increasing. While new battery systems with exceptional energy densities have been developed recently, these systems often do not provide sufficient power to meet the needs of many applications. In order to satisfy these requirements, bridging technologies are necessary. Type III supercapacitors represent a promising avenue towards this end. These devices are intended to store charge and then be discharged rapidly, giving more power than can be attained from a battery. Type III supercapacitors differ from Type I and Type II electrochemical cells in that they contain as active electrode materials both p-dopable and n-dopable components. During discharge, the materials are returned to their neutral states, meaning that all of the charge stored can be utilized. Type III supercapacitors also operate at significantly higher voltages than Type I or Type II supercapacitors, and are therefore able to deliver more power. When coupled with existing batteries, a system capable of storing considerable energy and delivering high power can be realized. Currently, there exist a great number of choices for the p-dopable component in supercapacitors. Polymers that are p-dopable are usually relatively stable to atmospheric oxygen and water in both their neutral and oxidized states. This stability leads to simplified construction and longer life for the devices. However, the choices for n-dopable polymers are much more limited. Polymers that can be electrochemically reduced tend to be very sensitive to oxygen and water while in their reduced states. In order to fabricate Type III supercapacitors with sufficient cycling stability and depth of discharge, it is necessary to devise a new group of n-dopable materials. Several approaches have been used to attain n-dopable polymers. The first, and most common, is to produce materials with regions of both high and low electron density. This goal is usually accomplished by copolymerization of electron-poor monomers with electron-rich units. Our efforts to produce n-dopable polymers have been focused exclusively upon the use of electron-deficient monomer units. Two different classes of monomers have been utilized in order to affect n-doping behavior, those with electron-withdrawing groups and those containing high-nitrogen heterocycles. In addition, the polymers can be further divided into two groups, those produced by electropolymerization to give the thin films necessary for device construction and those attained through chemical polymerization to give soluble materials which can then be processed by spin- or spray-casting. We will discuss our new n-dopable polymers as well as our working Type III supercapacitors with excellent energy and power densities and satisfactory cycle life.

#### 11:45 AM B5.11

**Nanostructured Supercapacitors by Combustion Chemical Vapor Deposition.** Yongdong Jiang, Todd A. Polley and Andrew T. Hunt; Electronics & Optics, nGimat Co., Atlanta, Georgia.

Supercapacitors have gained substantial attention since they offer outstanding advantages over conventional capacitors and batteries such as storing energy longer, discharging faster, longer shelf life, and excellent reversibility. Currently available supercapacitors utilizing carbon, metal oxide, and polymer electrodes and liquid or organic solid electrolytes have been technically successful in low cell voltage, low energy storage, and low operating temperature applications. With the predicted shift to wide band gap semiconductors, the allowable operating temperature of power electronics devices are expected to increase to over 200°C, at which point, the currently available passive components, specifically supercapacitors, will become the limiting

factor in thermal design. In this study, solid-state supercapacitors based on ceramic electrolytes (yttria stabilized zirconia, YSZ) and metal/ceramic (Pt/YSZ) nanocomposite electrodes were developed by the Combustion Chemical Vapor Deposition (CCVD) technique. Process parameters, such as deposition temperature, nanocomposite coating thickness, and metal particle loading, have been investigated. Electrochemical measurements on a specimen deposited with 50 vol.% metal loading (based on solution ratio) resulted in a specific capacitance of 87 F/m<sup>2</sup> at 550°C for a 4 μm thick coating, which corresponds to a specific capacitance of 22 F/m<sup>2</sup> per micron thickness. This specific capacitance is almost three times as high as the state-of-the-art. An energy density of 67 J/cm<sup>3</sup> could be achieved if 100 V were applied to this capacitor.

#### SESSION B6: Anodes

Chairs: Robert A. Huggins and Robert Kostecki  
Wednesday Afternoon, November 30, 2005  
Room 310 (Hynes)

#### 1:30 PM \*B6.1

**Novel Nitride Based Lithium Battery Negative Electrode Materials with Enhanced Stability: Study of Anti-Fluorite Type Lithium Manganese Oxynitrides.** M. Rosa Palacin and Jordi Cabana; Institut de Ciència de Materials de Barcelona, Bellaterra, Catalonia, Spain.

Although lithium transition metal nitrides have been considered as promising electrode materials since the mid 90's, the main drawback for their application is still their ambient air stability. With the aim of improving this aspect, we have undertaken the synthesis of oxygen containing related samples (i.e. oxynitrides). From the two structural families of known Li-M-N phases (Li<sub>3</sub>N-type and anti-fluorite type), we have focussed on the latter due to the fact that the coordination of nitrogen is more suitable for oxygen substitution. Among them, we have attempted the synthesis of manganese containing phases due to the rich redox chemistry of this metal and to the fact that it is environmentally friendly and non expensive. As a result of these experiments, we have succeeded in preparing a series lithium manganese oxynitrides of composition Li<sub>x</sub>MnN<sub>3.5</sub>O<sub>(x-5.5)/2</sub> by solid state reaction of lithium oxide, and lithium and manganese nitrides under nitrogen. These phases have been fully characterised from both a structural and an electrochemical point of view. Air stability tests indicate that even though they are not fully air stable, their degradation is considerably slower than that of the parent nitride Li<sub>7</sub>MnN<sub>4</sub> and hence can be processed without problems in a dry room environment. Their structure contains some cationic vacancies and is cubic anti-fluorite type with Li/Mn and O/N randomly occupying cationic and anionic sites respectively, in contrast to that of Li<sub>7</sub>MnN<sub>4</sub> in which Li/Mn ordering induce the appearance of a superstructure with doubling of the unit cell. The oxygen content was found to have a great influence on the voltage composition profile of the obtained oxynitrides. Indeed, higher oxygen amounts result in an increase of voltage and a decrease of the irreversible plateau at ca. 2V. The highest reversible capacity (310 mAh/g) was exhibited by the sample with x ≈ 8. This capacity value is similar to that of Li<sub>7</sub>MnN<sub>4</sub> but the oxynitride has the additional advantage of presenting lower capacity fade upon cycling. The structural changes taking place upon lithium intercalation/de-intercalation in these compounds have also been studied by means of *in situ* X-ray diffraction. The redox mechanism was found to be a classical intercalation-deintercalation process and, unlike in transition metal binary nitrides, no conversion reactions were observed. In summary, our results indicate that the study of lithium transition metal oxynitrides is a promising field in view of finding nitride based air stable compounds to be used as negative electrode materials in lithium ion batteries.

#### 2:00 PM \*B6.2

**The Development of Universal Lithium Anodes and Next Generation Li Batteries Based on Them.** Steven Joseph Visco, Eugene Nimon, Bruce Katz, Lutgard C. De Jonghe and May-Ying Chu; PolyPlus Battery Company, Berkeley, California.

The huge market for portable electronic devices has created strong incentives to develop next generation batteries capable of even higher energy densities than are possible with current Li-ion technology. Researchers at PolyPlus Battery Company have made a breakthrough in the development of lithium metal anodes de-coupled from liquid electrolytes through the use of a thin, multi-layer solid electrolyte membrane. Lithium anodes are thermodynamically unstable to all liquid electrolytes; however, with careful choice of the solvent system, the lithium electrode can be passivated by the formation of a suitable SEI (solid electrolyte interface). However, these SEIs are not true solid electrolytes, but rather multi-phase surface films specific to the particular solvent system in which they were formed. For the case of Li-ion batteries, the SEI layer is quite effective at protecting the

carbon anode from further reaction and leads to highly reversible cycling. Although lithium metal anodes can also form a passive surface through reaction with suitable electrolytes, this film is often disrupted on cell discharge (Li stripping), and on charge lithium dendrites are formed that easily break through the fragile SEI. The gravimetric capacity of lithium (3800 mAh/g and 2030 mAh/cc) is much higher than that of carbon providing a strong impetus to develop a stable lithium metal anode. In this talk, a unique approach is described where the lithium electrode is in contact with a solid electrolyte that is thermodynamically stable to lithium, followed by a second solid electrolyte that is stable to most aprotic and protic solvents, including water. Lithium metal reacts with virtually all battery solvents and most oxides to form a variety of lithium compounds. However, lithium is stable to fully reduced salts such as the halides, (LiCl, LiBr, etc.) and nitrides Li<sub>3</sub>N and Li<sub>3</sub>P. The low lithium ion conductivity of the halides precludes their use as electrolyte layer (except in very low rate applications), but the nitrides and phosphides have very high Li ion conductivity (~ 10-3 S/cm at RT). However, lithium nitride also has a narrow potential window of stability (~ 0.5 volts) and therefore would be oxidized by any useful positive electrode material. The LISICON [LiM<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>] electrolytes also exhibit excellent Li ion conductivity (~ 10-3 S/cm at RT), are air and water stable, but are unstable to reduction by lithium. A universal anode can be constructed by combining the properties of all 3 components, such that lithium metal is adjacent to the nitride or phosphide electrolyte that in turn is adjacent to the LISICON electrolyte. In this way a lithium metal anode is created that is stable in almost any conceivable liquid electrolyte, including aqueous systems. This enables the development of new battery chemistries with unprecedented energy densities, a number of which will be described in the presentation.

### 3:30 PM B6.3

**New Anode Materials for Lithium Batteries.** Quan Fan<sup>1</sup>, Peter Zavalij<sup>2</sup> and M. Stanley Whittingham<sup>1</sup>; <sup>1</sup>Chemistry, SUNY-Binghamton, Binghamton, New York; <sup>2</sup>University of Maryland, College Park, Maryland.

Graphite carbon anode in commercial lithium ion batteries has a relatively low capacity and may pose safety problems. Studies have been extensively carried out on various metals and alloys, which can reversibly react with lithium to form intermetallic phases at a potential around 500 mV above pure lithium (to minimize risk of lithium plating and thus enhance safety), and have higher volumetric energy densities than carbon. Pure bulk tin foil has a capacity of >600 mAh/g over more than 10 deep reaction cycles, and Sn-Bi eutectic alloy has similar capacity yet displays faster capacity drop. Binding the tin particles to a conducting substrate, such as copper, should mitigate the effect of particle-to-particle electronic isolation; factors such as copper surface roughness and tin thickness are being studied. The impact of electrolyte solvent and salt on the capacity retention has also been investigated with a comparison of LiPF<sub>6</sub> based and LiBOB based electrolyte. An alternative approach is to use oxide nanofibers, such as of manganese. This work is being supported by the US DOE FreedomCAR program.

### 3:45 PM B6.4

**Carbon Nanotubes: Electrochemical Applications.** Sanju Gupta, Physics and Materials Science, Missouri State University, Springfield, Missouri.

The isothermal conversion of chemical energy into mechanical work underlies the motility of all living systems - natural muscles. In this presentation, actuators built from a macro scale sheets of single-wall carbon nanotubes (bucky paper), which is among the growing list of several actuator materials since its pioneer demonstration, will be investigated. They are therefore dubbed as artificial muscles lying under the category of electro-chemo-mechanical devices, whereby the transformation of chemical energy into mechanical energy is triggered by electrical signal or dc bias. They operate as a result of double-layer (i.e. electrochemical double layer; ECDL) charge injection in electrodes having very high gravimetric surface area and gravimetric/specific capacitance and the output of the actuator may be a mechanical displacement that can be used to accomplish mechanical work. Despite several benefits (low operating voltages, conducting nature, high temperature performance, and unusual electro-mechanical coupling), some open questions concerning the actuation principle/mechanism remain. They stretch if they are electrically charged and stretching is due to the elongation of C-C bond (i.e. tangential displacement mode) - if bonding states are depopulated or if anti-bonding states are populated. This study addresses and presents these issues and aim to comprehend the various contributions by investigating the charge transfer dynamics on the surface of single-wall carbon nanotubes using in situ resonance Raman spectroscopy (RRS) and to determine the associated parameters include microscopic strain, fractional charge transfer and the corresponding shift in Fermi level through modeling [1,2]. We found the in-plane compressive strain (~ -0.25%) and the charge transfer per

carbon atom ( $f_c \sim -0.005$ ) as an upper bound for the electrolytes used i.e. CaCl<sub>2</sub>. These results can be quantitatively understood in terms of the changes in the energy gaps between the one-dimensional van Hove singularities in the electron density of states arising possibly due to the alterations in the overlap integral of bonds between the p orbitals of the adjacent carbon atoms. Moreover, the extent of variation of the absolute potential of the Fermi level or alternatively modification of band gap is estimated from modeling Raman intensity to be around 0.1 eV as an upper bound for CaCl<sub>2</sub>. The cyclic voltammetry and ac electrochemical impedance spectroscopy results will be discussed briefly which help to demonstrate well-developed capacitive behavior of single-wall carbon nanotubes sheet and to estimate the gravimetric/specific capacitances and the electrochemical storage capabilities as well. [1] S. Gupta, M. Hughes, A. H. Windle, and J. Robertson, *J. Appl. Phys.* 95, 2038 (2004) and references therein. [Selected for Virtual Journal of Nanoscale Science & Technology June Issue (2004)]. [2] S. Gupta, *Appl. Phys. Lett.* (Submitted, June 2005).

### 4:00 PM B6.5

**Composite Graphite and Fullerene Soot Li-Ion Negative Electrodes.** Robert E. Doe, Michael J. Erickson, Louis J. Rendek and Michael J. Wagner; Department of Chemistry, The George Washington University, Washington, District of Columbia.

Commercial Li-ion cells generally utilize synthetic graphite as the active material in the negative electrode, however high rate and extended cycling as well as deep depth of discharge cause rapid irreversible loss of capacity. The capacity loss is due primarily to electrolyte breakdown and growth of a passivation film at the electrode-electrolyte interface as well as exfoliation of the graphitic structure by the electrolyte. Several routes, including the introduction of non-graphitic carbonaceous materials into graphite, are being investigated to minimize capacity fade. Composite electrodes containing both graphite and an arc-generated fullerene soot show superior capacity retention upon extended cycling when compared to graphite alone electrodes. The mechanism underlying this performance is not fully understood in part because fullerene soot contains a variety of species including fullerenes, incomplete fullerenes, and polycyclic aromatic hydrocarbons. While some components of fullerene soot are responsible for the stabilization of anode capacity observed, others exhibit no effect or even a negative influence. The origin of the capacity retention is currently being investigated via EIS, ATR-IR, and MALDI-MS while probing the electrochemical limits of this material through various galvanostatic and potentiostatic tests. The results of our investigations into the mechanism for this unexpected behavior as well as which species in the fullerene soot are responsible for capacity fade stabilization of graphitic lithium-ion negative electrodes will be presented.

### 4:15 PM B6.6

**Optimization of Electrochemical Properties of Nanoparticulate Manganese Oxide Thin Films.** Suh Cem Pang, Yen Yuan Tay and Suk Fun Chin; Faculty of Resource Sciences & Technology, Universiti Malaysia Sarawak, Kota Samarahan, Sarawak, Malaysia.

Thin films of nanoparticulate tetrapropylammonium manganese oxide (TPA-MO) were being prepared on stainless steel foils by electrophoretic deposition (EPD) of preformed TPA-MO nanoparticles in stable colloidal suspensions. Electrochemical characterization of these films was conducted with a 3-electrode configuration setup in 1M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte using cyclic voltammetry. Among physical characterization techniques used include scanning electron microscope (SEM), pore size and surface area analyzer (BET), x-ray diffractometer (XRD), and thermogravimetric analyzer (TGA/DTA). Optimization of electrochemical properties was focused mainly on enhancing the charge capacity, specific capacitance, cycling reversibility and stability of TPA-MO thin films through altering parameters such as composition, sintering temperature, film thickness and loading of active materials. Optimized TPA-MO thin films were observed to exhibit excellent capacitive behaviors with their cyclic voltammograms almost perfectly rectangular in shape over the potential range of 0 to +1.0 V (vs SCE). Maximum charge capacity as high as 152 mF/cm<sup>2</sup> have been achieved for optimized TPA-MO thin films. Optimized films also showed high cycling reversibility and stability as evidenced by the anodic/cathodic current ratios remained close to 1 and total charge capacity loss of about 20% upon cycling for 1,600 cycles. The effect of microstructure on the electrochemical properties of nanoparticulate manganese oxide thin films was being further investigated through elucidation of the microstructure-property relationship. Thin films with enhanced electrochemical properties were being prepared by tailoring microstructural parameters such as the porosity, specific surface area and pore size distribution.

### 4:30 PM B6.7

**Novel Electrode Materials via Mechanical Treatment and**

**Chemical Vapor Deposition Methods.** Malgorzata K. Gulbinska<sup>1</sup>, Joseph S. Gnanaraj<sup>2</sup> and Steven L. Suih<sup>3</sup>; <sup>1</sup>Lithion, Inc, Pawcatuck, Connecticut; <sup>2</sup>Worcester Polytechnic Institute, Worcester, Massachusetts; <sup>3</sup>University of Connecticut, Storrs, Connecticut.

Carbonaceous materials are the most common commercial anodes in secondary lithium-ion batteries. Among carbon-based materials, natural graphite is the most promising anode material because of the high theoretical lithium intercalation specific capacity of 372 mAh/g, flat voltage potential profile, low irreversible capacity, and low cost. However, graphite electrodes fail in a number of commonly used electrolyte solutions, such as propylene carbonate (PC). Silicon-based powders provide an alternative to carbon-based anode materials due to the high theoretical capacity values (c.a. 4000 mAh/g), related to the high lithium-content silicides (e.g. Li<sub>4.4</sub>Si), formed during anodes operation. However, tremendous volume changes in silicon associated with the formation of lithium silicides cause mechanical degradation of the anode, and eventual capacity fading. Several experimental routes were taken in order to obtain successful anode materials: mechanical alteration of the powdered substrates, and composite materials formation. Particle size reduction of the silicon powders by milling was attempted to sustain the electrical contact between the current collector and the anode material upon repeated cycling of silicon-based anodes. The composites formation involved coating of the powdered substrates (graphite-, or silicon-based), thus modifying their surface properties and cycling performance. Natural graphite substrates (PNG) were coated with protective layer of disordered carbon in order to prevent the electrolyte reduction and to increase the cycling stability of PNG. Silicon coating was also deposited onto the graphite surface to provide sites for lithium intercalation, and to form the electronic conducting layer in the composite anode. Silicon powders were coated with protective carbon layer, derived from hydrocarbon precursors (toluene, propylene, and methane). Disordered carbon coatings provided protection against mechanical degradation of silicon-based anodes. Fluidized-bed Chemical Vapor Deposition (FBCVD) was a method of choice in forming both carbon, and silicon coatings on graphite and silicon powders, respectively. The advantage of fluidized bed CVD method over other coating processes is the ability to deposit uniform coating with the controlled thickness onto large quantities of substrate particles (silicon and graphite powders, respectively). Several instrumental techniques (X-ray diffraction methods, scanning electron microscopy, transmission electron microscopy, Auger electron spectroscopy, Raman spectroscopy, elemental analyses, etc.) were used to characterize the new anode materials. Coin cells were assembled and tested to evaluate the electrochemical properties of coated and milled materials.

#### 4:45 PM **B6.8**

##### **New Cu<sub>6</sub>Sn<sub>5</sub> Thin Film Electrodes for High Performance Thin Film Batteries: Synthesis and Characterization.**

Il-Seok Kim<sup>1</sup>, Orlando H. Auciello<sup>1</sup>, John T. Vaughney<sup>2</sup>, J. Elam<sup>3</sup>, J. A. Carlisle<sup>1</sup> and M. Pellin<sup>1</sup>; <sup>1</sup>MSD, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>CMT, Argonne National Laboratory, Argonne, Illinois; <sup>3</sup>ES, Argonne National Laboratory, Argonne, Illinois.

Thin film Cu<sub>6</sub>Sn<sub>5</sub> anodes were prepared by deposition of Cu<sub>6</sub>Sn<sub>5</sub> films on stainless steel disks using radio frequency (RF) magnetron sputtering. Different heterostructures, consisting of as-deposited Cu<sub>6</sub>Sn<sub>5</sub>, annealed Cu<sub>6</sub>Sn<sub>5</sub>, Cu<sub>6</sub>Sn<sub>5</sub>/Pt and Cu<sub>6</sub>Sn<sub>5</sub>/Ni, were prepared as film electrodes. The annealed Cu<sub>6</sub>Sn<sub>5</sub> films had a lower energy capacity when compared to the as-deposited film, most likely caused by grain growth during heat-treatment. The heterostructures that incorporate a Pt or Ni under-layer exhibit secondary phase(s) as revealed by XRD analysis. Notably, the Cu<sub>6</sub>Sn<sub>5</sub> anode with a Ni layer revealed a rapid fade in energy capacity suggesting that the secondary active phase(s) is detrimental in cycling performance of the electrode layer, while the Cu<sub>6</sub>Sn<sub>5</sub>/Pt anode displayed a high capacity of ~358 mAh/g or ~2964 mAh/ml with good capacity retention, which is more than 4 times higher than that of commercially used carbon anodes (850mAh/ml). Therefore, our initial results indicate that Cu<sub>6</sub>Sn<sub>5</sub> film anodes exhibit high volumetric/stable energy capacity, making this material an excellent candidate for thin film battery electrodes.

SESSION B7: Poster Session: Next Generation Batteries and Supercapacitors  
Chairs: Clare Grey and M. Stanley Whittingham  
Wednesday Evening, November 30, 2005  
8:00 PM  
Exhibition Hall D (Hynes)

#### **B7.1**

**Carbon Nanofiber Structure and Electrochemistry.** Kenneth J. Takeuchi<sup>1</sup>, Amy C. Marschillok<sup>1,2</sup>, Randolph A. Leising<sup>2</sup> and Esther Sans Takeuchi<sup>2</sup>; <sup>1</sup>Department of Chemistry, University at Buffalo, Buffalo, New York; <sup>2</sup>Research and Development, Greatbatch, Inc.,

Clarence, New York.

The preparation, characterization and electrochemistry of a new type of carbon nanofiber is reported. In addition, two different commercially available carbons are studied in parallel to benchmark the properties of our carbon nanofibers. Carbon electrochemistries are interrogated in coin sized cells versus lithium electrodes. Correlations are noted, and explanations are offered to describe broader carbon structure / function relationships.

#### **B7.2**

##### **Graphite Foam as Current Collectors for Lead-Acid and**

**Lithium-Ion Batteries.** Young-Il Jang<sup>1</sup>, Nancy J. Dudney<sup>1</sup>, James W. Klett<sup>2</sup> and Terry N. Tiegs<sup>2</sup>; <sup>1</sup>Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Graphite foam recently developed at Oak Ridge National Laboratory is a promising candidate for current collectors for various types of batteries. It is lightweight (0.6 g/cm<sup>3</sup>) and chemically inert with many aqueous and nonaqueous electrolytes. The conductive graphene layers are oriented along the walls of the foam, giving the monolithic structure high electrical and thermal conductivities (10<sup>3</sup> S/cm, 180 W/m K). When used as battery current collectors, the combination of excellent transport properties with high surface area and low mass density may provide dramatic improvement in performance of batteries. Electrochemical characterization has been performed on graphite foam as current collectors for lead-acid batteries. Graphite foam is electrochemically stable as the negative current collector. However, intercalation of sulfuric acid into graphite limits the use of graphite foam as the positive current collector. Intercalation of sulfuric acid is suppressed in non-graphitized foam, improving the electrochemical stability as the positive current collector. Electrochemical properties of graphite foam as current collectors for lithium-ion batteries will also be presented. This research was sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

#### **B7.3**

**Abstract Withdrawn**

#### **B7.4**

**Abstract Withdrawn**

#### **B7.5**

##### **Synthesis and Electrochemical Properties of Tin Oxide-Carbon Nanotube Composites as Anode Materials for Li-ion Batteries.**

Bingqing Wei and Subramanian Venkatchalam; Electrical and Computer Engineering, Louisiana State University, Baton Rouge, Louisiana.

Li-ion batteries are widely used in a range of consumer electronic devices such as camcorders, digital cameras, laptop computers, cellular phones, etc., mainly because of its light weight and high energy density. The present day commercial Li-ion battery uses predominantly LiCoO<sub>2</sub> as a cathode and carbonaceous material as anode where in the Li-ion intercalates and de-intercalates during charging and discharging process. Apart from carbon based anode materials, interest in the development of metal oxide based materials in nanoarchitectures have gained importance in recent years mainly due to advantages of increased energy and power densities of the battery system. Variety of metal oxides such as nanostructured TiO<sub>2</sub>, SnO<sub>2</sub>, MnO<sub>2</sub>, NiO, Fe<sub>2</sub>O<sub>3</sub> etc are ventured to be used as anode materials in Li-ion batteries. In this presentation, we present the synthesis and electrochemical properties of SnO<sub>2</sub>: Carbon Nanotube (CNT) composites. The SnO<sub>2</sub> nanoparticles were synthesized via a soft chemistry route using citric acid as a complexing agent. The composites of SnO<sub>2</sub> and CNT were made by adding nanoparticles of SnO<sub>2</sub> to the ethanolic solution of either single walled (SW) or multi-walled (MW) CNT. Prior to the addition of the SnO<sub>2</sub> nanoparticles, the SW or MW CNT is mixed well in an ethanolic solution overnight using a magnetic stirrer. Composites with different weight ratios of SnO<sub>2</sub> and CNT were prepared in order to optimize the system with best electrochemical properties. The structural properties of the synthesized materials were studied using XRD, SEM, TEM and surface area measurements. The electrochemical properties were evaluated in a two electrode test cell by galvanostatic cycling using Li-metal as an anode in a 1M LiPF<sub>6</sub>:EC:DMC non-aqueous electrolyte in a voltage range 0.02 to 3V at a current density of 0.5 mA/cm<sup>2</sup>. The rate capability of the different composites was studied by cycling the battery at different specific currents from 100 mA/g to 5 A/g. The redox reactions occurring during the Li-ion insertion and deinsertion properties were studied using Cyclic Voltammetry (CV) in a slow scan mode. The electrode kinetics of SnO<sub>2</sub>: CNT composites were studied at different voltages using electrochemical impedance

spectroscopy (EIS). Also, to further understand the electrode reactions occurring because of Li-ion insertion and deinsertion in the SnO<sub>2</sub>:CNT composite electrodes, ex-situ XPS measurements were performed and complemented with the EIS results. In this paper, an elaborate comparison of the structural, surface, electrochemical and compositional properties will be made and discussed in detail.

**B7.6**  
**Sprayed Transition Metal Oxide – Carbon Composites for Lithium-Ion Batteries.** S. A. Needham, G. X. Wang, K. Konstantinov, Y. Tournayre, G. Lao and H. K. Liu; University of Wollongong, Wollongong 2522, New South Wales, Australia.

Poizot et al. [1] first reported that electrodes made of nano-sized transition metal oxide particles of the form MO (M = Ni, Fe, Co) exhibit reversible capacities up to three times higher than electrodes composed of graphite. Researchers have long identified Li-ion battery material candidates by their ability to form reversible alloys with lithium or the existence of an open crystal structure. These divalent transition metal oxides do not display any of these characteristics. Rather, the reaction of these materials with lithium involves the reversible formation and decomposition of Li<sub>2</sub>O. It has also been shown that other forms of transition metal oxides such as Co<sub>3</sub>O<sub>4</sub> demonstrate a similar mechanism when reacted with lithium [1]. For Co<sub>3</sub>O<sub>4</sub>, electrochemical reaction with lithium is accompanied by the formation of a solid electrolyte interface (SEI) layer during the first discharge. Initial cycling can result this layer thickening and/or being partially dissolved [2]. The thickness of the SEI has proven to be a critical factor in the cyclability of the electrode. If the SEI layer is too thick, it will impede the reactivity between Co<sub>3</sub>O<sub>4</sub> and lithium thereby reducing the capacity retention of the electrode [3]. We have approached the problem of poor cyclability in Co<sub>3</sub>O<sub>4</sub> based electrodes by processing Co<sub>3</sub>O<sub>4</sub> - carbon composite powders using a chemical spray pyrolysis technique. The carbon was sourced from common sugar (sucrose) added to a 0.2 M cobalt nitrate precursor solution. SEM observation indicates highly porous spherical shaped particles. Preliminary electrochemical testing is encouraging and shows that the Co<sub>3</sub>O<sub>4</sub> - carbon composite electrodes possess excellent cyclability and a reversible discharge capacity in excess of 850 mAh/g. Further imaging techniques and electrochemical investigation (including a.c. impedance) are ongoing. \* Corresponding author, email: scott.needham@uow.edu.au, Fax: 61-2-42215731 Acknowledgements The authors would like to acknowledge financial support provided by the Australian Research Council. References [1] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J-M. Tarascon, Nature 407 (2000) 496-499. [2] S. Grugeon, S. Laruelle, R. Herrera-Urbina, L. Dupont, P. Poizot, and J-M. Tarascon, J. Electrochem. Soc. 148(4) (2001) A285-A292. [3] P. Poizot S. Laruelle, S. Grugeon, L. Dupont, and J-M. Tarascon, J. Power Sources 97-98 (2001) 235-239.

**B7.7**  
**Nano-Alloys Research Activities Aimed Towards the Elaboration of a Highly Performing Negative Electrode.** Ida Baglien<sup>2</sup>, Alan Chadwick<sup>4</sup>, Kristina Edstrom<sup>2</sup>, Costana Ionica<sup>3</sup>, Jean Claude Jumas<sup>3</sup>, Dominique Larcher<sup>1</sup>, Lippens Pierre-Emmanuel<sup>3</sup> and Mathieu Morcrette<sup>1</sup>; <sup>1</sup>Laboratoire de Reactivite de Chimie des Solides, Amiens, France; <sup>2</sup>Uppsala University, Uppsala, Sweden; <sup>3</sup>LAMMI, Montpellier, France; <sup>4</sup>University of Kent, Kent, United Kingdom.

The cycling performances of Li-alloys-based electrodes are well known to deteriorate upon cycling owing to large Li-driven volume swings (up to 200%). To get around these expansion issues, basic ideas based either on the use of 1) a "buffer matrix" (i.e., an electrochemically active phase imbedded in a non-electrochemically active matrix) to compensate for the expansion of the reactants or 2) inter metallic alloys that react towards Li through displacement reactions, and provide a stable host framework with limited volume expansion/contraction for both the incoming and extruded metal atoms, have been put into practice over the years. While elegant, electrodes made according to the above concepts still suffer from poor cyclability. Thus, from a fundamental point of view, it appears essential to know if the above reactivity mechanisms are different when the size of the alloys decreases down to the nano-size. Thus our mission, within the scope of ALISTORE, is to develop a scientific platform that could enable the practical use of single alloy elements such as Li<sub>x</sub>Si, which is theoretically very attractive but whose practical use is still very troublesome. Moving towards its mission, the nano-alloys group has, pursued studies aimed at providing a better understanding of Li reactivity mechanism in inter metallic alloys in the hope of distinguishing between alloying, displacement, restructuring and conversion-type reactions in both single elements and binary phases. Along that line MS<sub>b</sub>x and MS<sub>n</sub>x, where M is a metal that either alloys with Li (Mg, Sn) or does not (Cu ; Mn), have been defined as model compounds, and synthesized by ball-milling elemental powders. Their electrochemical performances together with the way that they react towards Li was carried out using an arsenal of

in situ characterization techniques involving X-Ray, Neutron diffraction as well as TEM, Mossbauer and absorption spectroscopy. An overview of the different reactivity of these materials will be presented in this communication.

**B7.8**  
**The Electrochemical Properties of Carbon Nanotubes Coated Cu as Anode of Lithium Ion Battery.** Chen Xiaohong and Song Huaihe; Beijing University of Chemical Technology, Beijing, China.

Carbon nanotubes coated Cu were prepared by the treatments of acid, sensitization, activation and copperizing. The microstructure and electrochemical properties of carbon nanotubes coated Cu were investigated by HREM, IR, XRD and discharge-charge measurement. Results showed that carbon nanotube coated Cu have higher initial capacities of discharge and charge which are 1365 mAh/g and 710 mAh/g respectively. After five cycles, the capacity can maintain 83 % of initial capacity.

**B7.9**  
**Sulfur-doped nanocrystalline diamond employed as anode in rechargeable Li batteries.** Joel De Jesus, Fabrice Piazza, Santander Nieto, Ram S. Katiyar, Donald Tryk, Carlos Cabrera, Brad R. Weiner and Gerardo Morell; University of Puerto Rico, San Juan, Puerto Rico.

Sulfur-doped nanocrystalline diamond was tested as anode material in Li batteries. Graphite is typically used in these batteries, with the well-known drawback of swelling and degradation. Ab initio calculations indicate that Li enters the diamond lattice interstitially, with minimum disruption of the lattice dimensions [1]. Therefore, conductive nanocrystalline diamond can represent a significant advantage over graphite anodes. We had previously shown n-type behavior in S-doped diamond [2]. A variety of sulfur-doped nanocrystalline diamond with different sp<sup>3</sup> C to sp<sup>2</sup> C content ratios were grown on Mo substrates by hot filament chemical vapor deposition to be tested as anodes in Li batteries. It was first observed that strong currents are generated that took the measuring system outside the measuring range typical for graphite anodes. Changes in the testing system were subsequently implemented in order to enable measuring the actual battery response with nanocrystalline diamond anodes. We thus report the results of these investigations centered around two important battery issues: the actual level of intercalation and its reversibility. [1] Kajihara et al, Phys. Rev. Lett. 66 (1991) 2010; Physica B 185 (1993) 144. [2] Gupta et al, Applied Physics Letters 83 (2003) 491.

**B7.10**  
**The Intercalation Potential of Li in Diamond Battery Anodes: Density Functional Theory Approach.** Hulusi Yilmaz, Brad R. Weiner and Gerardo Morell; Physics, University of Puerto Rico, San Juan, Puerto Rico.

Anode materials in rechargeable Li batteries have a strong impact in the overall battery performance. They should be able to intercalate large amounts of Li<sup>+</sup> reversibly at low voltages and with minimum lattice expansion. The ab initio calculations of Kajihara et al had shown that Li can enter the diamond lattice interstitially, with minimum disruption of the lattice dimensions [1]. In this study, using Density Functional Theory within generalized gradient approximation, the intercalation potential of lithium ions in (110) and (100) surfaces of both intrinsic diamond and S-doped diamond were examined. In this context, the dependence of the intercalation potential on the interstitial lithium ion density and substitutional sulfur atoms was analyzed. The structural deformations and the changes in electronic properties of Li-intercalated S-doped diamond are presented. [1] Kajihara et al, Phys. Rev. Lett. 66 (1991) 2010; Physica B 185 (1993) 144.

**B7.11**  
**The Electrochemical Properties of Carbon Aerogel Containing Nano-Si as Anode of Lithium-ion Battery.** Chen Xiaohong, Xia Sanyu and Song Huaihe; Beijing University of Chemical Technology, Beijing, China.

A carbon aerogel containing Si was synthesized by a series of processes such as sol-gelation, supercritical drying and carbonization using resorcinol(R), formaldehyde(F) and nano-Si powder. The microstructure of carbon aerogel containing nano-Si was characterized by SEM, XRD and electrochemical tests. The relative results of different molar ratios of R:F:Si indicated that when the ratio of R:Si equals 1, the composite has high capacity and excellent cyclability, the first discharge capacity and charge capacity of which is 663 mAh/g and 415 mAh/g, respectively. After 20th cycle, and the capacities of discharge and charge are 484mAh/g and 462mAh/g respectively. Carbon matrix would alleviate the volume effect of Si particles during charging/discharging, the conductivity of encapsulated composites

would also be enhanced by the carbon matrix, simultaneously. The original structure of Si is crystal in the composites, however, crystal Si would change to metastable amorphous during alloying/dealloying, which contributes to the first capacity loss.

#### **B7.12**

**Electrochemical performance of spherical LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> powders coated with metal oxide.** Seon Hye Kim<sup>1,2</sup>, Kook Jae Lee<sup>1,2</sup>, Kwang Bo Shim<sup>1</sup>, Kyoung Ran Han<sup>2</sup> and Chang Sam Kim<sup>2</sup>; <sup>1</sup>Department of Ceramic Engineering, Hanyang University, Seoul, South Korea; <sup>2</sup>Division of Materials Science and Engineering, KIST, Seoul, South Korea.

Layered LiMeO<sub>2</sub> (Me; transition metal) has been widely investigated as active cathode materials for lithium-ion batteries. Among them LiCoO<sub>2</sub> was the first material commercialized because of its good rate capability and high conductivity. However since its high cost and toxicity of Co in LiCoO<sub>2</sub>, a lot of studies to substitute Co to other transition metals, e.g. Ni or Mn, have been performed. LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> is one of the candidate materials for the alternatives, because of its high capacity, good thermal stability and low cost, but it also has some drawbacks such as lower tap density comparing with LiCoO<sub>2</sub>. The tap density is determined by the size, the size distribution and the morphology of particles. The properties of particles play a great role for the performance of the batteries too. So we tried to make fine and dense spherical LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> powders using ultrasonic spray pyrolysis method and subsequent sol-gel coating. The precursor solution was prepared by mixing LiNO<sub>3</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at a mole ratio of 3:1:1:1 in deionized water. The solution was atomized using an ultrasonic nebulizer with a resonant frequency of 1.67 MHz. The drops generated were introduced by a carrier gas to a vertical quartz reactor heated at 800 °C. The synthesized powder were annealed at 800 - 1000 °C and then coated with alumina or magnesia sol and heat-treated at 600-800 °C, successively. The collected powders were subjected to XRD analysis and observed by SEM and TEM. Capacity measurements and cycling tests were carried out in a voltage range between 3.0-4.5 V at 0.1-C rates using coin-type cells. The XRD pattern of synthesized powder without any coating conformed to a well developed R3m symmetry with I003/I104 ratio of 1.42. Its initial capacity was 175 mAh/g in the voltage range of 3.0-4.5 V. The effect of the alumina and magnesia coating on the morphology, microstructure and electrochemical performance will be discussed in detail.

#### **B7.13**

**Cathodic Electrosynthesis and Supercapacitive Properties of Manganese Oxide Based Thin Films.** Nandakumar Nagarajan, Harith Humadi, David S. Wilkinson and Igor Zhitomirsky; Materials Science and Engg, McMaster University, Hamilton, Ontario, Canada.

Cathodic electrosynthesis method has been developed for the deposition of manganese oxide films for application in electrochemical supercapacitors. The use of polyethylenimine (PEI) as an additive enabled the formation of adherent films, which exhibited enhanced resistance to cracking during drying. The polymer content in the deposits can be varied by changing the polymer concentration in the solutions. The mechanism for PEI deposition was proposed based on the use of PEI-Mn<sup>2+</sup> complexes. The deposition yield has been studied at different deposition durations. X-ray data of sintered films showed the crystallization of Mn<sub>3</sub>O<sub>4</sub> at 300 degC and Mn<sub>2</sub>O<sub>3</sub> at 500 degC. The electrochemical performance of the films sintered at different temperatures was studied by cyclic voltammetry (CV), chronopotentiometry and impedance spectroscopy in Na<sub>2</sub>SO<sub>4</sub> solutions. Obtained films showed excellent pseudocapacitive behavior in the potential window of 0-0.9V. The SC calculated from the CV data decreased from 425 to 318 F/g with increasing scan rate in the range of 10 - 100 mV/s. The SC measured from the chronopotentiometry data is about 470 F/g. After 1000 cycles of operation, the electrode can maintain ~ 80% of its initial capacitance. Microstructural analysis via FE-SEM was used to correlate the structural features of the films with their properties. These investigations showed changes in the film morphology and cracking during cycling, which can result in the reduction in the SC during 1000 cycles. The SC decreased with increasing sintering temperature in the range of 300-500 degC. Impedance measurements showed that the increase in electrode mass resulted in increasing electrical resistance. Mn-Co mixed oxides and layered materials were also investigated for supercapacitor applications, on various substrates. Cyclic-voltammetry, galvanostatic-charge-discharge and impedance data for these materials are also presented.

#### **B7.14**

Transferred to B6.6

#### **B7.15**

**Amorphisation and Recrystallisation Study of Nanocrystalline**

**Manganese Dioxide.** Phuti E. Ngoepe<sup>1</sup>, Thi X. T. Sayle<sup>2</sup>, Regina R. Maphanga<sup>1</sup>, Dean C. Sayle<sup>2</sup> and C. Richard A. Catlow<sup>3</sup>; <sup>1</sup>Materials Modelling Centre, University of Limpopo, Sovenga, 0727, Limpopo Province, South Africa; <sup>2</sup>DOES, Royal Military College of Science, Cranfield University, Shrivenham, Swindon, SN6 8LA, United Kingdom; <sup>3</sup>Davy Faraday Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, W1S 4BS, United Kingdom.

The Electrolytic Manganese Dioxide (EMD) serves as a cathode material in alkaline batteries, and is known to be a disordered random intergrowth of pyrolusite and ramsdellite manganese dioxide polymorphs. It has superior electrochemical discharge properties to other forms of manganese dioxide of similar composition and structure. Experimental methods such as X-ray diffraction and IR spectroscopy, which provide information on the long-range order are not sufficient to characterize EMD materials and hence there has been no efficient method to characterize their structures and thereby no means of relating their atomic scale arrangement with their behavior in batteries. In this work models of manganese dioxide nanoparticles, with full atomistic detail, have been generated using a simulated amorphisation and recrystallisation strategy. In particular, a 25,000-atom 'cube' of manganese dioxide was amorphised (tension-included) under molecular dynamics (MD). Long-duration MD, applied to this system, results in the sudden evolution of a small crystalline region of pyrolusite-structured manganese dioxide, which acts as a nucleating 'seed' and facilitates the recrystallisation of all surrounding (amorphous) manganese dioxide. The resulting manganese dioxide nanoparticle is about 8nm in diameter, and conforms to the pyrolusite structure (isostructural with rutile titanium dioxide, comprising '1x1' octahedra) and is heavily twinned. In addition, we suggest the presence of ramsdellite ('2x1' octahedra) intergrowths. The calculated radial distances compare reasonably with the experimental results.

#### **B7.16**

**Formation of LiNi(x)Co(1-x)O(2) by Decarbonization of Organic Gel Precursors by Low-Temperature Treatment with Nitric Acid and Hydrogen Peroxide.** Andrzej Deptula<sup>1</sup>, Kenneth C. Goretta<sup>2</sup>, W. Lada<sup>1</sup>, T. Olczak<sup>1</sup>, D. Wawrzczak<sup>1</sup> and B. Sartowska<sup>1</sup>; <sup>1</sup>Institute of Nuclear Chemistry and Technology, Warsaw; <sup>2</sup>Argonne National Lab, Argonne, Illinois.

Layered LiNiCoO compounds have received considerable attention as electrode materials in high-energy-density batteries. We have used our complex sol-gel process to synthesize LiNi(x)Co(1-x)O(2), where x = 0, 0.25, 0.5, 0.75, or 1. Starting sols were prepared from Ni-Co acetates + ascorbic acid aqueous solutions by alkalinizing with lithium hydroxide and ammonia. With thermal treatment in air, nickel carbonates formed in quantities roughly proportional to Ni content. The carbonate impurities could not be fully removed by heating in air to high temperatures. Because formation of pure layered oxides was inhibited by the presence of the carbonates, we developed a new way to remove the carbonates from just-formed precursors by treating the intermediate phases (e.g., those formed after calcination at 750C) with concentrated nitric acid and hydrogen peroxide. All resulting oxides were phase pure by X-ray diffraction, and exhibited powdery morphologies and excellent electrochemical properties. Work was supported by the Polish government and, at Argonne National Laboratory by the U.S. Department of Energy under Contract W-31-109-Eng-38.

#### **B7.17**

Abstract Withdrawn

#### **B7.18**

**Syntheses of LiCoO<sub>2</sub> for Cathode Materials of Secondary Batteries at Low Temperature by the High-Frequency Microwave.** Lihong Su, Chemical Engineering, Northwestern Polytechnical University, Xi'an, China.

The use of microwaves for solid-state synthesis is a fairly new development but promises advantages in time and energy efficiency. Synthesized LiCoO<sub>2</sub> by the high-frequency microwave is investigated in this paper. Using the superfine Co<sub>3</sub>O<sub>4</sub> powders as start material, acquired LiCoO<sub>2</sub> at 400-500C in 1 hours. Researched the factor affect the process. LiCoO<sub>2</sub> has well-crystallized with the layered structure. The consequences in terms of the phase purity, crystallization, and particle sizes are described. The charging capacity is up to 185mAh/g, and both the platform charging curve and time for charging/discharging demonstrate the electrochemical activity of the microwave synthesized LiCoO<sub>2</sub>.

#### **B7.19**

**On the use of XAS and Mossbauer spectroscopies for lithiated iron phosphates.** Charles Delacourt<sup>1</sup>, Dominique Bonnin<sup>2</sup> and Christian Masquelier<sup>1</sup>; <sup>1</sup>LRCS - Chemistry, Universite Picardie

Jules Verne, Amiens, France; <sup>2</sup>ESPCI, Paris, France.

Recent studies have demonstrated the reversible electrochemical reaction of lithium with hydrated iron phosphates  $\text{FePO}_4 \cdot n\text{H}_2\text{O}$  at attractive average operating voltages of 3.1 V vs.  $\text{Li}^+/\text{Li}$ . This was demonstrated either for very fine particles ( $< 100$  nm) of amorphous compositions or for highly crystalline forms such as phosphosiderite  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ . Additionally, there is a tremendous effort worldwide to fully understand and further improve the surprisingly fast response of  $\text{LiFePO}_4$  towards electrochemical extraction at fast rates. Optimal electrochemical properties and true understanding of the electrochemical mechanism are highly dependent on the high purity of the samples, on the local environment of iron and on its oxidation state. To tackle these issues we investigated in details a whole series of  $\text{Li}_x\text{FePO}_4 \cdot n\text{H}_2\text{O}$  and  $\text{Li}_x\text{FePO}_4$  samples through XAS and Mossbauer spectroscopies.

#### **B7.20**

##### **Enhanced Li-ion Intercalation Performance in Vanadium Pentoxides through Engineering of Nanostructure and Interlayer Structure.** Ying Wang<sup>1</sup>, Katsunori Takahashi<sup>1,2</sup> and

Guozhong Cao<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Washington, Seattle, Washington; <sup>2</sup>Steel Research Laboratory, JFE Steel Corporation, Chuo-ku, Chiba, Japan.

This research aims to improve the Li-ion intercalation performance of  $\text{V}_2\text{O}_5$  by engineering its nanostructure and interlayer structure. We have prepared single-crystalline  $\text{V}_2\text{O}_5$  nanorods by using the template based electrodeposition method followed by sintering at  $485^\circ\text{C}$  to obtain the pure orthorhombic phase. The resultant nanorod arrays consist of uniformly-sized and 10-micron long nanorods of  $\text{V}_2\text{O}_5$  projecting from the substrate surface. High-resolution transmission electron microscopy (TEM) micrographs and electron diffraction patterns of  $\text{V}_2\text{O}_5$  nanorods clearly show the single-crystalline nature of nanorods with a growth direction of [010]. The growth mechanism of single-crystalline  $\text{V}_2\text{O}_5$  has been discussed. The Li-ion intercalation property of the nanostructured  $\text{V}_2\text{O}_5$  electrode has been compared to a film electrode of similar  $\text{V}_2\text{O}_5$  mass and geometric area. Electrochemical analysis have demonstrated that nanorod arrays deliver significantly improved storage capacity than  $\text{V}_2\text{O}_5$  film at high discharge rate, due to the larger surface area and the shorter diffusion path. Although at a low specific current of 50 mA/g, the Li-ion intercalation capacities of nanorod arrays and films are similar and reach the maximum of 148 mAh/g, nanorod arrays can store 5 times  $\text{Li}^+$  than  $\text{V}_2\text{O}_5$  films do at a higher specific current such as 700 mA/g. Further enhancement in Li-ion intercalation property has been accomplished by introducing a small controlled fraction of water between adjacent layers in  $\text{V}_2\text{O}_5$ . Electrochemical characterizations have demonstrated that  $\text{V}_2\text{O}_5 \cdot 0.3\text{H}_2\text{O}$  film exhibits higher Li-ion intercalation capacity and more sustainable cycling life than anhydrous crystalline  $\text{V}_2\text{O}_5$  film or other  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  film ( $n = 0.1, 0.6, 1.6$ ). At a high specific current of 850 mA/g, the  $\text{V}_2\text{O}_5 \cdot 0.3\text{H}_2\text{O}$  film showed a stable cycling performance with a capacity of 185 mAh/g for 50 cycles. At a low specific current of 85 mA/g, the capacity of this film can reach 390 mAh/g. Such an enhanced electrochemical property is ascribed to the modulated water content in  $\text{V}_2\text{O}_5$ . The small amount of water intercalated between the layered structure of  $\text{V}_2\text{O}_5$  makes the interlayer spacing twice that of anhydrous crystalline  $\text{V}_2\text{O}_5$ , resulting in a higher Li-ion intercalation capacity. Simultaneously, water in  $\text{V}_2\text{O}_5 \cdot 0.3\text{H}_2\text{O}$  film is much less and more tightly bound than that in  $\text{V}_2\text{O}_5 \cdot 1.6\text{H}_2\text{O}$  xerogels, and thus deflects the damaging effect of water reacting with lithium on the cycling life.

#### **B7.21**

##### **Energetics of Lanthanide-doped Hafnia.** Petra Simoncic and Alexandra Navrotsky; Thermochemistry Facility, UC Davis, Davis, California.

$\text{HfO}_2$  is a candidate for solid electrolytes, ceramic toughening agents, nuclear waste forms, and alternative gates dielectrics. Crystallographic phases, phase transitions and energetics of  $\text{HfO}_2$  are therefore of special interest for these applications.  $\text{HfO}_2$  occurs in three polymorphs at atmospheric pressure: (1) monoclinic, (2) tetragonal, (3) cubic fluorite structure, with transition temperatures at  $1700^\circ\text{C}$  and  $2600^\circ\text{C}$ . Oxides with a disordered cubic fluorite structure display a high oxygen mobility and find applications as ionic conductors. The cubic fluorite structure of  $\text{HfO}_2$ , usually only stable at very high temperature, can be stabilized at lower temperature by doping with various elements such as Y or lanthanides.  $\text{Hf}_{1-x}\text{R}_x\text{O}_{2-x/2}$  samples with  $x = 0.4$  and  $\text{R} = \text{Sm, Gd, Dy, Yb}$  were prepared by co-precipitation. The resulting precipitates were dried overnight at  $150^\circ\text{C}$  and calcined at  $900^\circ\text{C}$  for 8 hours. The powders were annealed at  $1500^\circ\text{C}$  and quenched into liquid nitrogen. Present phases were analyzed by powder X-ray diffraction (XRD) with a Scintag (Cupertino, CA) PAD-V using  $\text{Cu K}\alpha_1$  radiation. Synchrotron powder X-ray diffraction for lattice parameters and site

occupancies by Rietveld refinement are performed on beamline X14A at NSLS, Brookhaven. Calorimetric measurements were performed with (1) a Netzsch DSC 404 determining crystallization temperature of the solid solutions, and (2) a custom built Tian-Calvet calorimeter for the determination of the enthalpy of formation. Drop solution calorimetry was carried out with all  $\text{Hf}_{1-x}\text{R}_x\text{O}_{2-x/2}$  samples ( $\text{R} = \text{Sm, Gd, Dy, Yb}$ ) using sodium molybdate solution ( $3 \text{ Na}_2\text{O} \cdot 4\text{MoO}_3$ ) at  $700^\circ\text{C}$  with  $\text{O}_2$  bubbling and flushing for better dissolution. 10 mg pellets of Hf-R solid solution powders were calibrated against the heat content of 5 mg pellets of  $\alpha\text{-Al}_2\text{O}_3$ . All  $\text{Hf}_{1-x}\text{R}_x\text{O}_{2-x/2}$  samples ( $\text{R} = \text{Sm, Gd, Dy, Yb}$ ) were cubic fluorite single phase as determined by XRD. Lattice parameters and occupancies for Hf and R sites will be presented based on synchrotron XRD data. Crystallization temperature determined by Netzsch DSC 404 for the  $\text{Hf}_{1-x}\text{R}_x\text{O}_{2-x/2}$  samples lie between  $712.1 \pm 0.6^\circ\text{C}$  ( $\text{R} = \text{Sm}$ ) and  $519.5 \pm 2.8^\circ\text{C}$  ( $\text{R} = \text{Yb}$ ). The enthalpy of formation of  $\text{Hf}_{1-x}\text{R}_x\text{O}_{2-x/2}$  samples is calculated by a thermodynamic cycle based on the enthalpies of drop solution of  $\text{HfO}_2$ ,  $\text{RO}_{1.5}$  and  $\text{Hf}_{1-x}\text{R}_x\text{O}_{2-x/2}$ .

#### **B7.22**

##### **Clusters of Iron Nanoparticles as an Alternative Energy**

**Carrier.** David B. Beach, Solomon D. Labinov and Bobby G. Sumpter; Chemistry, Oak Ridge National Lab, Oak Ridge, Tennessee.

We have recently begun an investigation of the combustion characteristics of iron nanoparticles. Due to the high surface-to-volume ratio of nanoparticles, combustion occurs entirely in the solid phase, without the very high temperatures encountered in conventional metal combustion. Furthermore, the nanostructuring is preserved through cycles of combustion, reduction, and passivation, so that the cost of nanostructuring is only paid once. The particles may be engineered to a given application by varying the size of the particle, the thickness of the passivating oxide coating, and the assembly of the particles into clusters. We believe that this control of combustion properties by nanostructuring will offer unprecedented advantages in energy transfer to remote sites because of the high energy density of metal fuels, the ability to transport them at ambient temperature and pressure, and the ability to remotely regenerate the particles. Data will be presented on peak combustion temperatures, reaction efficiency, and regeneration of the particles.

#### **B7.23**

##### **Unidirectional Conducting Nano-Structured Electrode**

**Materials for Supercapacitors.** Muge Acik and Gursel Sonmez; Materials Science & Engineering, Sabanci University, Istanbul, Orhanli/Tuzla, Turkey.

Unidirectional alignment of organic conducting polymers is presented. Monomers (i.e., pyrroles, N-methyl pyrroles, thiophenes, 3,4-ethylenedioxythiophenes) have been polymerized inside the pores of polycarbonate and alumina membranes using template synthesis technique. As a chemical approach from a different perspective to these template-synthesized polymers, a special reaction medium can be devised due to the intrinsic behavior of each kind of polymer. In developing such kind of systems that would be amenable to create various special nanostructures, both polycarbonate and alumina membranes are applied. Resulting behavior of the nano-fabricated conducting polymer based nano-arrays is investigated. The application of these conducting nano-structured materials in the development of electrodes for supercapacitors is discussed.

#### **B7.24**

##### **Rechargeable Battery based on $\text{LiNi}_1/3\text{Mn}_1/3\text{Rh}_1/3\text{O}_2$**

**Cathode material.** Maharaj S. Tomar, Osbert Oviedo, Surinder P. Singh and Rahul Singhal; Physics, University of Puerto Rico, Mayaguez, Puerto Rico.

Several oxide based materials are important for thermal coatings and cathode materials. Our ab initio calculations indicated that  $\text{LiNi}_1/3\text{Mn}_1/3\text{Rh}_1/3\text{O}_2$  is potentially important cathode material for Li-ion based rechargeable battery. However, there has been problem in the synthesis of complex oxides due to high temperature process involved in solid state reaction. The solution chemistry route was used to synthesize  $\text{LiNi}_1/3\text{Mn}_1/3\text{Rh}_1/3\text{O}_2$  material and characterized for its structural and electrochemical behavior. The results indicate that such cathode material is suitable for low voltage battery applications.

#### **B7.25**

##### **Tunnel Manganese Oxides with Orthorhombic $\text{Na}_0.44\text{MnO}_2$ Structure as Electro-Catalysts for Oxygen Reduction.**

Shaun Alia<sup>1</sup>, Katana Ngala<sup>1</sup>, Arthur Doble<sup>2</sup> and Steven L. Suib<sup>1</sup>; <sup>1</sup>Chemistry, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Lithion, Inc, Pawcatuck, Connecticut.

The tunnel compounds  $\text{NaMnO}_2$  and  $\text{Na}_x\text{TiyMn}_{1-y}\text{O}_2$  are being investigated as low cost potential catalysts for application in metal-air batteries and low energy fuel cells. The structure of this type of



materials consists of both octahedral and square pyramidal Mn ions. The manganese oxide units join to form S-shaped tunnels along the c lattice parameter. The MnO<sub>5</sub> units act as distorted octahedral units, which may facilitate oxygen transport across the structure. The compounds Na<sub>0.44</sub>MnO<sub>2</sub> and Na<sub>0.44</sub>Ti<sub>0.2</sub>Mn<sub>0.8</sub>O<sub>2</sub> have been synthesized by solution-assisted solid state synthesis in the presence of sucrose as template. The properties of these materials as oxygen reducing catalysts are of interest.

#### **B7.26**

**Structural and Electrochemical Impedance Studies of an AlPO<sub>4</sub> Nanoparticle Coating on LiCoO<sub>2</sub>.** Anjuli T. Appapillai and Y. Shao-Horn; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Application of nanoscale coatings on transition metal oxides has become a promising approach to improving the capacity retention and thermal stability of these cathode materials for lithium-ion batteries. We study the electrochemical and structural properties of an AlPO<sub>4</sub>-nanoparticle coating on LiCoO<sub>2</sub> as a cathode material. Through electrochemical impedance spectroscopy of coin-type cells, the electronic and charge-transfer resistance of the AlPO<sub>4</sub>-coated LiCoO<sub>2</sub> are compared to that of the pristine LiCoO<sub>2</sub> at various states of charge. Along with composite cathodes, cathodes comprised of active material pressed into gold foil discs will also be studied in coin cells to examine the impedance properties in the absence of the carbon and binder additives used in composites. Using an atomic force microscope, nanoscale impedance measurements of single LiCoO<sub>2</sub> crystals will be used to characterize localized transport properties and their variation across the crystal surface. In combination with cross-sectional transmission electron microscopy, which will be used to characterize the internal microstructure of the cathode particles, these studies may elucidate the correlation between the microstructure and performance characteristics of the coated and pristine LiCoO<sub>2</sub>.

#### **B7.27**

**Novel Method for Fabricating of Nano-Porous Platinum Thin Films.** Woo Sik Kim, Avner Rothschild, Joshua Hertz and Harry L. Tuller; Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nano-porous noble metal thin films such as Pt, Au, and Ag, with high specific surface area, are attractive in a wide variety of applications including batteries, electronics, sensors, clinical diagnostics, and fuel cells. The typical methods for fabricating porous thin or thick metal films are commonly based on liquid processes such as electroplating on pre-prepared templates or sel-gels using block copolymers. These fabrication techniques offer precise control over the size and structure of the final porous structure but are generally suffer from contamination and reproducibility. In this work, we report a strategy for fabricating nano-porous noble metal thin films by physical vapor deposition compatible with other film deposition processes. We obtain nano-porous Pt thin films by rf magnetron sputtering of nano-composites followed by subsequent removal of the sacrificial phase. We observe the change of microstructure of the Pt film according to the deposition conditions and discuss the relationship between the porosity and the electrochemical properties of nano-porous Pt thin films.

#### **B7.28**

**A Finite-Element Modeling for the Discharge Behavior of a Lithium-Polymer Battery.** Chee Bum Shin<sup>1</sup>, Ui Seong Kim<sup>1</sup>, Tae Hyuk Kang<sup>2</sup> and Chi-Su Kim<sup>2</sup>; <sup>1</sup>Chemical Engineering, Ajou University, Suwon, South Korea; <sup>2</sup>Battery R&D Center, VK Corporation, Pyeongtaek, South Korea.

The lithium-polymer battery is a preferred candidate as a power source for hybrid electric vehicle (HEV) and electric vehicle (EV) due to its outstanding characteristics such as high energy density, high voltage, low self-discharge rate, and good stability among others. However, much larger lithium-polymer batteries than those available in the market for consumer electronics are required for HEV and EV applications. The performance of a battery electrode is influenced by the aspect ratio, the placing of current collecting tabs, and the total amount of the current flowing through an electrode. If an electrode is not designed optimally, the potential and current density will be non-uniformly distributed, and the utilization of the active material over the electrode will be non-uniform. Accelerated degradation of the electrode may result due to excessive localized utilization of the active material on the electrode. That effect becomes more pronounced, as the size of the electrode becomes larger. Therefore, an optimum design of the electrode is pertinent for the production of larger lithium-polymer batteries. By using the finite element method, a two-dimensional modeling is performed to calculate the potential and current density distribution on the electrodes of a lithium-polymer battery comprising a LiMn<sub>2</sub>O<sub>4</sub> cathode, a graphite anode, and a plasticized electrolyte during the discharge in this work. The

distribution of the depth of discharge (DOD) on the electrode is predicted as a function of discharge time from the calculated potential and current density distribution. Based on the distribution of DOD, the effects of the aspect ratio of the electrode, the size and placing of current collecting tabs, and discharge rates on the battery performance are evaluated.

#### **B7.29**

**Gel Electrolyte for Safe, Sustainable and Low Cost Lithium-ion Batteries.** Zonghai Chen and Khalil Amine; Chemical Engineering Division, Argonne National Laboratory, Argonne, Illinois.

When lithium-ion batteries were thermally or electrically abused, a serious safety concern would occur because of the possible leakage of volatile and flammable non-aqueous electrolyte. In a gel-electrolyte system, the non-aqueous electrolyte is confined in the polymer framework, and the possibility of electrolyte leakage can be significantly reduced even under abuse condition. The non-liquid characteristics of the gel-electrolyte also enable the manufacturer to shift from the rigid package to a light flexible package, which can impact both the cost of the battery and its gravimetric energy density. Generally, the chemical gellation of the electrolyte can be thermally initiated with the help of some radical precursors, such as benzoyl peroxide (BPO). However, the LiPF<sub>6</sub>-based electrolyte starts to decompose at a low temperature (~55°C), and the small amount of decomposition products can lead to a significant degradation of the cell performance and the cleavage of the polymer framework. Therefore, effort was devoted to developing a gel-electrolyte system that can be gelled at room temperature. By using the proposed gel-electrolyte, the LiFePO<sub>4</sub>/graphite cells can be cycled up to 300 cycles with less than 10% capacity loss. Moreover, the impact of carbon coating on LiFePO<sub>4</sub> surface and the polymer content in the electrolyte was also investigated. Acknowledgements: This research is funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract W-31-109-Eng-38.

#### **B7.30**

**Conduction measurements of electrolyte and Bi filled nanostructures using AFM.** Karen Jo Long, Victor H. Gehman, Francisco Santiago and Kevin A. Boulais; Dahlgren Division Naval Surface Warfare Center, Dahlgren, Virginia.

This work explores electrical conduction measurements of various electrolytes and Bi confined by insulating nanostructures, <200nm, using a conducting AFM. Interest exploring Bi alloyed nanowires for thermoelectric systems together with findings in novel electrical conduction properties of confined ions may open many opportunities to develop technologies that feature the integration of thermoelectric systems with their power sources. By using electrowetting we have found that alumina nanostructures can easily be wetted/filled and by using a conducting probe with a DI 3100, I/V curves from individual nanochannels can be obtained. We will report results from measurements using a setup that features conducting AFM with temperature and atmosphere control with the goal of observing electrical conduction of low dimensional, confined structures at 77K. This work is the foundation work to develop a nanobattery operated thermoelectric system.

#### **B7.31**

**Catalytic Efficiency of FePt/C Catalyst Prepared by Using Polyol Method for Polymer Electrolyte Fuel Cells.** Yutaro Sawada<sup>1</sup>, Yoshinori Sato<sup>1</sup>, Takashi Itoh<sup>2</sup>, Balachandran Jayadevan<sup>1</sup>, Atsuo Kasuya<sup>2</sup> and Kazuyuki Tohji<sup>1</sup>; <sup>1</sup>Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; <sup>2</sup>Center for Interdisciplinary Research, Tohoku University, Sendai, Japan.

Carbon supported Pt-M alloy (M = Fe, Co, Ru, etc) catalysts show improved catalytic activity towards the oxidation-reduction reaction (ORR) in polymer electrolyte fuel cells (PEFC) [1- 4]. The role of metal M for the ORR has been investigated and assumed resulting from the shortening of Pt-Pt interatomic distances by alloying [5] or more favorable Pt-Pt distance for the ORR [6]. Here, we report preparation of FePt/C catalyst by co-reducing iron and platinum ions to deposit nanosize FePt particles with narrow size distribution on carbon support by using polyol process. The advantage of this method is that the polyol not only reduces transition metal ions like Fe, Ni, Co and their alloys, but also works as an oxidation inhibitor. The preparation process of the catalysts can be described as follows: first the salts of platinum and iron are dissolved in EG and then the carbon support is dispersed in the same. The reduction reaction was carried out by refluxing and stirring at 453 K for 3 h under nitrogen gas flow. FePt/C were obtained by filtrating, washing with acetone and drying at 333 K for 12 h. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and cyclic voltammetry (CV). For the CV measurement, a conventional three-electrode method, in which reference, counter and working electrodes were separated, was used. Pt foil and Ag/AgCl

were used as counter and reference electrodes, respectively. The working electrode was a thin layer of Nafion-impregnated catalyst casted on a glassy carbon disk and measured area (contact with electrolyte) was inside of the o-ring (diameter was 6 mm). The electrolyte, 1N H<sub>2</sub>SO<sub>4</sub> solution was purged with argon gas for nearly 30 min before starting the experiment. In this study, we compared the performance of Pt/C prepared by polyol method with commercially available catalysts to evaluate the technique used for the preparation of carbon-supported catalyst. FePt/C with varying physical properties were synthesized by controlling the reaction parameters to examine the effect of the particle size and the most appropriate atomic ratio (Fe:Pt) for ORR. Furthermore, the effect of carbon support was also studied by using different carbon materials such as carbon nanotubes, Ketjen black, etc. We will discuss the factors that determine the ORR rate and the potential of FePt/C prepared by polyol process for PEFC. [1] T. Toda et al., *J. Electrochem. Soc.*, **146**, 3750, 1999. [2] H. Igarashi et al., *Phys. Chem. Chem. Phys.*, **3**, 306, 2001. [3] L. Xiong and A. Manthiram, *Electrochemistry Communications*, **4**, 898, 2002. [4] T. Kim et al., *Electrochimica Acta*, **50**, 817, 2004. [5] V. Jalan and E. J. Taylor, *J. Electrochem. Soc.*, **130**, 2299, 1983. [6] S. Mukerjee and S. Srinivasan, *J. Electroanal. Chem.*, **357**, 201, 1993.

### **B7.32**

**Single wall carbon nanotube-based electrochemical capacitors for space exploration applications.** Heather Fireman<sup>1</sup>, Jud Ready<sup>2</sup>, Tom Reynolds<sup>3</sup>, Padraig Moloney<sup>1</sup>, Olga Gorelik<sup>4</sup>, Pasha Nikolaev<sup>4</sup>, Sivaram Arepalli<sup>4</sup> and Leonard Yowell<sup>1</sup>; <sup>1</sup>NASA Johnson Space Center, Houston, Texas; <sup>2</sup>Georgia Tech Research Institute, Atlanta, Georgia; <sup>3</sup>Reytech Corporation, Bend, Oregon; <sup>4</sup>ERC Inc./NASA Johnson Space Center, Houston, Texas.

Electrochemical double-layer capacitors, or supercapacitors, have tremendous potential as high-power energy sources for use in low weight hybrid systems for human space exploration. Electrodes based on single wall carbon nanotubes (SWCNT) offer exceptional power and energy performance, due to the high surface area, high conductivity, and the ability to functionalize SWCNTs to optimize capacitor properties [1]. We will report on the preparation of electrochemical capacitors incorporating SWCNT electrodes and on their performance compared with existing commercial technology. Preliminary results indicate substantial increases in both power and energy performance. The effects of nanotube growth and processing methods on electrochemical capacitor performance, including purification and functionalization, will be presented. Compatibility of different SWCNTs and electrolytes was studied by varying the type of electrolyte ions that accumulate on the high surface area electrodes and comparing with results of molecular modeling studies. Electrochemical performance was studied and correlated to material attributes such as porosity and surface area using SEM, TEM, and BET surface area analysis. [1] Reynolds, et. al., NASA Tech Briefs, June 2005, p. 70

### **B7.33**

**MoO<sub>3</sub>-Pt thin film electrodes as a nanocomposite host for rechargeable lithium ion battery.** Youn-Su Kim<sup>1</sup>, Hyo-Jin Ahn<sup>1</sup>, Hee-Sang Shim<sup>1</sup>, Yung-Eun Sung<sup>2</sup> and Won-Bae Kim<sup>1</sup>; <sup>1</sup>MSE, GIST, Gwangju, South Korea; <sup>2</sup>Seoul National Univ., Seoul, South Korea.

Effects of platinum nanoparticles, which are embedded in the molybdenum trioxide (MoO<sub>3</sub>) matrix, on the microstructure and electrochemical behaviors were investigated. The Pt-MoO<sub>3</sub> nanocomposite thin film electrodes were prepared through co-sputtering process with MoO<sub>3</sub> and Pt targets. Transmission electron microscopy (TEM) results exhibited particle size and amount of Pt nanophases were controlled. The electrochemical behaviors of Pt-MoO<sub>3</sub> nanocomposite thin film electrodes were described as the function of particle size and amount of Pt nanophases. From the electrochemical experimental results for the lithium insertion and extraction process, Pt-MoO<sub>3</sub> nanocomposite thin film electrodes show enhanced cycling performance and discharge capacity compared to those of MoO<sub>3</sub> single thin film electrodes in the absence of Pt nanoparticles.

### **B7.34**

**Laser Modifications of Electrochemical Materials during Deposition.** Guodan Wei and Craig B. Arnold; Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey.

An innovative approach to the processing and optimization of materials during deposition for micropower sources is presented. In this study, the influence of incident laser as well as secondary laser irradiation during direct-write deposition is studied and exploited in order to modify electrochemical materials during deposition. Key systems of hydrous ruthenium oxide for ultracapacitor applications and titanium oxide for solar cell applications are examined. Titanium oxide and hydrous ruthenium oxide electrodes are deposited using the laser direct write process with varying incident laser energies. The

nature of the laser interaction is probed through structural, optical, and electrochemical characterization of the deposited films. At low transfer energy density, below 0.1 J/cm<sup>2</sup>, the materials maintain their structural, morphological, and electrochemical properties in comparison to control samples. However, higher energy density produces noticeable changes to the morphology, structure, and electrochemistry leading to improved performance at high discharge rates. Secondary laser irradiation during the material deposition enables further modifications to these materials enabling additional control of material properties. This work was supported by NSF-DMR-0346497.

### **B7.35**

**EELS Analysis of Niobium Oxide Compounds For Support of Next Generation Solid Electrolytic Capacitors.** Matthew Olszta, Jinguo Wang and Beth Dickey; Penn State University, University Park, Pennsylvania.

On the forefront of capacitor technology sits the field of electrolytic capacitors. Electrolytic capacitors are produced from powders of valve metal (e.g., Nb) or valve metal oxides (e.g., NbO) to create high-charge, dielectric materials. By utilizing the high CV/g of these materials, smaller capacitors (e.g., surface mount devices (SMDs)) can be produced to accommodate the electronics industries push towards miniaturization, such as for use in cell phones and laptops. In order to fully characterize the properties of these new materials, as well as provide failure analysis, it is pertinent that electron energy-loss spectroscopy (EELS) be utilized due to the spatial resolution required. Before analysis of these materials can be performed, standard samples must be analyzed in order to determine the qualitative and quantitative differences between each of the stable oxides. Qualitative and quantitative electron energy loss spectroscopy (EELS) analyses have been performed on niobium (Nb) and stable niobium oxides (NbO, NbO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub>). The k-factors for each oxide compound were measured versus the edge integration window width ( $\Delta$ ), with each converging at  $\sim 0.055$  at  $\Delta = 150$  eV and the measurements at  $\Delta 50$  and 100 eV matching data reported for Nb<sub>2</sub>O<sub>5</sub> in literature. The theoretical cross-sections of each element (Hartree-Slater model for Nb M edges and the hydrogenic model for O K edge) were found to predict the stoichiometry of oxides within a standard deviation at certain integration energy windows ( $\Delta$ ). Normalized M<sub>2,3</sub> white line intensities were measured versus 4d occupancy for each compound. The data are in correspondence with that observed in the literature for 3d and 4d transition metals using normalized L<sub>2,3</sub> white lines. Lastly, a distinctive energy-loss near-edge structure (ELNES) of O-K edge was observed for each oxide, with more detail appearing in NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> as compared to NbO. The analysis of this series of stable niobium oxides provides guidelines for analysis of next generation electrolytic capacitors.

### **B7.36**

**Phase Transformations of the Pb<sub>1-x</sub>Sn<sub>x</sub>F<sub>2</sub> Solid Solution on Ball-Milling.** Georges Denes, Matthieu Kerne, M. Cecilia Madamba and Marc Poizat; Chemistry and Biochemistry, Concordia University, Montreal, Quebec, Canada.

The high temperature form of lead(II) fluoride,  $\beta$ PbF<sub>2</sub>, is the highest performance fluoride-ion conductor among the binary fluorides, i.e. containing only one metallic element. Several combinations of PbF<sub>2</sub> with SnF<sub>2</sub>, result in highly enhanced ionic conductivity. The best combination is PbSnF<sub>4</sub>, the conductivity of which is three orders of magnitude higher than that of  $\beta$ -PbF<sub>2</sub>, making it the highest performance fluoride ion conductor known to date. This remarkable fluoride ion conductivity has been applied by a Japanese group for the fabrication of an ambient temperature amperometric oxygen sensor. However, PbSnF<sub>4</sub> undergoes several phase transitions, the phase obtained in a given preparation is highly sensitive to the method of preparation, and several of the phase transitions are highly sluggish. In addition, PbSnF<sub>4</sub> is much more sensitive than PbF<sub>2</sub> to oxidation when heated, and in addition, it suffers from a tremendous amount of preferred orientation due to its highly layered structure. High preferred orientation makes it impossible to have randomly oriented samples, and in case of conduction anisotropy, it is about impossible to make several samples that will have the same performance. For all the above reasons, the fabrication of a device with well defined properties, that will be stable over a long period of time, necessitates a material with a reasonably good chemical stability, suffering with minimal or no preferred orientation, and that can be obtained in the form of a phase that has no phase transition. A wide Pb<sub>1-x</sub>Sn<sub>x</sub>F<sub>2</sub> solid solution ( $0 \leq x \leq 0.50$ ) was prepared earlier in our laboratory, and later by others. Its fluoride ion conductivity increases from  $x = 0$  ( $\beta$ -PbF<sub>2</sub>) to reach a maximum for  $x = 0.50$  (PbSnF<sub>4</sub>), however, for  $x = 0.40$ , the conductivity is close to that of PbSnF<sub>4</sub>, and it changes little at higher  $x$  values. For  $0 \leq x \leq 0.30$ , the Pb<sub>1-x</sub>Sn<sub>x</sub>F<sub>2</sub> solid solution has the cubic fluorite-type structure, with full Pb/Sn disorder. For  $0.30 < x \leq 0.50$ , a lattice distortion takes place to give the tetragonal  $\beta$ -PbSnF<sub>4</sub> structure, with partial Pb/Sn order. Therefore, for  $x$  values

large enough to have a sufficiently high conductivity, yet low enough to have reduced preferred orientation and a lower sensitivity to oxidation, one must have a material more reliable than  $\text{PbSnF}_4$ , with similar performance. In the present work, we have studied the behavior of the  $\text{Pb}_{1-x}\text{Sn}_x\text{F}_2$  solid solution when ball-milled. It was found that the behavior of the solid solution when milled is very much a function of  $x$ , the fraction molar of tin. For  $x = 0$  ( $\beta\text{-PbF}_2$ ), a partial transformation to orthorhombic  $\alpha\text{-PbF}_2$  takes place, and the rate of this transformation increases for low values of  $x$  ( $x \leq 0.025$ ). For  $x > 0.025$ , it decreases dramatically with increasing  $x$  such that for ca.  $x \geq 0.12$ , no  $\alpha\text{-PbF}_2$  is formed on milling, and no phase transition takes place on ball-milling; only a slow decrease of the crystallite dimension is observed. For  $x > 0.30$  the  $\beta\text{-PbSnF}_4$  type tetragonal solid solution undergoes a transformation to a cubic fully disordered nanocrystalline  $\beta\text{-PbF}_2$  type, with a rate increasing when  $x$  increases.

### **B7.37**

**Preparation of Nanosuperionic Materials by Ball-Milling.** Georges Denes, M. Cecilia Madamba, Abdualhafed Muntasar and Alena Peroutka; Chemistry and Biochemistry, Concordia University, Montreal, Quebec, Canada.

The best fluoride-ion conductors were, for a long time the  $\text{MF}_2$  ( $M = \text{Ca, Sr, Ba}$  and  $\text{Pb}$ ) compounds that have the fluorite-type structure, with  $\beta\text{-PbF}_2$  having the highest performance from far. The superior performance of the fluorite-type materials has been explained by the presence of a large number of empty  $\text{F}_8$  cubes (half of them, the other half being occupied in its center by a  $\text{M}^{2+}$  cation) that can be used as interstitial sites for a Frenkel defect type of conduction. However, Dénès has shown that this mechanism does not explain why  $\beta\text{-PbF}_2$  has a conductivity that is much higher than that of  $\text{BaF}_2$ , since the  $\text{F}_8$  cubes of  $\text{BaF}_2$  are large enough to take a fluoride ion without local strain, when the  $\text{F}_8$  cube of  $\beta\text{-PbF}_2$  requires local distortion and should therefore be less efficient. Furthermore, new materials, most containing divalent tin prepared in the last two decades, have a fluoride ion conductivity much higher than any other fluoride known before, and can therefore be labeled *superionics*. This is the case of the  $\text{MSnF}_4$  materials ( $M = \text{Ba \& Pb}$ ), the conductivity of which is three orders of magnitude higher than that of the corresponding  $\text{MF}_2$ , and also of disordered systems such as  $\text{PbSn}_4\text{F}_{10}$  and the  $\text{Pb}_{1-x}\text{Sn}_x\text{F}_2$  solid solution. Furthermore, new materials, the conductivity of which has not been measured yet, have been prepared in our laboratory, such as  $\text{Pb}_2\text{SnF}_6$ ,  $\text{CaSn}_2\text{F}_6$  and the  $\text{Ca}_{1-x}\text{Sn}_x\text{F}_2$  solid solution. In a new development of this work, nanocrystalline disordered phases of many of the materials containing tin(II) and either lead(II) or Ba have been prepared and studied. They were obtained by mild ball-milling, for a very short time (1-5 minutes for all the  $\text{PbSnF}_4$  phases, up to 40 minutes for  $\text{BaSnF}_4$ ). The order-disorder transition has been studied by X-ray diffraction, and  $^{119}\text{Sn}$  Mössbauer spectroscopy was used to investigate the tin electronic structure and eliminate the possibility of electronic conduction. All materials studied so far by electrical methods have a fluoride ion transport number equal to 0.99 or higher.

### **B7.38**

**Studies on Dielectric Properties of Ionically Conducting Polymer Nanocomposite Films.** Dillip K. Pradhan, B. K. Samantaray, R. N. P. Choudhary and Awalendra K. Thakur; Physics and Meteorology, IIT, Kharagpur, West Bengal, West Bengal, India.

Solid polymer electrolytes (SPEs) have received considerable attention for energy conversion/ storage devices over the last three decades. Primary emphasis has, however, been basically on applications with little attention on ion transport behaviour of such a complex multi phase systems. A better understanding of the ion transport behavior, ionic and molecular interaction in solid polymer electrolytes can be obtained from studies on dielectric relaxation properties, in view of the intimate relation of the permittivity and conductivity parameters. It is believed that the dielectric properties of an ionically conducting solids arises due to dielectric relaxation caused by reorientation dynamics of molecular dipoles resulting in an electrical conduction due to the mobility of ions. The origin of dipolar relaxation in polymer electrolytes can be traced to the presence of relaxing dipoles due to cation-anion pair or relaxation due to clustering of ions. The information on relaxing dipoles in the sample may be obtained from an analysis of the complex permittivity since the appearance of a peak in the imaginary part of permittivity indicates energy absorption by the samples. The dielectric relaxation and frequency dependent conductivity are both sensitive to the motion of charge species and dipoles in a SPE, and can provide sufficient insight into the charge transport behavior. The present paper aims to emphasize the problems associated with the dielectric analysis of an ionically conducting solid electrolyte and provide an in depth analysis of conduction behaviour from dielectric analysis. The results of dielectric and conductivity analysis of a Na<sup>+</sup>-ion conducting polymer nanocomposite film having general formula  $\text{PEO}_{25}\text{-NaClO}_4 + x\text{wt.}\% \text{Na}^+ \text{Montmorillonite}$ . The freestanding polymer nanocomposite films

have been prepared by tape casting technique using a self-design tape caster. The dielectric properties of the materials have been carried out using impedance spectroscopy on application of a small a. c. signal across the sample cell using blocking electrode. The dielectric permittivity and electrical conductivity shows frequency dispersion. The appearance of peaks in the dielectric loss spectrum suggests the presence of relaxing dipoles in the conducting polymeric films. The dielectric properties and conductivity have also been observed as a function of temperature and are found to be well correlated. The results of the electrical properties have been observed to be in good agreement with the sample microstructure.

## SESSION B8: Characterization and Other Battery Chemistries

Chairs: Isobel Davidson and Clare Grey  
Thursday Morning, December 1, 2005  
Room 310 (Hynes)

### **8:00 AM \*B8.1**

**NMR Studies of Short-range Structure and Dynamics in Li Battery Materials.** Steve Greenbaum, Physics Dept., Hunter College of CUNY, New York, New York.

Structural studies of materials utilized in lithium battery technology are often hampered by the lack of long-range order found only in well-defined crystalline phases. Powder x-ray diffraction, while being an indispensable technique in the characterization of electrode materials, yields only structural parameters that have been averaged over hundreds of lattice sites, and is unable to provide structural information about amorphous compounds. Our laboratory utilizes solid state nuclear magnetic resonance (NMR) methods to investigate structural and chemical aspects of lithium ion cathodes, anodes, electrolytes, and interfaces. NMR is element- (nuclear-) specific and sensitive to small variations in the immediate environment of the ions being probed, especially  $\text{Li}^+$ . NMR is also a powerful tool for probing ion and molecular motion in polymer electrolytes, with a dynamic range spanning some nine orders of magnitude through spin-lattice relaxation and self-diffusion measurements. Several recent investigations will be described, including amorphous nanostructured  $\text{Li}_2\text{MnO}_3$ , which is electrochemically active as compared to its crystalline state (principal collaborators J.J. Xu and C.P. Grey); lithiated silver vanadium oxide, an important medical battery material (principal collaborators R.A. Leising and T. Reddy); using NMR to identify and quantify SEI formation on anodes and cathodes; (principal collaborator C.P. Grey); and ion transport in ionic liquid/lithium salt solutions and membranes prepared from these solutions (principal collaborator J.J. Xu). Research funded by the U.S. Department of Energy, the National Science Foundation, and the Director of Central Intelligence Postdoc Program.

### **8:30 AM B8.2**

**Mechanical and Electromechanical Characterization of Rechargeable Lithium Ion Batteries.** Timothy Chin, Urs Rhyner, Yukinori Koyama and Yet-Ming Chiang; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The mechanical and electromechanical response of lithium rechargeable batteries is of interest to applications where the cells are under mechanical load, or where volume changes over time are of concern. In addition, we are interested in the potential for using electrochemically-induced strain for mechanical actuation. Here we have studied the mechanical response of several prismatic lithium ion cells of stacked construction. Since  $\text{LiCoO}_2$  expands by 1.9% by volume as Li is de-intercalated during charging, and simultaneously graphite expands 10.4% in the c-axis direction and 1.2% in the basal plane, this system exhibits a net expansion (contraction) upon charging (discharging). We observed free strain in the thickness direction of the batteries of 2-3% upon charging. Uniaxial loading in the absence of electrochemical cycling showed viscoelastic creep deformation, after which cycling under fixed prestress yielded 1.5-2% cyclic strain. The mechanical energy density produced reached surprisingly high values of  $150 \text{ kJ/m}^3$ , exceeding that of many other actuators such as piezoelectrics, although at lower speeds. Thus, even in an unoptimized state, electrochemical actuators exceed the actuation energy density of piezoelectrics, albeit with a much lower actuation speed, suggesting numerous possible applications, some of which will be demonstrated in this presentation. This work was sponsored by the DARPA Nastic Materials Program under contract no. W911W6-05-C-0013.

### **8:45 AM \*B8.3**

**In Situ Microprobe Studies of Local Detrimental Processes in Li-Ion Battery Composite Cathodes.** Robert Milosz Kostecki, Marie Kerlau, Jinglei Lei and Frank McLarnon; Environmental Energy Technologies Division, Lawrence Berkeley National

A steady degradation of the electrochemical properties of lithium-ion batteries often limits the performance of portable electronic devices and presents a significant barrier for transportation applications such as electric and hybrid-electric vehicles. Lithium-ion intercalation/deintercalation into anode and cathode active material is coupled with electron injection/removal into/from the crystal lattice of the electrode active material. The impedance growth that is observed at both electrodes is associated with an ion-blocking surface film as well as an electronically insulating barrier formed within the composite electrode [1,2]. Thus, the resistances to both ion and electron transfer constitute the overall charge transfer impedance and contribute to the overall electrode impedance. Interfacial phenomena occur and manifest themselves at nano- or micro-scales and can be detected and characterized only by techniques of suitable sensitivity and resolution [5]. Ex situ Raman mapping of cathodes that were removed from tested high-power Li-ion cells, which suffered substantial power and capacity loss, showed that the state of charge (SOC) of oxide particles on the cathode surface was highly non-uniform despite deep discharge of the Li-ion cells at the end of the test. In situ Raman microprobe monitoring of the SOC of selected oxide particles in the composite cathode in a sealed spectro-electrochemical cell revealed that the rate at which particles charge and discharge varied with time and location. The inconsistent kinetic behavior of individual oxide particles was attributed to degradation of the electronically conducting carbon matrix in the composite cathode upon testing. These local micro-phenomena are most likely responsible for the overall impedance rise of the cathode and contribute to the mechanism of lithium-ion cell failure. Conductive carbon additive behavior contributes significantly to the impedance of the composite electrodes. SEM images of aged composite cathodes as well as pure carbon electrodes revealed surface deposits and morphology changes. Surface analysis revealed that surface decomposition products originate from  $\text{LiPF}_6$  decomposition. Oxygen and water adsorbed at carbon additives,  $-\text{C}-\text{O}-\text{H}$ ,  $-\text{C}=\text{O}$  surface functional groups catalyze and/or react with the electrolyte. Surface reaction products create electronic and ionic barriers in the composite electrode, which contribute to the impedance of the composite electrodes. References 1. Arora, P.; White R. E.; Doyle, M. J. *Electrochem. Soc.* 1998, 145, 3647-3667 2. Nobili, F.; Tossici, R.; Marassi, R.; Croce, F.; Scrosati, B. *J. Phys. Chem. B*, 2002, 106, 3909-3915. 3. 1. Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B*, 2003, 107, 6668-6697.

#### 9:15 AM B8.4

**X-ray Absorption Spectroscopy study of lithium insertion mechanism in  $\gamma$ -MnO<sub>2</sub> materials.** Emilie Machefaux<sup>1</sup>, Stephanie Belin<sup>2</sup>, Dominique Guymard<sup>1</sup> and Guy Ouvrard<sup>1</sup>; <sup>1</sup>Institut des Materiaux Jean Rouxel, NANTES, France; <sup>2</sup>Soleil, Saint Aubin, France.

Due to low cost of raw material, and their non-toxicity, manganese oxides, and especially  $\gamma$ -MnO<sub>2</sub> materials, present a strong interest as active material in the positive electrodes for Li metal primary and secondary batteries. The  $\gamma$ -MnO<sub>2</sub> structure can be seen as resulting from two types of structural defects in a Ramsdellite structure: intergrowth of rutile-type structural units (noted Pr) and microtwinning (noted Mt). Thus, these compounds are characterized by their structural parameters (Pr, Mt). We have shown recently that the versatile electrochemical-hydrothermal method allows to synthesize  $\gamma$ -MnO<sub>2</sub> compounds with various amounts of structural defects. In this system of an obvious industrial interest, several questions are related to the Li insertion process: (i) Are there structural phase transitions induced by Li insertion? Is it possible to detect them also at the short-range order scale? (ii) What are the redox processes involved in these reactions? (iii) Are the different electrochemical behaviors observed in the various compounds linked to the parameters mentioned in (i) or (ii), or are they related to other parameters (various Li diffusion mechanisms, interface diffusion mechanisms in a two-phase system etc...)?  $\gamma$ -MnO<sub>2</sub> compounds obtained in this study show a relatively high degree of crystallization compared to compounds synthesized by more traditional methods. The relative amounts of pyrolusite intergrowth, Pr, and microtwinning defects, Mt, can be determined from the position of the (110), (221) and (420) peaks. To characterize  $\gamma$ -MnO<sub>2</sub> compounds upon lithiation, ex-situ XRD were performed after the charge (at 4V) and the discharge (at 2V) for the first two cycles. After the discharge, a marked shift in the  $\gamma$ -MnO<sub>2</sub> peaks, as well as additional peaks are visible on the XRD patterns, while after the charge, the XRD patterns show strong similarities with that of the non lithiated  $\gamma$ -MnO<sub>2</sub> compound. However, the complexity of the XRD patterns does not allow yet to get a complete understanding on the Li insertion mechanism. The local structural environments and the electronic

states of manganese in the lithiated and pure  $\gamma$ -MnO<sub>2</sub> compounds have been investigated by X-ray absorption spectroscopy (XANES and EXAFS) at the Mn K edge. The data show a reversible evolution of the pre-edge intensity and of the edge position. The absorption edges are shifted to lower energy with increasing the lithium content in agreement with manganese reduction. The shape of the XANES spectra are significantly transformed after discharge. EXAFS data are consistent with the reversible evolution of the absorption edge upon lithiation and delithiation. These data show that for strongly lithiated compounds, the octahedral manganese environment is distorted by Jahn-Teller stabilization. Results of EXAFS refinements as well as results of simulation of the absorption spectra will be presented.

#### 9:30 AM B8.5

**Determination of the Transition Metal Ion Distribution in  $\text{Li}(\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z})\text{O}_2$  via the Magnetic Properties.**

Natasha A. Chernova<sup>1</sup>, Miaomiao Ma<sup>1</sup>, Jie Xiao<sup>1</sup>, Peter Y. Zavalij<sup>2,1</sup> and M. Stanley Whittingham<sup>1</sup>; <sup>1</sup>Institute for Materials Research, SUNY-Binghamton, Binghamton, New York; <sup>2</sup>Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland.

Magnetic properties of the promising cathode material for the rechargeable lithium batteries  $\text{Li}(\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z})\text{O}_2$  are studied with the aim to understand charge states of the transition metal ions and their distribution, i.e. migration to the lithium layer and ordering. Temperature and magnetic field dependences of the DC magnetization as well as AC susceptibility are measured for  $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-2y}\text{O}_2$  ( $0.9 \leq x \leq 1.25$ ,  $y=0.5, 0.45, 0.4, \frac{1}{2}$ ) using SQUID magnetometer. At high temperatures, the Curie-Weiss behavior is observed. The average magnetic moment per transition ion is consistent with  $\text{Ni}^{2+}$  ( $S=1$ ),  $\text{Mn}^{4+}$  ( $S=3/2$ ),  $\text{Co}^{3+}$  ( $S=0$ ) oxidation states for  $x=1$ . For  $x < 1$ , the magnetic moment increases as a fraction of  $\text{Co}^{3+}$  ions becomes  $\text{Co}^{2+}$  ( $S=\frac{1}{2}$ ); for  $x > 1$ , the magnetic moment decreases as part of  $\text{Ni}^{2+}$  becomes  $\text{Ni}^{3+}$  ( $S=\frac{1}{2}$ ). The negative Curie-Weiss temperature indicates antiferromagnetic exchange which is getting stronger as the magnetic moment increases. At lower temperatures, a strong increase of the DC susceptibility is observed indicating a phase transition; the transition temperature  $T_c$  increases with increasing magnetic moment. Below  $T_c$  the temperature dependences of the DC susceptibility measured under zero-field cooling (ZFC) diverge from that under field-cooling (FC) conditions. The irreversibility temperature and the difference between the FC and ZFC magnetizations decrease with increasing Co or Li content. The hysteresis of magnetization is found below  $T_c$ , whose size increases with decreased Co and Li content. AC susceptibility shows pronounced frequency dependence around and below  $T_c$  for all the materials. In  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  the peak of both real and imaginary components observed around 100 K shows no temperature shift when the AC frequency is varied. In Co-containing materials as well as in Li-rich ones, the peak shifts towards the lower temperatures with decreasing AC frequency. Based on these results, ferrimagnetic ordering is proposed for  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , while cluster glass or spin-glass phase appear in other materials at low temperatures. The magnetic properties in these compounds are closely related to the distribution of transition metal ions, which is changing upon the variation of Co and Li content. Increasing Co or Li content prevents Ni ions from migrating to the Li layer. As a result, the transition metal layers become magnetically separated; random distribution of magnetic  $\text{Mn}^{4+}$  and  $\text{Ni}^{2+}$  ions diluted with non-magnetic  $\text{Co}^{3+}$  ions provides a spin-glass behavior in  $\text{LiNi}_{\frac{1}{3}}\text{Mn}_{\frac{1}{3}}\text{Co}_{\frac{1}{3}}\text{O}_2$ . When  $\text{Ni}^{2+}$  ions occur on Li sites, magnetic clusters are formed that have net magnetic moment when ordered, therefore cluster-glass is observed in  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ . In  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  ferrimagnetic ordering is proposed, which indicates that the Ni and Mn ions may be ordered in this compound, as proposed by the NMR, structural and modeling studies.

#### 10:15 AM \*B8.6

**Lithium metal battery study by Electrochemical impedance spectroscopy.** Renaud Bouchet<sup>1</sup>, Lucas Sannier<sup>2</sup>, Delphine Guy<sup>4</sup>, Bernard Lestriez<sup>4</sup>, Michel Rosso<sup>3</sup>, Dominique Guymard<sup>4</sup> and Jean-Marie Tarascon<sup>2</sup>; <sup>1</sup>MADIREL, Marseille cedex 20, France; <sup>2</sup>LRCS UMRS 6007, Amiens, France; <sup>3</sup>LPMC 7643, Palaiseau, France; <sup>4</sup>Institut des Materiaux Jean Rouxel, Nantes, France.

The electrochemical impedance spectroscopy (EIS) is a powerful analytical technique because it allows a frequency deconvolution of the different physico-chemical processes involved in a global electrochemical mechanism. Generally, one can follow at high frequencies, the evolution of the electrical properties of materials, then in lower frequencies, the evolution of the parameters linked to the reactions at the interface electrode/electrolyte, and finally, at low frequencies, the charge transport (by diffusion) and the charge accumulation in the electrolyte, in the electrode, and at their interface, are observed. Hence, EIS allows theoretically a complete

characterisation of an electrochemical system from the materials to their interface. The aim of this presentation is to show the ability of EIS to do so in the case of lithium metal battery. The analysis of both the anode interface lithium/electrolyte and the electrolyte properties are first presented. The electrolyte is varied from model solid polymer electrolyte PEO to gelled PEO/PVdf-HFP based polymer. The lithium electrode rate determining step and the charge transport across the electrolyte are determined. Then, the cathode composite properties are analysed in the framework of their texturation which drives the efficiency of the electronic percolation through the composite and therefore their electrochemical performances.

#### 10:45 AM B8.7

**Correlation of Surface Chemistry to Hydrogen Gas Evolution of Green Zinc Battery Powders.** Martin Gerardo Perez, Matt O'Keefe and Tom O'Keefe; Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri.

Zinc powders serve as the anode material in an alkaline battery. The anode is a paste composed of Zn powder, 35-45% KOH solution (ZnO saturated), proprietary additives, and a gelling agent. While in storage, an alkaline battery is in a state of partial discharge. As the Zn anode discharges or corrodes, Zn<sup>2+</sup> and hydrogen gas are generated. Excessive hydrogen gas may break the battery seals and cause the KOH electrolyte to leak out. Air atomized Zn alloy powders were analyzed to detect differences in chemical composition between powder manufacturing runs. The comparisons were made between powders that generated acceptable and unacceptable levels of hydrogen gas inside a test cell containing a strong KOH solution. As late as the mid-1990s, Hg and Pb additions to the alloys inhibited Zn corrosion. The on-going development of next generation, environmentally friendly Zn alloy powders contain no added Hg and Pb but still must minimize hydrogen gas evolution. Alloy additions of Bi and In act to inhibit Zn corrosion; Mg or Al may also be added as a third alloying element to act as possible deoxidants or grain refiners. Differences in alloy concentrations or chemistry will affect Zn corrosion and the hydrogen gas evolution properties of the Zn anode. The amount of surface ZnO formed during the air atomization process may influence the chemical reactivity of the powders. It has been reported that increasing amounts of surface ZnO increase the hydrogen gassing property of the Zn powders. No ZnO surface layer was detected in scanning electron microscope (SEM) images. However, the surface oxide content was determined by dissolving any ZnO present in a 5 wt.% ammonia aqueous solution and measuring the ZnO content via atomic absorption spectroscopy. Other chemical analyses included energy dispersive spectroscopy (EDS) on the bulk microstructure to detect differences in the Bi and In concentrations; inert gas fusion for the bulk oxygen content of the Zn powders; and X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to determine alloy concentrations close to the powder surfaces. No chemical differences were detected in the bulk content of Bi and In per EDS. No differences were detected in the O content of the powders. Several replications of XPS and AES analyses detected differences in surface chemistry. X-ray photoelectron spectroscopy detected a higher Al content on the surface of the failed powders, and AES detected a higher In content on the surface of the powder that passed gas testing.

#### 11:00 AM B8.8

**Material Design and Structure-Processing-Property Relationships of Li-ion Battery Cathodes.** Susan J. Babinec, H. Sean Tang and Andrew Talik; CR&D, The Dow Chemical Company, Midland, Michigan.

Traditional engineering composite designs employ well established mechanical theory to optimize physical properties, such as modulus, impact strength, and flexibility. Electroactive composites have been developed with the sole objective of electrochemical optimization: energy density, cyclife, electrochemical stability, etc. These disparate worlds must merge as energy storage devices make their way into physically demanding applications such as EV and HEV. This study is a preliminary comparison of properties achieved when using these two paradigms for preparation of electroactive composites based on the traditional materials of construction for a Li-Ion cathode - LiCoO<sub>2</sub>, poly(vinylidene fluoride) (PVDF), carbon black, and liquid electrolyte. In our model system, the structure-processing-property relationships of the cathode and the effects of different processing variables are examined, including the compositional ratio, electroactive particle size, crystallinity of the binder, melt vs. solution processing, processing temperature, etc. The microstructure of the composites is studied using electron microscopy (scanning and transmission electron microscopy), X-Ray diffraction, DSC, and surface analysis (atomic force microscopy, X-Ray photoelectron spectroscopy), the mechanical properties are evaluated via dynamical mechanical test, tensile test and nano-indentation, and the electrochemical properties via standard button cell tests. The learnings from this study should serve as preliminary guidelines for

design and processing of similar cathode composites.

#### 11:15 AM B8.9

**A Novel bi-functional Air Electrode for a Rechargeable Battery.** Masatsugu Morimitsu<sup>1</sup>, Shunji Taniguchi<sup>2</sup> and Masanao Takahashi<sup>2</sup>; <sup>1</sup>Department of Environmental Systems Science, Doshisha University, Kyo-tanabe, Kyoto, Japan; <sup>2</sup>Research Laboratory, Kyushu Electric Power Co., Inc., Fukuoka, Fukuoka, Japan.

A metal-air battery such as zinc-air and iron-air batteries has potentially a high energy density and could operate under high current load, because the active mass of the positive electrode is oxygen, and the gas-diffusion type of electrode provides a high active surface area so as to reduce the substantial current density. The air electrode usually consists of the mixture of carbon powders partially modified with ORR catalysts and PTFE particles. The carbon-based air electrode is also possible to act for oxygen evolution, if appropriate catalysts for OER are loaded on the carbon powders. However, the electrode's durability in this case is much lower than that only for oxygen reduction, since the carbon powders are consumed by the oxidation to carbon dioxide together with oxygen evolution. This results in the formation of macro- and micro-pores in the electrode and finally induces the electrolyte leakage through the electrode. Therefore, the metal-air battery for rechargeable uses needs another stable electrode material for oxygen evolution and reduction along with a bi-functional catalyst. In this paper, the authors present the performances of a novel bi-functional air electrode for a metal-air secondary battery. The electrode uses nickel powders as a base material, iridium oxide-based catalyst, and PTFE powders. The obtained air electrode shows good polarization behaviors for oxygen evolution and oxygen reduction in concentrated KOH solutions and has demonstrated the excellent durability for the charge-discharge cycle test over 1000 cycles. This is attributed to iridium oxide-based bi-functional catalysts mixed with corrosion-resistant nickel powders. A new class of rechargeable hydrogen-air cell using the developed air electrode and MH electrode will be also proposed.

#### 11:30 AM B8.10

**Explanation of the Memory Effect in "Nickel Electrode" Batteries.** Robert A. Huggins, Materials Science & Engineering, Stanford University, Stanford, California.

A large number of commercial batteries have nickel positive electrodes. Such batteries often exhibit a so-called memory effect in which the available capacity at useful voltages noticeably decreases if they are used under conditions in which they are repeatedly only partially discharged before being recharged. Upon charging, these electrodes exhibit two potential plateaus. On the first one the reversible H<sub>2</sub>NiO<sub>2</sub> - HNiO<sub>2</sub> (or Ni(OH)<sub>2</sub> - NiOOH) reaction takes place. This requires the transport of protons through an outer layer of the H<sub>2</sub>NiO<sub>2</sub> phase, which is in contact with the electrolyte. This phase is predominantly an ionic conductor and acts as a solid electrolyte, transporting protons to and from the two-phase H<sub>2</sub>NiO<sub>2</sub> / HNiO<sub>2</sub> boundary. This boundary is thus displaced as the reaction proceeds. When the electrode is fully charged, or oxidized, only HNiO<sub>2</sub> is present. Upon discharge the interface moves toward the current collector, and in the end its structure consists of only H<sub>2</sub>NiO<sub>2</sub>. When the H<sub>2</sub>NiO<sub>2</sub> solid electrolyte has disappeared and the HNiO<sub>2</sub> phase comes into contact with the aqueous electrolyte it is still possible to extract further hydrogen. This leads to a higher plateau, and a new process takes place, resulting in the rapid evolution of gaseous oxygen and a modification of the solid phase. The label gamma-NiOOH is often used in this connection. During discharge the potential retraces these two plateaus, and if there has been a substantial amount of overcharge the capacity of the main plateau is reduced and an additional discharge plateau at about 0.8 V vs. H<sub>2</sub> appears. The total charge capacity remains constant, but more of it gradually resides on the lowest plateau, where it is not useful. This gradual reduction in the capacity above 1 V, where it can be utilized, is what is called the memory effect. It is commonly known that if the cell is deeply discharged, it is possible to regain the initial high voltage capacity, and the lower discharge plateau disappears. That is, the memory effect can be reversed by this procedure. There has been considerable controversy over many years concerning the formation of this lower voltage plateau and the fact that this loss of useful capacity can be cured by a deep discharge. Although not generally recognized by workers in this field, it was found that another phase, HNi<sub>2</sub>O<sub>3</sub>, can be formed during overcharging on the upper voltage plateau. It forms as an amorphous product, but its crystal structure and composition were determined after hydrothermal crystallization. Consideration of the effect of the presence of HNi<sub>2</sub>O<sub>3</sub> upon the thermodynamics of the ternary H-Ni-O system shows that upon discharge the composition of the electrode moves into a ternary triangle with a potential comparable to that experimentally observed for the second plateau. Upon further hydrogen extraction HNi<sub>2</sub>O<sub>3</sub> is no longer stable, the phase stability shifts back to that present before the charging cycle, and the memory effect is cured.

11:45 AM **B8.11**

**Combustion-Based Synthesis Routes to Novel Lithium Ion Electrode Nanomaterials.** Richard Charles Breitung and Andrew Hunt; Nanomiser, nGimat, Atlanta, Georgia.

Combustion Chemical Vapor Deposition and Condensation (CCVD, CCVC) routes were used to synthesize anode and cathode nanomaterials with novel morphology and improved cycling performance. During the process, chemical precursors containing the metal of interest are dissolved in suitable solvents, which also act as a fuel for combustion. The chemical precursor solution is atomized to a sub-micron level within nGimat's proprietary Nanomiser device and droplets are then mixed with the oxidizer and ignited to generate a diffusion flame spray. The flame flash vaporizes the solvent and precursors, which then decompose to yield reactive vapor intermediates that ultimately combine and form a coating or nanoparticles. The synthesized nanoparticles are then captured in a powder collector, or a continuous film may be formed on a substrate held near the flame. Tin-based anode-solid electrolyte composites with improved rate capability were prepared using both flame generation of anode and electrolyte powders and flame-based thin film deposition techniques. Tin (IV) and tin (II) oxides were prepared using flame-based methods as were lithium titanium phosphate-based solid electrolytes. The solid electrolyte materials prepared exhibited Li ion conductivities as high as  $2 \times 10^{-5}$  S/cm, which is significantly larger than is observed for Lipon and other state of the art compounds. Electrochemical performance was assessed using the potential window from 1.2 to 0.05V. Specific first charge capacities in excess of 790 mAh/g Sn were achieved at 25 mA/g rates with powder-based composite materials while those attained at 100 mA/g rates were as high as 700 mAh/g Sn in the thin film electrodes. Longer term cycling performance in the thin films was superior to that obtained with the tape-cast powder based layers. This is attributed to morphological and resistive differences between the types of layers. Additionally, cobalt-substituted lithium nickel oxide layered nanostructured materials with good first cycle charge and discharge capacities were prepared using combustion chemical vapor condensation techniques. This is significant since nanopowders of these compounds are attractive for their potential to deliver greater rate capability and reversibility, and because preparing nano domains of the correct phase is especially difficult due to the potential for hard agglomeration to occur at the required temperatures, and the possibility of layered structure decomposition to NiO and Li<sub>2</sub>O at elevated temperatures. In preliminary efforts, first cycle charge capacities exceeded 120 mAh/g which in conjunction with X-ray diffraction data suggest the presence of the layered LiCo<sub>x</sub>Ni<sub>1-x</sub>O<sub>2</sub> phase. Additionally, SEM results indicate primary particle sizes ranging from 50 to 200 nm and larger agglomerates on the order of 300-500 nm.

SESSION B9: Electrolytes

Chairs: Gerbrand Ceder and Steven Greenbaum  
Thursday Afternoon, December 1, 2005  
Room 310 (Hynes)

1:30 PM **\*B9.1**

**Lithium-doped Plastic Crystal Electrolytes for Ambient Temperature Secondary Batteries.** Ali Abouimrane and Isobel Davidson; Institute for Chemical Process and Environmental Technology, National Research Council Canada, Ottawa, Ontario, Canada.

Plastic crystal electrolytes which can combine the benefits of plastic-like pliability with the high ionic conductivity of a crystallographically ordered structure are good candidates for utilization in solid-state lithium ion batteries. Studies on succinonitrile-based plastic crystal electrolytes will be presented. Cyclic voltammetry and physical properties of plastic crystal phases as a function of the composition and concentration of dopant salts will be reported. Comparisons will be made of the electrochemical performance with various combinations of anodes and cathodes.

2:00 PM **B9.2**

**Architecture and Function in Layered Polymer Electrolytes.** Jodie Lutkenhaus<sup>1</sup>, Amit Desai<sup>2</sup> and Paula T. Hammond<sup>1</sup>; <sup>1</sup>Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Polyethylene oxide (PEO) has been a polymer electrolyte of interest because of its low glass transition temperature, its ability to coordinate with cations, and its relative electrochemical stability. However, the crystallinity of pure PEO detracts from its ability to transport ions through the electrolyte matrix. In addition roughly 30 percent of the ionic current is carried by the cation rather than the

anion, and in a lithium battery, this property can cause concentration polarization. To reduce crystallite formation in PEO and promote the conduction of a single ion, we introduce two different systems that both utilize the power of the layer-by-layer (LBL) assembly method where a substrate is alternately exposed to aqueous solution of polymer A and then polymer B. The LBL method is particularly advantageous for electrolytes because it provides a platform to enhance the electrode-electrolyte interface, for which every crevice of an electrode is conformally coated by the LBL film. The assembly technique also produces ultrathin films of nanometer-scale controlled thickness that behave as amorphous blends. In this case, we investigate how hydrogen bonded layered architectures of PEO and polyacrylic acid compare with hydrogen bonded composites of Laponite clay and PEO. Through differential scanning calorimetry, dynamic mechanical analysis, scanning electron microscopy, and electrochemical characterization, we illustrate how the morphology of each system can be tuned and refined to give different thermal and electrochemical properties. Laponite, a synthetic hectorite clay, is of particular interest because the clay behaves as a single ion conductor or cation exchange medium. Combining clay and PEO with the layer-by-layer assembly technique allows the construction of ultrathin films with electrochemical functionality and tunable structure.

2:15 PM **B9.3**

**Electrical Properties of Vertically Aligned Carbon Nanofiber-Electrolyte Interfaces.** Kiu-Yuen Tse, Sarah E. Baker, Patrick Warf and Robert J. Hamers; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin.

Due to their high accessible surface area, good conductivity and chemical inertness, VACNFs are seen as a potential candidate for use as electrodes for a new generation of supercapacitors. However, the effects of chemical and/or molecular layers have not been well characterized. We have explored the electrical properties of bare and chemically functionalized VACNFs in both aqueous and non-aqueous electrolyte solutions using electrical impedance spectroscopy and cyclic voltammetry, and how these properties are affected by chemical changes including (1) oxidation, and (2) covalent functionalization with molecular monolayers. On bare fibers, measurements on nanofibers up to ~2 micron in length show that the capacitance is proportional to the average nanofiber length, demonstrating that the fiber sidewalls are electrically active. Using simple aqueous electrolytes, the electrical double-layer at the VACNF-aqueous electrolyte interface shows a high capacitance of ~1000  $\mu\text{F}/\text{cm}^2$  macroscopic electrode area, which is weakly frequency-dependent; these measurements indicate the facile access of ions to the nanofiber sidewalls. Measurements using a redox couple show that the charge transfer kinetics at the nanofibers-electrolyte interface can be very fast. Quantitative measurements of the capacitance and electron-transfer rates at the clean and functionalized surfaces have been obtained, providing direct information on the ability to tune the electrical properties of nanofiber forests via chemical means.

2:30 PM **B9.4**

**Controlled Electrical Conductivity in Carbon Black-Polymer Composites.** Sidhartha Gupta, Runqing Ou and Rosario Gerhardt; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Composites of carbon black and insulating polymers have been studied for many years because the addition of carbon black imparts enhanced electrical conductivity, thermal dissipation and radiation hardness to the polymer matrix. While many studies have reported widely varying changes in electrical conductivity, limited data exists on how to achieve a desired value of electrical conductivity for the same polymer system. In this paper, we will report on three different methods that can be used to fabricate carbon black filled polymer composites using ABS (Poly(acrylonitrile-co-butadiene-co-styrene)) as the polymer matrix. The first is based on dissolution of ABS in Butan-2-one, the second is mechanical mixing of the precursor materials and the third is obtained by a combination of the previous two methods. Microstructural characterization was done using SEM and optical microscopy. Electrical conductivity was determined by analysis of complex impedance plots. The percolation threshold for composites fabricated using these three different methods was found to be drastically different, with composites fabricated using the dissolution method having the highest percolation threshold (~3 vol% CB), and those fabricated with the manual mixing method having the lowest percolation threshold (< 0.01 vol%). It is to be noted that these values rival those reported for single walled carbon nanotube-polymer composites. Combining the two methods described above results in conductivities that fell in between those of the composites fabricated by the first two methods. At a given carbon black composition, it is possible to vary the electrical conductivity by as much as 12 orders of magnitude.

3:15 PM **B9.5**

**Self-Filling Electrochemical Cells by Dual Laser Processing.** Craig B. Arnold<sup>1</sup> and Alberto Pique<sup>2</sup>; <sup>1</sup>Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; <sup>2</sup>Materials Science and Technology Division, Naval Research Laboratory, Washington, District of Columbia.

The fabrication of small-scale energy storage components for microdevices is necessary to meet growing demands in these emerging technologies. Successful microbatteries and ultracapacitors electrodes have previously been fabricated, but the completed electrochemical cells require assembly or additional processing. One particular complication is the addition of a controlled amount of liquid electrolyte to activate the device. In this paper, we present recent results on a dual-beam laser processing technique that is able to complete the required fabrication including forming electrodes and electrolyte filling in a single processing step. We focus on the system of hydrous ruthenium oxide electrode material with liquid sulfuric acid electrolyte. Electrode and electrolyte material is deposited by laser direct write and the cells are fabricated in a planar geometry. Results show high capacity and material utilization with linear discharge indicative of typical capacitor behavior. The implications of this technique are discussed in the context of improving the efficiency of these small energy storage devices as well as enabling direct integration on existing microdevices.

**3:30 PM B9.6**  
**Molecular Dynamics Simulation Studies of Structure and Charge Transport at Carbon Anode/Liquid Electrolyte and Carbon Anode/Polymer Electrolyte Interfaces.** Grant D. Smith, Materials Science and Engineering, University of Utah, Salt Lake City, Utah.

Overcoming interfacial impedance is one of the critical technological challenges that must be faced in efforts to improve the low temperature performance of Li-ion batteries and to develop Li-polymer batteries with acceptable Li<sup>+</sup> transport properties. We have utilized atomistic molecular dynamics simulations in order to better understand (1) the role of the electrode/electrolyte interface and (2) the role of model SEI layers on transport of Li<sup>+</sup> to graphite electrodes. In these studies we have investigated the structure and ionic transport properties of the electrolyte/graphite interface for liquid electrolytes, dry polymer electrolytes, single ion conductors based upon comb-branch polymer architectures, ionic liquids, and gel electrolytes based upon comb-branch polymers as a function of temperature. Simulations reveal that the structure of the polymer and the mobility of the anion play important roles in the transport of Li<sup>+</sup> through the electrode/electrolyte interface. Furthermore, barriers to transport imposed by polymer structure and low anion mobility become greater with decreasing temperature. Our studies of transport of Li<sup>+</sup> through model SEI layers have revealed that while Li<sup>+</sup> is readily transported through common SEI components at high temperature, with conductivity comparable to that found in liquid electrolytes, the mobility of Li<sup>+</sup> in the SEI layer decreases much more dramatically with decreasing temperature than in the bulk electrolyte.

**3:45 PM B9.7**  
**Density Function Theory Study of Redox Shuttles for Lithium-Ion Batteries.** Zonghai Chen and Khalil Amine; Chemical Engineering Division, Argonne National Laboratory, Argonne, Illinois.

The lithium-ion batteries have been widely used in portable electronics, and a lots of research has been devoted to the development of robust lithium-ion batteries with higher tolerance to thermal abuse and overcharge abuse. Overcharge generally occurs when a current is forced through the batteries and the charge delivered exceeds the charge-storing capability of the battery. Lots of industrial and scientific interested has been focused on searching for redox shuttles to enhance the overcharge tolerance of lithium-ion batteries. The redox shuttle (S) is an additive to the electrolyte that can act as the intrinsic overcharge protection agent for lithium-ion batteries. For instance, benzene derivatives are a class of redox shuttles for 4V class lithium-ion batteries. When the battery is overcharged, S (redox shuttle) is oxidized at the positive electrode, then shuttles back to the negative electrode as S<sup>•+</sup> and then is reduced to S again. The chemical stability of the radical cation S<sup>•+</sup> greatly determines the overcharge protection capability of the redox shuttle. For instance, 1-bromo 2,5-dimethoxybenzene was claimed as a redox shuttle for lithium-ion batteries[1,2], and was finally reported unstable and can only provide very limited overcharge protection capability by Chen et. al.[3]. At the same time, Chen et. al. also propose 2,5-diterbutyl-1,4-dimethoxybenzene as a super stable redox shuttle[3]. In order to understand the criteria of a good redox shuttle, the density function theory was employed to study the impact of the substitution groups on the benzene ring. Current effort was focused on the charge distribution of the oxidized redox shuttle (S<sup>•+</sup>) and its possible degradation pathway. It is also our objective to search for the optima structure whose radical cation is stable in the lithium-ion

battery environment. Acknowledgements: This research is funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Division of Chemical Sciences, under Contact W-31-109-Eng-38. References [1] M. Adachi, U.S. Pat. 5,763,119 (1998) [2] M. Adachi, K. Tanaka, and K. Sekai, J. Electrochem. Soc., 146 (1999): 1256 [3] J. Chen, C. Buhrmester, and J. R. Dahn, Electrochem. Solid-State Lett., 8(2005): A59.

**4:00 PM B9.8**  
**Modeling and Simulation of Li-ion Conduction in Poly(Ethylene Oxide).** Larisa Gitelman<sup>1</sup>, Moshe Israeli<sup>2</sup>, Amir Averbuch<sup>3</sup>, Menachem Nathan<sup>4</sup>, Diana Golodnitsky<sup>5</sup> and Zeev Schuss<sup>6</sup>; <sup>1</sup>Faculty of Mathematics, Technion, Haifa, Israel; <sup>2</sup>Faculty of Computer Science, Technion, Haifa, Israel; <sup>3</sup>School of Computer Science, Tel Aviv University, Tel Aviv, Israel; <sup>4</sup>Department of Physical Electronics, Tel Aviv University, Tel Aviv, Israel; <sup>5</sup>School of Chemistry, Tel Aviv University, Tel Aviv, Israel; <sup>6</sup>School of Mathematical Sciences, Tel Aviv University, Tel Aviv, Israel.

We present results of modeling and simulations of Li-ion conduction in a single poly(ethylene oxide)(PEO) helical channel. PEO with a Li-salt (e.g. Li-I) serves as a solid polymer electrolyte (SPE) candidate in 3-dimensional (3D) thin-film microbatteries (M. Nathan et al., MRS Proceedings, vol. 835, K.10.10.1 - K.10.10.6, 2004) and its ionic conductivity is a key parameter in their performance. We develop an analytical model that can predict the change in polymer conductivity as a function of its stretching, the salt concentration and the temperature. The simulation results are compared with recent theoretical and experimental results. We use Langevin-based simulation methods originally developed for an analogous problem of ion conduction through biological channels by Z. Schuss et al, Phys. Rev. E, vol. 64(2-3) 036116, pp.1-14, 2001. The numerical simulations are based on a coarse-grained theory of ionic permeation in a single polymer channel bound by two electrodes. The polymeric film is assumed to comprise a layer of randomly oriented helical structures. Each helix forms a random angle  $\alpha$  with a "stretching" axis positioned perpendicularly to the electrodes. Upon mechanical stretching,  $\alpha > 0$ . For this configuration, we assume that the main Li transport mechanism is diffusion inside the helix (in-channel diffusion). The ion transport inside the polymer is assumed as due to the thermal motion of the polymer, and occurs by diffusion in the electrostatic field of mobile ions and permanent polymer charges, as well as due to the voltage across the battery. For channels parallel to the electrodes, the main transport mechanism is assumed to be inter-channel hopping. For intermediate SPE channel geometries the transport is assumed to be mixed in-channel diffusion and inter-channel hopping. Anions (I) are assumed to move by diffusion outside the channels. Our computed dependence of the normalized current in non-dimensional units on the angle  $\alpha$  at 60C is in good agreement with literature experimental results, as well as with the predictions of a model proposed by Nitzan et al., J. Phys. Chem. B vol. 106, pp. 6149-6155, 2002. Nitzan's model is based on the idea that a highly conducting phase is associated with oriented molecular structures surrounded by poorly conducting boundary regions and is evaluated within the framework of differential effective medium theory. In contrast with Nitzan's model, which predicts a weak temperature dependence (factor of 2-3) upon the decrease of temperature from 60 to 40C, our simulations correctly predict the much larger (order of magnitude) actually observed decrease

**4:15 PM B9.9**  
**Study of Ionic Conductivity of Electrospun Nano Fibers of PEO/LiClO4.** Natarajan Tirupattur Srinivasan and K. P. Rajesh; Physics, Indian Institute of Technology Madras, Chennai, Tamilnadu, India.

Polymer electrolytes often exhibit macroscopic mechanical properties which are typical of a solid, but their local relaxation processes are liquid-like and permit short-range ionic motion at the atomic level. PEO is a lithium ion carrier and can be formed into thin films and fibers to improve the energy density. Current commercial Li-ion batteries use liquid electrolytes, which are highly flammable, and further the volume of electrodes usually changes during discharge-charge cycle so a metal house has to be used to prevent possible leakage and to withstand high pressures. This results in a prohibitive manufacturing cost. In contrast, batteries based on polymer electrolytes formed as a flexible film or a bunch of fibers do not need heavy metal housing. This is so because, polymer electrolyte can easily change its shape and deform to contact with the electrode closely, therefore a laminate of aluminum foil and plastic is enough to house the battery. This demands less space and weighs less than the metal counterpart. The present paper is an attempt to form the electrolyte in the form of nano fiber by electrospinning so that it is even better than forming thin films, we believe. We measure the Li ion conductivity in PEO nano fibers and compare it with those reported for PEO films. The fibers are formed by using PEO and LiClO4 dissolved in acetonitrile solvent for different Li:O ratios. The

electrospun fibers are characterized by scanning electron microscopy (SEM), X-ray diffraction, differential scanning calorimetry (DSC) and FTIR. The crystallinity of the fibers is compared with the film using XRD and DSC techniques. The surface morphology of the membrane is studied using SEM. It is observed that the conductivity of Li in PEO has been enhanced inside the fibers. This is a very useful result and an attempt is also made to fabricate a Li Battery using these electrospun fibers. The results of the investigations are discussed in detail.

**4:30 PM B9.10**

**Conductive Polymer Clay Nanocomposites for Lithium Battery.** Awalendra K. Thakur, S. R. Mahapatra and R. N. P. Choudhary; Physics & Meteorology, I. I. T. Kharagpur, Kharagpur, West Bengal, India.

The rapidly changing technologies in different area, e.g. miniaturization of an electronic device with much enhanced power than before, is imposing pressing demand for development and commercialization of small and portable power sources (batteries, capacitors etc.) with higher energy and power densities. Amongst a larger variety of such devices, lithium batteries appear to be the most promising one due to high voltage, higher energy density, possibility of miniaturization and absence of memory effect. To achieve the desirable objectives, development and evaluation of suitable solid electrolyte materials in thin film form (having liquid like conductivity in solid state, better mechanical, thermal, electrochemical and interfacial stability, higher cation transport etc.) for the purpose is the first step. Composite polymer electrolytes studied now for over two decades have not yielded anything substantial. This has provided the ground sufficient enough to explore other possibilities such as synthesis and evaluation of nanocomposite electrolytes.

Nanostructured polymer based composites provide exceptional structure, working temperature and barrier properties in comparison to the conventional micro scale composites due to greatly enhanced filler-polymer interaction. The well dispersed polymer nanocomposite electrolyte has great advantage compared to typical solid polymer electrolyte. It shows an overall increase of conductivity at the room temperature, low interfacial resistance with electrode, higher cation transport number and enhanced mechanical strength. The present work reports how modification of montmorillonite (MMT) to the organo clay complex influence the interlayer distance and consequently structure, interaction of polymer salt complex with clay layers and end use properties (conductivity and stability etc.) of PEO based lithium ion conducting nanocomposite films prepared using casting technique with a self designed tape caster. Structural and microstructural changes have been studied over a wide range of clay compositions that, in turn, has been optimized in terms of conductivity and stability properties. It is observed that physical properties of polymer salt intercalated clay nanocomposite films have improved considerably.