SYMPOSIUM B
Next-Generation Batteries, Supercapacitors and Other Storage Materials
November 28 - December 1, 2005

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* Invited paper
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 or the power source is limited to micrometer 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 3-D electrode fabrication is based on combining silicon micromachining with colloidal processing of electrode powders. Silicon molds with 60 micron dimension holes are fabricated using DRIE. The core material of the 3-D electrode materials including vanadium oxide nanorods (VONR) and carbon (MCMB) are dispersed in an appropriate solvent and filled into the mold by filtration methods. The electrodes are released from the molds by immersing in a hydroxylic solvent. A backside 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 comprising the VONR electrode material exhibited an areal normalized capacities ranging from 0.29 mAh/cm² to 2.56 mAh/cm² for aspect ratios of 0.5 and 2, respectively. By comparison, the same VONR electrode material prepared with a stainless steel collector exhibits an areal capacity of only 0.17 mAh/cm² 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 9B.1.2 Colloidal-Scale Self-Organized Lithium Batteries
Yen-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 colloidal-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 electroconductive 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 LiCoO2 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. F49620-02-1-0466. RW was supported by a DCT Postdoctoral Fellowship.

8:45 AM 9B.3 Coating Monolithic Macroporous Carbon Electrodes with Polymeric and Inorganic Electrolytes
Nicholas S. Engargi1, Justin C. Lytle1, KY T. Lee1, Seung M. Oh1 and Andreas Stein1; 1Chemistry Department, University of Minnesota, Minneapolis, Minnesota; 2School 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 wall networks with wall thicknesses of tens of nanometers that allow for shortened diffusion pathlengths, thereby improving the rate capability. Various electrolytes from anodes such as SnO2 and carbon to cathodes such as V2O5, LiNiO2, LiCoO2, and LiPnO2 have been synthesized with these macroporous structures. Rate studies of 3DOM LiCoO2 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 electrosorption is believed to be a good method for uniform, thin, pinhole free polymer coatings due to the self-limiting nature of the rod 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 architecture on the uniform electodeposition 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, LiPnO3/Li0.5Pn0.5O2. The organic-inorganic composite films improved capacity and cycling stability due to coating uniformity and thickness. The pore structure of the modified gelatin 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 9B.4 Three-Dimensional Battery Nanoarchitectures

A new Li-ion microbattery approach is presented where both electrodes are assembled in a planar configuration by electrochemical deposition (ECD) and electrodeposited in situ (EES). 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 architectures. In this paper, the individual 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 microbattery architectures of size and shape, based on both lithium 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 Garcia1 and Yet-Ming Chiang1; 1Materials Engineering, Purdue University, West Lafayette, Indiana; 2Materials 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, allowing the optimization of battery architecture. 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 LiCoO2 and Li4RuO4. Arnold M. Stux1 and Karen Swider-Lyon1; 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 LiCoO2 in the cathodes with Li4RuO4. LiCoO2 is a standard active material used in Li-ion batteries, and Li4RuO4 is a highly stable Li-insertion compound with high electronic and Li-ion conductivity. Batteries with LiCoO2 or Li4RuO4 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 LiCoO2/Li4RuO4 cathode blend have a disproportionate increase of 25 and 30% in their expected specific capacity and energy, respectively, relative to LiCoO2 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 LiCoO2 and Li4RuO4 phases are distinct in the electrodes. Analysis of discharge curves in combination with electrochemical impedance spectroscopy shows that Li4RuO4 lowers the electrical resistance of the electrodes when combined in parallel to the LiCoO2. 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. Sadownik 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 copolymer electrolyte 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 reaction can occur and decreasing distances within the electrode. We begin with templates of microphase-separated 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) methacrylate)-block-poly(butyl methacrylate), POEM-b-PBMA and free-radically synthesized poly(oxyethylene)9 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 components between the polymer electrolyte precursors of vanadium and prehydrolyzing the precursor ion to incorporation, up to 30wt% (13x%) 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-actiue vanadium oxide domains.

10:45 AM B1.9
High capacity 3D-microbatteries with electrochemically deposited composite thin-film cathodes. Menachem Nathan1, Diana Golodnitsky2, Vladimir Yuft1, Ella Strauss2, Kathrin Frankman2, Larisa Burstein2, Michael Gliklich2, and Michael Peled2; 1Department of Physical Electronics, School of EE, Tel Aviv University, Tel Aviv, Israel; 2School of Chemistry, Tel Aviv University, Tel Aviv, Israel; 2Wolfson 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, K10.10.1 - K10.6.04). 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 microbatteries onto oxysulfide cathodes that allow an almost doubled 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 spheres or assembles of spheres. XPS and TOFSIMS 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 (-CH2-CH2-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 Morris3, Thomas Gennis1,2, Brett M. Gall1, Brian Dixon5, Chaiwat Engtrakul2, Jeffrey Blackburn2 and Michael J. Heben2; 1Chemistry, Rochester Institute of Technology, Rochester, New York; 2National Renewable Energy Laboratory, Golden, Colorado; 3Phoenix 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 traditional 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 12cm2 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, CN1-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 reversible and cyclable secondary cells with specific energies exceeding 400Wh/kg and pulse power exceeding 3kW/kg.
11:30 AM BL12
Electrochemically Active Nanoparticles Made by Flame Spray Pyrolysis. Francesco Scintu1, Lucia E. Einzinger1, Joachim F. E. Fath1, and Petr Novak2; 1Particle Technology Laboratory, ETH Zuerich, Zuerich, Switzerland; 2Electrochemistry 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 compared to 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 formation 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 Co3O4, MnO2, LiMnO2, Li2TiO2, and LiFeO2 particles with spinel structure (normal, normal distorted, mixed, and mixed inverse) were made by flame spray pyrolysis at production rates of 10 to 20 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 LiMnO2 and Li2TiO2 as potential cathode and anode material, respectively, in secondary lithium-ion batteries.

11:45 AM BL13
High rate charge/discharge properties of nanostructured electrodes synthesized through soft solution processes. Itaru Honma1, Fumikazu Yon1, Takashi Hasobe2, and Hoshen Zhou; ETRI, AIST, Tsukuba, Ibaraki, Japan.

For the system in which not only high-energy but also high-power operation is required as pure and hybrid electric vehicle such as 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 attention 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 have 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 sonochemistry to synthesis of manganese oxide with controlled nanostructure of manganese oxides are reviewed and novel non-aqueous preparation is proposed to obtained improved high rate charge/discharge electrode properties. Mesoporous Titanias are also prepared by sol-gel process. The high surface area and electrochemical high power properties are also demonstrated.

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

1:30 PM B2.1
An Initio Study of Olivine Cathode Materials. Dane Morgan1, Fei Zhou2, Thomas Macixsch3, Kishik Kang3, Matteo Cococcioni4, Chris A. MacMillan1, and Gerbrand Ceder2; 1Department of Materials Science and Engineering, University of Wisconsin - Madison, Madison, Wisconsin; 2Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

Some of the most promising materials for next generation cathodes come from the olivine 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 method is known 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 LiFePO4 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 Li/Li Solid-State 2D Exchange NMR. L. S. Cahill1, 2, R. P. Chapman3, and Giliam Gemard4; 1Department of Chemistry, McMaster University, Hamilton, Ontario, Canada; 2Brockhouse 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 2Li/Li NMR studies of the monoclinic Li3V2(PO4)3 material, and several members of the electrochemically cycled materials, Li5.33V2(PO4)3). We correlate our results with related studies of the parent material, and chemically delithiated members of the Li5.33V2(PO4)3 family. 2Li NMR spectra act as a 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 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 measurements of hopping rates and activation energies for the lithium transport process are obtained. These results are correlated to interionic 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 Li chemical shift as a function of discharge.


3:30 PM B2.3
The Hydrothermal Synthesis of LiFePO4 Revisited. Jiajun Chen and M. Stanley Whittingham; Chemistry Department, Binghamton University, Binghamton, New York.

LiFePO4 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 LiFePO4 in 2001 (Electrochem. Comm. 3, 505); however, it did not exhibit 100% utilization due to the presence of ca. 7%-8% iron occupancy on the lithium site (Electrochem. Comm. 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 LiFePO4. However, a collaboration at LBNL in 2004 reported the successful hydrothermal formation of LiFePO4; however without much detail. This study focuses on optimizing the hydrothermal conditions to obtain structurally sound material with optimal electrochemical behavior. Samples of FePO4.5 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 sulfur, ascorbic acid and amoniacal solutions. Samples were formed approximately 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 LiFePO4/C composite. We also attempt 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 Basic Energy and Vehicle Technologies, through the BATT program at LBNL.

3:45 PM B2.4
Effect of dopants on lithium and electron transport in olivine LiFePO4. Jack Treger, Sharon Dalton-Castor, Karen Thomas-Altern, Dmitri Novikov and Per Onnerud; TIAX LLC, Cambridge, Massachusetts.

LiFePO4 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.

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Morgan et al. [1] have performed quantum mechanical calculations which imply that diffusion is facile only along the b axis of the Pr2MnO4 space group. In addition, localized and persistent defects at the I-D path are responsible for the low experimentally observed diffusivity (on order 10-17 cm2/s). Their study has led some to speculate that dopants on the lithium site would block the I-D paths, thereby increasing lithium ion transport. 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 also present our findings 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 LiFePO4. Fei Zhou and Gerbrand Ceder, MIT, Cambridge, Massachusetts.

LiFePO4 is a promising rechargeable Li-ion cathode material. At room temperature the LiFePO4 system is well known experimentally to phase separate into FeO4 and Fe3O4. The phase stability of the system is essential for 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 LiFePO4 at intermediate (0<x<1) lithium concentrations [Phys. Rev B 79 201101 (2009)]. We have thoroughly studied the LiFePO4 phase diagram with the LDA+U method. At intermediate lithium concentrations the ordering of Fe3+-Fe2+ 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 lithium in FePO4 and vacancy in LiFePO4 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 Lissie Dhaubhadel, Chemistry, CNRS - L SDMS, Montpellier Cedex 5, France.

Development of density functional theory (DFT) and computer capabilities 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-binding electronic levels of the host at the Fermi level. This method has been applied to early transition metal pnictides LiMnP4 (M = Ti, V ; Pu = N, P, As) and validated by experiments. These systems are built on nearly isolated M4+ 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. These results have then been extrapolated to middle and late transition metal pnictides and to more suitable binary MxPy systems.


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 and supercapacitors can store electricity and release it in 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 important effects and postulate that the I-D path is responsible for the low experimentally observed diffusivity (on order 10-17 cm2/s). Their study has led some to speculate that dopants on the lithium site would block the I-D paths, thereby increasing lithium ion transport. 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 also present our findings 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.

SESSION B3: Layered Cathodes

Chairs: Gillian Goward and M. Stanley Whittingham
Tuesday Morning, November 29, 2005
Room 310 (Hyenes)

8:00 AM **B3.1** Li De-intercalation Mechanism in LiNi0.5Mn0.5O2 Cathode Material: Electrochemical and Electron Diffraction Studies. Yang Shao-Horn1, Ying Shirley Meng2, Sundep Kumar3, Clare P. Grey4, Julien Breger3 and Gerbrand Ceder1, 5 Massachusetts Institute of Technology, Cambridge, Massachusetts; 6State University of New York at Stony Brook, Stony Brook, New York.

As a new potential cathode material, layered Li0.5Li0.5Mn0.5O2 has attracted much interest in recent years. Structural changes of LiNi0.5Mn0.5O2 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 electronic 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 LiNi0.5Mn0.5O2 after the first charge-discharge process with different cut-off voltages, as well as the structural changes after extended cycling. By combining 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 LiNi0.5Mn0.5O2. References: 1 W. S. Yoon, S. Iannopollol, 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, 3168 (2003).

8:30 AM **B3.2** Structure and Properties of Overlithiated Li(Li,Ni,Mn)O2 Materials as Positive Electrode for Lithium-Ion Batteries. Laurent Crouergrenon, Nicolas Collevez, Jeremy Le Roy, Erik Willnau, Maxime Moulin, Claude Claret and Claude Delmas; Institut de Chimie de la Matiere Condensee de Bordeaux (ICMCB-CNRS) and ENSCPB, PESSAC, France.

Layered Li+ x(Ni,Mn)O2-xO2 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 Li1+x(Ni,Mn)O2 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 tetrahedral oxidation state for all the transition metal ions. To explain this overcapacity phenomena, some proposed that a simultaneous loss of lithium ions and oxygen extraction occurs during the plateau while others claimed the additional mechanism of an exchange between Li+ and H+ 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+/H+ exchange reaction is only a side-reaction.

9:00 AM **B3.3** Processing-Structure-Property Relation in Layered...
LiNi2MnO4 has been proposed as a promising cathode material with high reversible capacity and better thermodynamic stability than LiCoO2 in advanced Li-ion batteries. It has been shown that the electrochemical properties of the material depend on the synthesis conditions, including the presence of certain temperature treatments and the presence of certain cations in the structure. Analysis of 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 planes plays an essential role in determining the long-range ordering of this material and is crucial for the electrochemical properties of the compound. In this study, we systematically studied the short-range and long-range ordering in LiNi2Mn1/2O2 synthesized under different synthesis conditions. Electrochemical performance will be compared among different samples and correlated to the three-dimensional crystal structure of LiNi2Mn1/2O2. The knowledge of the processing-structure-property relationships is essential for optimizing the performance of the LiNi2Mn1/2O2 and its derivatives. References: 1. T. Ohzuku and Y. Makimura, Chemistry Letters, 744 (2001). 2. Z. H. Lu, L. Y. Beaulieu, R. A. Donabarger, 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. Iannopollo, 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 Chernysh, and Stanely Whittingham, Chemistry, State University of New York at Binghamton, Binghamton, New York.

LiNiO2.45Mn0.45Co0.1O2 combines the advantages of both LiNiO2 M1/2O2 and LiCoO2 and has been synthesized at different temperatures varying from 700°C to 1000°C by co-procipitation method. XRD, TEM and magnetic studies show the evolution of the layered structure with rising temperature and lithium content; increasing temperature decrease 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 highest electrochemical behavior, with the actual capacity depending on the charging voltage. Cyclic voltammetry 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

The thermal decomposition of manganese carbonate gives an X-ray amorphous manganese oxide in a narrow temperature range below 400°C. Using a precipitated mixed manganese and 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 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 structure. Commonly, these materials can be successfully used in lithium batteries at a potential around 3V vs. Li/Li. Step-potential electrochemical spectroscopy shows that the initial discharge gives rise to a 2-phase transition and is followed by stable, reversible, single-phase electrochemical processes depending on the charging current and on the manganese valence of the discharging material. Best results are obtained on a cobalt-doped manganese oxide (Co:Mn molar ratio 1:3), which can sustain more than 100 charge-discharge cycles with a 175 mAh/g 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 the variations in local structure around Mn on discharge are much smaller than in long-range ordered compounds such as LiMnO2 spinels, 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, Michigan, Michigan.

First-principles computational schemes have reached a stage 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 that in principle can 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(Ni0.5Mn0.5)O2, a new but poorly characterized Li-intercalation compound.

10:45 AM B3.7
Computational Structure Determination of LiNi1/2Mn1/2O2 Yongsun, Yik Shirley Meng, Kikuo Kang and Gerhard 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 though the short range structure cannot be detected in powder X-ray and neutron diffraction [5]. NMR [5] has indicated that a significant amount of Li in the transition metal layer and gives evidence that thesis Li ions have a strong preference to be surrounded by 8 or 9 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 (the ‘flower’ structure) proposed by us predicted 8.3% Li composition in TEM layer. This model agrees well with both NMR and TEM experimental observations. 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. Reference: T. Ohzuku and Y. Makimura, Chemistry Letters, 744 (2001). 1. Z. Z. Lu, Z. H. Chen, and J. R. Dahn, Chemistry of Materials, 15, 3214 (2004). 2. W. Y. Yoon, S. Iannopollo, C. P. Grey, et al., Electrochemical and Solid State Letters 7, 1677 (2004). 3. C. G. Meng Y. S., Grey C. P., Yoon W. S., and Hoh-Yoro Y., Electrochemical and Solid State Letters 7, A155 (2004). 4. Z. Z. Lu, L. Y. Beaulieu, R. A. Donabarger, 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, Kikuo Kang and Gerhard 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 dendrite grain size, morphology of defects in the structure and so on. In our work we use first principles computations of the
11:15 AM B3.9

**Effect of Metal Ions Doping on the Structural and Electrochemical Properties of Layered Li-Ni-Co-O**

**Compound:** Santanu Mandal, Niloy N. Maiti, Mahajan Tomar, Subhashis B. Majumder and Ram S. Katyar

**1st Physics, University of Puerto Rico, San Juan, Puerto Rico; 2**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 an cathode material for Li-ion rechargeable batteries. Among them LiCoO2 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 LiNiO2 is difficult to synthesize, due to difficult oxidation of Ni2+ to Ni3+ and the volatility of the lithium compounds, nonstoichiometric oxides are usually obtained and in the charged state migration of Ni ions from the 2b octahedral site to 3a octahedral site (occupied by Li ions) poses high polarization loss and poor reversibility in the formation of the desired 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 CR2025 coin-type cell using lithium metal as anode. The discharge capacities of LiNi0.8Co0.2O2, LiNi0.8Co0.15Mn0.05O2 and LiNi0.8Co0.15Zr0.05O2 cathodes, measured at constant current-densities 0.48 mAh/cm2 were 100.5, 155, and 103 mAh/g respectively. Thus better discharge capacities are obtained in M (M=Mo, Zr) doped LiNi0.8Co0.2O2 cathode. After 20th charge-discharge cycles the discharge capacities for LiNi0.8Co0.2O2, LiNi0.8Co0.15Mn0.05O2 and LiNi0.8Co0.15Zr0.05O2 were 72.47, 138 and 103 mAh/g respectively. Hence the capacity retention of M doped cathodes was also better as compared to LiNi0.8Co0.2O2 cathode. Results of XRD diffraction and Raman spectroscopic studies show that the 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, Rimma Sirotina, Todd Bofinger, Fan Zhang and Steve Huckey

**Gillette Technical Center, Needham, Massachusetts; 2**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 \( \gamma \)-MnO2. Heating the lithium substituted MnO2 to 350-400 °C results in a partially ordered HEMD like MnO2 (LiMD50) 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 MnO2 phase (LiMD450). More exhaustive replacement of structural protons by lithium results in formation of a \( \gamma \)-MnO2 phase substantially losing about 1.8% \( \delta \)-Li. This highly substituted lithium containing MnO2 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 MnO2 to 500 °C in formation of a lithium containing MnO2 (LiMD 350 MnO2 phase as with the previous partially lithium substituted MnO2. Additional heating of the highly lithium substituted MnO2 to 450-480 °C under oxygen results in formation of the new LiMD450 phase in substoichiometric phase. XRD and TEM studies of the new material suggest it has a monoclinic unit cell described by Chabere and Pannetier, consisting of alternating 1x1 and 2x1 tunnels. The proposed structure is also similar to that described by Verbaere and Hili 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 LiMn2O4 spinel after 100 deep discharge cycles.

**SESSION B4: Vanadium Oxide and Other Cathodes**

**Chairs:** Marie Lissa Doublet and Debra Rollison

**Tuesday, November 29, 2005**

**Room 310 (Hynes)**

1:30 PM B4.1

**The Origin of 5 V Electrochemical Activity Observed In Divalent Cations Doped LiM0.5-xMn1.5+xO4 (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. LiMn2O4 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 LiMxMn2-xO4 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, and the Sob, et al. studies have shown that some of these mixed oxide spins 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 LiNi0.5-xMn1.5+xO4 (where, 0<x<0.5) provides an additional 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 Ni2+ to Ni4+. Copper, on the other hand have 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 LiMn2O4 spinel compounds of the type LiCu0.5-xMn1.5+xO4. 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 lithium Mn spinel compounds. Synchrotron based In-situ XANES and XRD results points that the strong tetrahedral site prefernece 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[Li0.33Mn0.67]O2, as Electro-Catalysts for Li-Air Batteries.** Katana Ngah1, Arthur Dobley2, Saul Alia2 and Steven L. Suib1


The proton-exchanged compounds of the layered materials, Li[Li1/3Mn2/3]O2 and Li[Li1/2Mn1/2]O2, have indicated suitable properties as potential catalysts for Li-air batteries. Acid treatment of Li[Li0.33Mn0.67]O2 materials at room temperature leads to a decrease in particle size, as a result of proton exchange with the Li+ 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[Li0.33Mn0.67]O2 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 Li0.11H0.9[Li1/3Mn2/3]O2 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 Extraction-Insertion Electrode for Rechargeable Li Batteries.** Giuseppe de Ghetto1, Rozier Patrick2, Dupont Loic1, Swajaw Olivier1, Bodemus Vincent1, Murphy Don1 and Tarazon Jean-Marie1; 1Laboratoire de Reactivite et de Chimie des Solides, Amiens, France; 2CEMES, 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 Li3CuO3. The peculiar chemical property of such a compound was ascribed to both structural considerations (presence of anchoring oxygen giving the V4O11 layers a flexibility), and electronic considerations, such as the existence of a delicate balance between the two CuO6 coordination spheres for a Na12O31 compound, was carried out in the hope of better adjusting the redox value of Nb5+/Nb7+ to that of Cu. A survey of numerous (Cu)-Nb-O compounds (Cu2Nb2O11, Cu2Nb2O7, Cu2Nb2O7), 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 authors have revisited the literature of old insertion materials such as CuTi2S4, which is 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 Macrocyclic Frameworks: Positive Electrodes for Lithium Batteries, Fleurin Carg1, Lahire Biette 1, Mathieu Morcrette1, Christine Surcin2, NDB, Reine Biesme, Jacques Livage1 and Renal Backov1, 2Centre de Recherche Paul Pascal (UPR-CNRS 8641), Pessac, France, 3Laboratoire de Reactivite et de Chimie des Solides (UMR-CNRS 6607), Amiens, France, 3Laboratoire 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 macroscopic shape is an emerging area of technological interest towards heterogeneous catalysis, phase separations, artificial bone structures, thermal and/or acoustic insulation, ion-exchange operation, and so forth. Different patterns can be used at the macrosopic length scale as bimetal[1] or air-liquid foams.[2]

Different inorganic polymers can be used toward specific applications mentioned above, and those, extensive interest is focused over vanadium oxides mainly for their structural and textural[3] diversity and potential applications in various domains as for instance, heterogeneous catalysis, cathode materials for advanced lithium batteries, visible light photocatalysis and electro-chemical devices. Present work[3] extends the recently reported study[3] 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 macrocyclic frameworks. Results will be discussed both in terms of interlayer distance parameters and carbon nanotubes percentages associated to the V2O5/Carbon nanotube composites. Charge-discharge cycling experiments will be presented. F. Carg, A. Colin, M.-F. Achard, H. Deleuze, E. Sellier, M. Birot, R. Backov J. Mater. Chem., 2004, 14, 1370- 2-F. Carg, A. Colin, M.-F. Achard, H. Deleuze, C. Sanchez, R. Backov Adv. Mater., 2005, 17, 62- 3-F. Carg, N. Steunou , A. Colin, J. Livage, R. Backov Chem. Mater. 2006, 17, 644.

3:45 PM B4.5
Electrospinning of Novel Vanadium Oxide Nanofibers. Chummei 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 oxytrispropoxide gels; the composite fibers, so formed, are then hydrothermally treated around 160°C for 24 hours. These vanadium 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 vanadium 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 vanadium nanofibers exhibits the characteristic vibration bands at about 1664 and 1263 cm⁻¹, corresponding to the V=O vibration bands and V=O bands; these suggest a double sheet structure as in MxVO410 and the vanadium oxide nanotubes. Electron diffraction patterns suggest that each fiber is a single crystal, and the triospincrodite 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 nanostuctures will be discussed. This work is supported by NSF-DMR 0313903.

4:00 PM B4.6
From vanadium oxide gels to Li1+x+αV3O8/-Li1/3V2O5/C nanocomposites, Joel Gaubichelle1, M. Dubarry1, P. Moreau1, D. Guyomard2, O. Duruphy2, N. Steunou2, J. Livage2, N. Dupre3 and C. P. Grey3, IMN, Nantes, France, 3Laboratoire de Chimie de la Matiere Condensee, Universite Pierre et Marie Curie-Paris VI, Paris, France; SUNY, Stony Brook University, Stony Brook, New York.

Li1+x+αV3O8 (α=0.1-0.2) has been extensively studied during the past 20 years for its attractive electrical 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 depends on the drying temperature of the xerogel: samples prepared upon heating at 580°C exhibit a stable capacity of 180 mAh/g upon cycling, whereas those heated at 350°C, exhibit a larger initial capacity (300 mAh/g) that decreases rapidly upon cycling. The purpose of this paper is to examine the reaction mechanisms that occur from the pristine solute species to anhydrous Li1+αV3O8 as well as their consequences regarding the electrochemical behaviors, and on an other hand, to improve capacity retention of low temperature prepared Li1+αV3O8. Unlike V2O5 gel, the Li1+αV3O8 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 Li1+αV3O8 gel-like precipitate via solubilized vanadic species will be proposed. Formation of anhydrous Li1+αV3O8 from the xerogel has been studied from thermogravimetric analysis in vacuum. MAS NMR. Completion of dehydration leads to a sample characterized by a bimodal grain size distribution, with a size distribution 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 Li1+αV3O8. As capacity fading of low temperature prepared Li1+αV3O8 was ascribed to electrolyte/material intercalation, modification of the surface was investigated by thermal carboxeroduction.

Li1+αV3O8/y-beta-Li1/3V2O5/C nanocomposites (n ≈ 0.3) were obtained upon heat treatment of a carbonized gel using a fast firing technique under an inert 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

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. An alternative to intercalation materials is to utilize the covalent bonding, conversion and reversible conversion compounds where multiple electronic bands 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 high 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 to make 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 insulating properties and very low 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 low voltage macromaterials and our group (Biesme) 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 the past, a number of systems have been shown to exhibit near theoretical conversion voltages (2.3-2.3V) and specific capacities from 400 to 700 mAh/g. Systems including fluorides and in some cases oxyfluorides of Fe, Ni, Cu, Cr, Bi, and Cu have been investigated. This paper will review the latest work with this area with discussion of reaction mechanisms and challenges that remain.

SESSION B5: Supercapacitor
Chairs: Glen Amatucci and Laurence Crouquen
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 Lerouz3, Encarnacio Raymond-Pinoz4 and Francois Beguin5;3Materials Chemistry, Universite Blaise Pascal, Aubiere, France; 4Centre 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 is due to 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 material 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. The specific surface area range to 2500 m2/g is measured for samples prepared initially via the monomer intercalation and its subsequent in-situ polymerization. The carbons have been characterized as active electrode material of supercapacitors in sulfuric acid medium by means of galvanostatic charge/discharge cycles measured according to the Anai's van ostad 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, Université Paul Sabatier, Toulouse, France.

Electrodes used in most of the electrochemical energy and power sources can be divided into active material film/current collector interface. 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 contact 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 devices. 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 Allistore, a European Network of excellence headed by Prof. Tarascou. 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 Technical Applications, 377-416 (1999) [2] P. Poizat, S. Laruelle, S. Grueion, L. Dupont et J.-M. Tarascou Nature (407/8803), 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
Byoung Jeong Wei and Subramanian Venkataramlan; 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 supercapacitors. 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/tranition 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 MnO2-single walled carbon nanotube (a-MnO2/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, XPS, FTIR, 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 Na2SO4 electrolyte. The dependence of capacity and current, 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 Kennedy1, Justin Raj2, Judith John Vijaya1 and Ganesan Sekaran2;1Environmental Technology, CLR, Chennai, Tamil Nads, India; 2Chemistry, 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 EDLC using activated carbon as an electrode was characterized using cyclic voltammetry and galvanostatic charge/discharge techniques using 1 M H2SO4 as an electrolyte. The BET surface area of the prepared C700, C800 and C900 carbon materials were in the range 345, 379 to 440m2/g. The specific capacitance values were linearly related with BET surface area of activated carbon. The cyclic voltamgram 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 143 mF/g respectively. The capacity was maximum of about 143 mF/g for activated carbon containing 60% mesopore concentration. The specific capacitance of the mesoporous activated carbon was majorly dependent on the surface functional groups such as hydroxyl, carboxyl and carbonyl groups determined through FT-IR technique. The stability of the activated carbon capacitors was examined by conducting repeated charge-discharge cycles to the maximum 100 cycles demonstrate that the capacitor has stable capacitance with cycling efficiency of about 99.5%.

9:30 AM B5.5
Double Layer Capacitance of Carbide-Derived Carbon in Organic Electrolyte.
John Chimola1, Gleb Yushin1, Cristelle Portet3, Pierre Louis Taberna3, Patrice Simon3 and Yury Gogotsi2; 1Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; 2CIRIMAT, 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 Na2BF4/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 600°C and 1200°C. A systematic study using cyclic voltammetry, impedance spectroscopy and galvanostatic cycling characterization revealed the presence of the reviews 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 graphic structure, which led to enhanced capacitance. These results supported the hypothesis that the synthesis temperature had the opposite effect on specific capacitance. CD/C showed very promising initial performances, with a specific capacitance in excess of 100 F/g and a series resistance of 0.5 Ω cm² or less, which shows the ability of C/D to be used in high-power applications.

10:15 AM B5.6 Highly Reversible Nanocrystalline Vanadium Nitride Based Pseudocapacitors, Prashant Nagesh Kumta 1,2, Davion Cho 1 and George E. Blomgren 3, 4.


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 aerogels 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 expansive 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 2 mV/s and 554 F/g when tested at high charging rates of 100 mV/s using 1M KOH. Such a high capacitance performance has never observed before in transition metal nitrides or carbides. The excellent capacitor response exceeding that of RuO2 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 225 F/g. In our study, nanocrystalline VN powders were synthesized via 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 microscopy (HRTEM) images 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 m²/g. Detailed X-ray diffraction, Rietveld refinement, thermogravimetric and mass spectrometric 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. Deming, Chemistry Division, Naval Research Laboratory, Washington, District of Columbia.

Carbon aerogels and related nanoarchitectures are appealing as electrode structures for energy storage 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 for charge and ions to interact with the extended electric field. 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 electrical area of the nanocomposite 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, in the use of electroreduction conditions where polymer growth is self-limiting, which for azlactone monomers is achieved by performing the electropolymerization in aqueous electrolytes with pH > 2. The resulting ultrathin, polyaniline (PANI) coating can be employed by exposure to aqueous acid electrolytes. When incorporated into carbon aerogels, the faradaic pseudocapacitance of the polymer coating enhances the overall gravimetric capacitance by > 90% 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-MnO2 coatings in which the MnO2 phase exhibits high capacity and electrochemical reversibility even in cyano-based aqueous electrolytes. Future hybrid electrodes will be designed to exploit the functions of both the electroactive carbon and the electroactive nanocomposite architectures 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. Pethak, J.C. Farmer, C.T. Alviso, D.T. Tran, S.T. Mayor, J.M. Miller, and B. Dunn, J. Non-Cryst. Solids, 225, 74 (1998). [3] U. Fischer, R. Saliger, V. Bock, R. Petricevic, and J. Frische, J. Porous Mater., 4, 281 (1997). [4] J.W. Long, B.M. Dening, C.P. Rhodes, M.S. Doevers, 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 Supercapacitor Electrolyte Properties. Nandakumar Nagarajan, Elizabeth A. McNally, Harith Humadi, Hallun 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 nanotubular oxides 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, chronoamperometry and impedance spectroscopy in KOH (NiO and Co3O4) and Na2SO4 (MnSO4) 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 theoretical values from chronopotentiometry. Obtained 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.


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 nanocomposites, such as inorganic composites with inorganic nanocomposites, such as inorganic composites such as nano-platelet SiO2 for high dielectric strength or H2O2 for high dielectric constant. Crucial to the use of such nano-composite systems is an understanding of the properties of such systems, both for 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 method based on first principles density functional theory, of alpha quartz SiO2 and cubic H2O2 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 parameterization of the net field induced polarization in nano-particles into bulk and surface/interfacial parts, with the bulk part (if large enough) resulting in the bulk dielectric properties, and the surface/interfacial 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 respond) regimes to nano-scale SiO2 and H2O 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 the use of the surface/interfacial 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. Clonson, 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 therefore are able to deliver more power. When coupled with existing batteries, a system capable of storing sufficient 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 materials 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 find a 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 incorporating electron deficient monomers into 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 as outstanding Type III.

11:45 AM B5.11
Nanostructured Supercapacitors by Combustion Chemical Vapor Deposition.
Yongdong Jiang, Todd A. Polley and Andrea T. Hunt; Electronics & Optics, nGimat Co., Atlanta, Georgia.

Supercapacitors have gained increasing 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. These devices are limited 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. In 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/m² at 550°C for a 4 μm thick coating, which corresponds to a specific capacitance of 22 F/m² per micron thickness. This specific capacitance is almost three times as high as the state-of-the-art. An energy density of 67 J/cm³ could be achieved if 100 V were applied to this capacitor.

SESSION B6: Anodes
Chairs: Robert A. Huggins and Robert Kosteczi
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. Ross Palacin and Jordi Cabana; Institut de Ciencia 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 study of oxygen containing related samples (i.e. oxynitrides). From the two structural families of known Li-M-N phases (Li3N-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 Li12Mn24ON2x−(5/3)x by solid state reaction of lithium oxide, lithium and manganese nitrides under nitrogen. These phases have been fully characterised from both a structural and an electrochemical point of view. Amongst others, X-ray powder diffraction and spectroscopy tests indicate that even though they are not fully air stable, their degradation is considerably slower than that of the parent nitride Li2Mn24N24 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 Li2Mn24N24 in which Li/Mn ordering induces 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 irreversable plateau at ca. 2V. The highest reversible capacity (311 mAh/g) was obtained from sample with x = 8. This capacity value is similar to that of Li12Mn24N24 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 this compound have 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 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 Vico, 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 battery technologies capable of delivering more 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 reduction of a stable electrolyte 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 other anode materials, including a strong 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 to further stabilize the anode material. 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 nitrates LiNO3 and Li3PO4. The low lithium ion conductivity of the halides precludes their use as electrolyte layer (except in very low rate applications), but the nitrates and phosphates have very high Li ion conductivity (~10-3 S/cm at RT). However, lithium nitride also has a much higher rate of stability (~ 0.5 volt) than other lithium compounds and therefore be oxidized by any useful positive electrode material. The LISICON (Li2M2[PO4]2) electrolytes also exhibit excellent Li ion conductivity (~10-3 S/cm at RT), are air and water stable, but are unstable to reduction by hydrogen. The LISICON electrolyte 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 Fan1, Peter Zavali2 and M. Stanley Whittingham3, 1Chemistry, SUNY-Binghamton, Binghamton, New York; 2University 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 density of about 1 Wh/cm³. Pure bulk carbon has a capacity of >600 mAh/g over more than 10 deep charge cycles, and Si-Bn 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 interactions; 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 LiPF6 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. Suna Jang, 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 electronic-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; ECCL) charge injection in electrodes having gravimetric surface area and gravimetric/capacitive 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 bond-stretching is 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 using high resolution panchromatic in-situ resonant 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
Chemical Vapor Deposition Methods, Malgorzata K. Guibinska1, Joseph S. Gnanaraj2 and Steven L. Suib3, 1Lithion, Inc, Pawcatuck, Connecticut; 2Worcester Polytechnic Institute, Worcester, Massachusetts; 3University of Connecticut, Storrs, Connecticut.

Carbonaceous materials are the most common commercial anodes in secondary lithium-ion batteries. Among carbon-based materials, 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 solvents (e.g. propylene carbonate (PC)). Silicon-based powders provide an alternative to carbon-based anode materials due to the high theoretical capacity values (e.g. 4000 mAh/g), related to the high lithium-content silicides (e.g. Li4Si), 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 Chemical Vapor Deposition (FCVBD) 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, X-ray micro-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 B7.8

Thin film Cu4Sn5 anodes were prepared by deposition of Cu4Sn5 films on stainless steel disks using radio frequency (RF) magnetron sputtering. Different heterostructures, consisting of as-deposited Cu4Sn5 anode, Cu4Sn5/Sn, Cu4Sn5/SnOx/Al, and Cu4Sn5/Al, were prepared as film electrodes. The annealed Cu4Sn5 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 Cu4Sn5 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 Cu4Sn5/Pt anode displayed a high capacity of ~350 mAh/g or ~3964 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 Cu4Sn5 film anodes exhibit a metastable or stable capacity, indicating 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)

B7.4

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.

B7.5

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 LiCoO2 as a cathode and carbonaceous material as anode, where in the Li-ion insertion/desinsertion and charging discharging process. Apart from carbon based anode materials, interest in the development of metal oxide based materials in nanomaterials 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 TiO2, SnO2, MnO2, NiO, Fe2O3 etc are ventured to be used as anode materials in Li-ion batteries. In this presentation, we present the synthesis and electrochemical properties of SnO2 Carbon Nanotube (CNT) composites. The SnO2 nanoparticles were synthesized via a soft chemistry route using citric acid as a capping agent. The composites of SnO2 and CNT were made by adding nanoparticles of SnO2 to the ethanolic solution of either single walled (SW) or multi-walled (MW) CNT. Prior to the addition of the SnO2 nanoparticles, the SW or MW CNT is mixed well in an ethanolic solution overnight using a magnetic stirrer. Composites with different weight ratios of SnO2 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 LiPF6/EC:DMC non-aqueous electrolyte in a voltage range 0.02 to 3V at a current density of 0.5 mA/cm2. 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 SnO2: 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 SnO2/Cr2O3/Cr electrodes, electrochemical 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. Kostantinou1, 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 their ability to maintain an open crystal structure. 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 Li2O. It has also been shown that other forms of transition metal oxides such as Co3O4 demonstrate a similar mechanism when reacted with lithium [1]. For Co3O4, electrochemical reaction with lithium is accompanied by the formation of a solid electrolyte interface (SEI) layer during the first discharge. Initial cycling can result in 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 reduce the reversibility between Co3O4 and lithium thereby reducing the capacity retention of the electrode [3]. We have approached the problem of poor cyclability in Co3O4-based electrodes by processing Co3O4 - carbon composite powders using a chemical spray pyrolysis technique. The carbon was sourced from common sugar (sucrose) added to 0.2 M cobalt nitrate precursor solution. SEM observation indicates highly porous spherical shaped particles. Preliminary electrochemical testing is encouraging and shows that the carbon-coated Co3O4 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 4221 5731.*

Acknowledgements


**B7.7**
Nanoparticles Research Activities Aimed Towards the Elaboration of a Highly Performing Negative Electrode. Ida Baglioni1, Aliaksandr Baranau2, Cristiana Bonomi3, Jean Claude Jumas3, Dominique Larcher1, Lippens Pierre-Emmanuel2 and Mathieu Moretette4; 1Laboratoire de Reactivite de Chimie des Solides, Amiens, France; 2Uppsala University, Uppsala, Sweden; 3LAMH, Montpellier, France; 4University of Kent, Kent, United Kingdom.

The cycling performances of Li-alloys-based electrodes are well known to deteriorate owing to the self-discharge reactions (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) intermediate 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 these types of 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 reactive 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 LiS2, which is theoretically very attractive but whose practical use is hampered by a troublesome “metallic” phase towards its mission, the nano-alloys group has, pursued studies aimed at providing a better understanding of Li reactivity mechanism in intermetallic alloys in the hope of distinguishing between alloying, displacement, restructuring, insertion/extraction-type reactions and also their interplay in a binary phase. Along that line MgxSn and MnxSn, where M is a metal that either alloys with Li (Mg, Sn) or does not (Cu ; Mn), has been defined as model compounds, and synthesized by ball-milling elements 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. A variety of the different combination 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 Huahe; Beijing University of Chemical Technology, Beijing, China.

Carbon nanotubes coated Cu were prepared by the treatments of acid, sensitization, activation and copper plating. The microstructure and electrochemical properties of carbon nanotubes coated Cu were investigated by HREM, IR, XRD and discharge-charge measurements. Results showed that carbon nanotubes 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 D. 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, a nanocrystalline diamond can have a significant advantage over graphite anodes. We have previously shown n-type behavior in S-doped diamond [2]. A variety of sulfur-doped nanocrystalline diamond with different contents 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. 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 LiIn Diamond Battery Anodes: Density Functional Theory Approach. Holuk Vimalas, 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+ reversibly at low voltages and with minimum lattice expansion. The ab initio calculations of Kajihara et al had shown that Li can enter interstitial 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 electrical 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, Xiu Sanyu and Song Huahe; 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(B), 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 nolar ratios of RF-Si indicated that when the ratio of RF-Si equals 1, the composite has the highest capacity and excellent cyclability, the first discharge capacity and charge capacity of which is 663 mAh/g and 415 mAh/g, respectively. After 200th cycle, and the capacities of discharge and charge are 484 mAh/g and 462 mAh/g respectively. The matrix would alleviate the volume effect of Si particles during charging/discharging, the conductivity of encapsulated composites

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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/deallloying, which contributes to the first capacity loss.

**B7.12**

Electrochemical performance of spherical LiNi1/3Co1/3Mn1/3O2 powders coated with metal oxide. Seon Hye Kim1,2, Kook Jae Lee1,2, Kwang Bo Shin3, Kyoung Ran Han2 and Chang Sam Kim2; 1Department of Ceramic Engineering, Hanyang University, Seoul, South Korea; 2Division of Materials Science and Engineering, KIST, Seoul, South Korea.

Layered LiMnO2 (Me; transition metal) has been widely investigated as active cathode materials for lithium-ion batteries. Among them LiCoO2 was the first material commercialized because of its good rate capability and high conductivity. However since its high cost and toxicity of Co in LiCoO2, a lot of studies to substitute Co to other transition metals, e.g. Ni or Mn, have been performed. LiNi1/3Co1/3Mn1/3O2 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 LiCoO2. 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 LiNi1/3Co1/3Mn1/3O2 powders using ultrasonic spray pyrolysis method and subsequent sol-gel coating. The precursor solution were prepared by mixing LiNO3, Co(NO3)2·6H2O, Ni(NO3)3·6H2O, Mn(NO3)3·6H2O at a mole ratio of 3:1:1:1 in deionized water. The solution was atomized using an ultrasonic spray nozzle 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 powders were annealed at 800 - 1000 °C—celsius—and then coated with alumina or magnesia, sol-treated at 600-800 °C—celsius, 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 0.1-1C rates using coin-type cells. The XRD pattern of synthesized powder without any coating conformed to a well developed R3m symmetry with I001/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 method has been developed for the deposition of manganese oxide films for application in electrochemical supercapacitors. The use of polyethyleneimine (PEI) as an additive enabled the formation of adherent films with excellent adhesion and 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 and Zn+ complexes. The deposition yield has been studied at different deposition durations. X-ray data of sintered films showed the crystallization of Mn3O4 at 300 degC and Mn2O3 at 500 degC. The electrochemical performance of the film sintered at different temperatures was studied by cyclic voltammetry (CV), chronopotentiometry and impedance spectroscopy in Na2SO4 solutions. Obtained films showed excellent pseudocapacitive behavior in the potential window of 0-0.5 V. 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 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 increased 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. 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. Pluți E. Ngoepe1, Thi X. T. Sayle2, Regina R. Maphanga1, Dean C. Sayle2 and C. Richard A. Catlow2; 1Materials Modelling Centre, University of Limpopo, Sovenga, 0727, Limpopo Province, South Africa; 2Inorganic Materials Group, Department of Science, Cranfield University, Shrivenham, Swindon, SN6 8LA, United Kingdom; 2Davy Faraday Laboratory, The Royal Institution of Great Britain, 21 Alabmarle 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 pyroslite 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 (sinteration-included) under molecular dynamics (MD). Long-duration MD, applied to this system, results in the sudden evolution of a small crystalline region of pyroslite-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 consists of the pyroslite structure (isotrophic with rutile titanium dioxide, comprising 1x1 octahedra) and is heavily twinned. In addition, we study the influence 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 Deptula3, Kenneth G. Goretta, W. Lada1, T. Olczak1, D. Wawszczyk2 and B. Sartowska1; 4Institute of Nuclear Chemistry and Technology, Warsaw; 5Argonne National Lab, Argonne, Illinois.

Layered LiNiOx 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 + acetic acid aqueous solutions by alkalinization 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 750°C) 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 LiCoO2 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 LiCoO2 by the high-frequency microwave is investigated in this paper. Using the superfine Co3O4 powders as starting material, acquired LiCoO2 at 400-500°C in 1 hours. Researched the factor affect the process. LiCoO2 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 LiCoO2.

**B7.19**

On the use of XAS and Mossbauer spectroscopies for lithiated iron phosphates. Charles Delacourt1, Dominique Bonnin2 and Christian Masquelier; 1LRC - Chemistry, Universite Picardie
Recent studies have demonstrated the reversible electrochemical reaction of lithium with hydrated iron phosphates FePO4.nH2O at attractive average operating voltages of 3.1 V vs. Li+/Li. This was demonstrated either for very fine particles (<100 nm) of amorphous compositions or for crystalline forms such as phosphoehedrite FePO4.2H2O. Additionally, there is a tremendous effort worldwide to fully understand and further improve the surprisingly fast response of LiFePO4 towards electrochemical extraction at fast rates. Optimal electrodeactive properties and true plating of the material require that 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 detail a whole series of LiFePO4.nH2O and LiFePO4 samples through XAS and Mossbauer spectroscopies.

**BT.20**
Enhanced Li-ion Inter-calation Performance in Vanadium Pentoxides through Engineering of Nanostructure and Interlayer Structure. **Ying Wang**, Katsunori Takahashi and Guozhong Cao; Materials Science and Engineering, University of Washington, Seattle, Washington; **Steel Research Laboratory, JFE Steel Corporation, Chuo-ku, Chiba, Japan.**

This research aims to improve the Li-ion intercalation performance of V2O5 by engineering its nanostructure and interlayer structure. We have prepared single-crystalline V2O5 nanorods by using the template base electrodeposition method followed by sintering at 485°C to obtain the pure orthorhombic phase. The resultant nanorod arrays consist of numerous nanorods with diameters of 5-10 nm and lengths of 4-5 μm, projecting from the substrate surface. High-resolution transmission electron microscopy (TEM) micrographs and electron diffraction patterns of V2O5 nanorods clearly show the single-crystalline nature of nanorods and the layer direction of growth. The growth mechanism of single-crystalline V2O5 has been discussed. The Li-ion intercalation property of the nanostructured V2O5 electrode has been compared to a film electrode of similar V2O5 mass and geometric area. Electrochemical analysis have demonstrated that nanorod arrays deliver significantly improved storage capacity than V2O5 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 capacity of nanoparticulated nanorod arrays and films is similar and reach the maximum of 148 mAh/g, nanorod arrays can store 5 times Li+ than V2O5 films do at a higher specific current such as 700 mA/g. Further enhancement in Li-intercalation property has been accomplished by introducing a small controlled fraction of water between adjacent layers in V2O5. Electrochemical characterization have demonstrated that V2O5-0.3H2O film exhibits higher Li-ion intercalation capacity and more sustainable cycling life than anhydrous V2O5-V05 film or other V2O5-nH2O film (n = 0.1, 0.6, 1.0). At a high specific current of 850 mA/g, the V2O5-0.3H2O 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 V2O5. The small amount of water intercalated between the layered structure of V2O5 makes the interlayer spacing twice that of anhydrous V2O5, resulting in slightly enhanced intercalation capacity. Simultaneously, water in V2O5-0.3H2O film is much less and more tightly bound than that in V2O5-1.6H2O xerogel, and thus deflected the damaging effect of water reacting with lithium on the cycling life.

**BT.21**
Energetics of Lanthanide-doped Hafnia. **Patra Simonic** and Alexandra Niezgoda; Thermochemistry Facility, UC Davis, Davis, California.

HfO2 is a candidate for solid electrolytes, ceramic toughening agents, nuclear waste forms, and alternative gates dielectrics. Crystallographic phases, phase transitions and energetics of HfO2 are therefore of special interest for these applications. HfO2 occurs in three polymorphs at atmospheric pressure: (1) monoclinic, (2) tetragonal, (3) cubic fluorite structure, with transition temperatures at 1700 °C and 2600 °C. Oxides with a disorder cubic fluorite structure display a high oxygen mobility and find applications as ionic conductors. The monoclinic HfO2, usually only stable at very high temperature, can be stabilized at lower temperature by doping with various elements such as Y or lanthanides. Hf1–xRxO2–y/2+ samples with x = 0.4 and R = Sm, Gd, Dy, Yb were prepared by a modified fluoride method. The resulting powders were dried over night at 150 °C and calcined at 900 °C for 8 hours. The powders were annealed at 1500 °C and quenched into liquid nitrogen. Present phases were analyzed by powder X-ray diffraction (XRD) with a Scintag (Pertinio, CA) PAD-V using Cu Ka radiation. Synchrotron powder X-ray diffraction to determine lattice parameters and site occupancies by Rietveld refinement are performed on beamline X14A at NSLS, Brookhaven. Calorimetric measurements were performed with 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 Hf1-xRxO2–y/2+ samples (R = Sm, Gd, Dy, Yb) using a small volume titration method. The calorimeter was heated to 700 °C with O2 bubbling and flushing for better dissolution. 10 mg pellets of Hf-R solid solution powders were calibrated against the heat of combustion of Mg. All Hf1–xRxO2–y/2+ samples (R = Sm, Gd, Dy, Yb) were measured in 10–20 mg pellets, heated to the growth temperature of the single crystal, and the enthalpy of formation of Hf1–xRxO2–y/2+ was calculated by a thermodynamic cycle based on the enthalpies of drop solution of HfO2, HfO1.5 and Hf1–xRxO2–y/2+.

**BT.22**

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 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 over 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.

**BT.23**

Unidirectional alignment of organic conducting polymers is presented. Monomers (i.e., pyroles, N-methyl pyroles, 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 membranes 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.

**BT.24**
Rechargeable Battery based on LiNi1/3Mn1/3Rh1/3O2. **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 LiNi1/3Mn1/3Rh1/3O2 is potentially important cathode material for Lithium 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 LiNi1/3Mn1/3Rh1/3O2 material and characterized for its structural and electrochemical behavior. The results indicate that such cathode material is suitable for low voltage battery applications.

**BT.25**

The tunnel compounds NaNMnO2 and Na0.44TiMn1-yO2 are being investigated as low cost potential catalysts in applications for 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 P2O5 units are also present in units, which may facilitate oxygen transport across the structure. The compounds Na0.44MnO2 and Na0.44Ti0.25Mn0.8O2 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 AIPO4 Nanoparticle Coating on LiCO2O. Anjili T. Appappillai 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 AIPO4-nanoparticle coating on LiCO2O as a cathode material. Through electrochemical impedance spectroscopy of coin-type cells, the electronic and charge-transfer resistance of the AIPO4-coated LiCO2O are compared to that of the pristine LiCO2O 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 LiCO2O 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 LiCO2O.


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 self-assembly 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-composite targets 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. Ue Seung-Ki Kim, Tae Hyuk Kang and Chi-Su Kim; 1Chemical Engineering, Ajou University, Suwon, South Korea; 2Battery 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, the lithium-polymer battery is unavailable 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 of the current collector tabs, and the 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 on 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 current collector tabs is pertinent for the total amount of the current-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 employing a Lithium 2P04 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 the 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 electrolyte. Based on the discharge behavior, 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.

B7.30 Conduction measurements of electrolyte and Bi filled nanostructured using AFM. Karen Jo Long, Victor H. Gehman, Francisco Santiago and Kevin A. Boullais; 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. Yutaka Sagiwa1, Yoshinori Sato1, Takashi Itoh2, Balachandran Jayadevan1, Atsuo Kasuya2 and Kazuyuki Tojii1, 1Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; 2Center 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 the Pt-M steps by less than the Pt-Pt steps in ORR by more favorable Pt-Mr 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 poloyr 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 FeCl3 and 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. FePt/C were obtained by filtering, 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 cast on an 


B.7.32 Single wall carbon nanotube-based electrochemical capacitors for space exploration applications. Heather Fireman, J. Jud Ready, Tom Reynolds, Padraig Moloney, Olga Gorelik, Pasha Nikolaev, Sivaram Arapahoi and Leonard Yowell, NASA Johnson Space Center, Houston, Texas; 2Georgia Tech Research Institute, Atlanta, Georgia; 3Raytheon Corporation, Bend, Oregon; 4ERC 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 geometric 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 effect of a new method of one-step purification, including 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, July 2005, p. 70.

B.7.33 MoO3-Pt thin film electrodes as a nanocomposite host for rechargeable lithium ion battery. Youn-Su Kim1, Hye-Jin Ahn1, Hee-Sang Shim1, Yung-Eun Sung2 and Won-Bae Kim2, IMSE, GIST, Gwangju, South Korea; 2Seoul National Univ., Seoul, South Korea.

Effects of platinum nanoparticles, which are embedded in the molybdenum trioxide (MoO3) matrix, on the microstructure and electrochemical behaviors were investigated. The Pt-MoO3 nanocomposite thin film electrodes were prepared through co-sputtering process with MoO3 and Pt targets. Transmission electron microscopy (TEM) results exhibited particle size and amount of Pt nanophases were controlled. The electrochemical behaviors of Pt-MoO3 nanocomposite thin film electrodes were described as the function of particle size and amount of Pt and amount of Pt nanophase. From the electrochemical experimental results for the lithium insertion and extraction process, Pt-MoO3 nanocomposite thin film electrodes show enhanced cycling performance and discharge capacity compared to those of MoO3 single thin film electrodes in the absence of Pt nanoparticles.


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 ultracapacitors 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, the material (CMR) retains their structural, morphological, and electrochemical properties in comparison to control samples. However, higher energy density produces noticeable changes to the morphology, structure, and electrochemical performance and 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.

B.7.35 EELS analysis of Niobium Oxide Compounds For Support of Next Generation Solid Electrolytic Capacitors. Matthew Olseta, Jinguo Wang and Beth Dickey: Penn State University, University Park, Pennsylvania.

On the forefront of capacitor technology sits the field of electrochemical capacitors. Electrochemical capacitors are produced from powders of valve metal (e.g., Nb) or valve metal oxides (e.g., NbO) to create high, charge-dense materials. By utilizing the high CV/ks 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 further 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, standards 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 niobium oxide (Nb2O5). The extent 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. Normalized M2.3 white line intensities were measured versus 4d occupancy for each compound. The data are in correspondence with those observed in the literature for 3d and 4d transition metals using normalized L2.3 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 and Nb2O5 as compared to NbO. The analysis of this series of stable niobium oxides provides guidelines for analysis of next generation electrolytic capacitors.

B.7.36 Phase Transformations of the Pb1−xSnxF2 Solid Solution on Ball-Milling. Georges Denes, Matthieu Kernech, M. Cecilia Madamba and Lucie Pozziar; Chemistry and Biochemistry, Concordia University, Montreal, Quebec, Canada.

The high temperature form of lead(II) fluoride, PbF2, is the highest performance fluoride-ion conductor among the fluorides, containing only one metallic element. Several combinations of PbF2 with SnF2 result in high density ionic solid, the best combination is PbSnF4, the conductivity of which is three orders of magnitude higher than that of PbF2, 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, PbSnF4 undergoes several phase transitions, the phase obtained in a given preparation is highly sensitive to the method of preparation, and several of these phase transitions are highly sluggish. In addition, PbSnF4 is much more sensitive than PbF2 to oxidation when heated, and in addition, it suffers from a substantial 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 be comparable in the same way. 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 Pb1−xSnxF2 solid solution (0<x<0.50) was prepared earlier in our laboratory, and later by others. Its fluoride ion conductivity increases from x = 0.2 (8×10−4 S/cm) to reach a maximum at x = 0.5 (8×10−2 S/cm) for x = 0.40, the conductivity is close to that of PbSnF4, and it changes little at higher x values. For 0<x<0.30, the Pb1−xSnxF2 solid solution has the cubic fluorite-type structure, with full Pb/Sn disorder. For 0.40<x<0.50, a lattice distortion gives rise to the rhombohedral β-PbSnF4 structure, with partial Pb/Sn order. Therefore, for x values

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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 PbSnF₄ with similar performance. In the present work, we have studied the behavior of the Pb₁₋ₓSnₓF₂ 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, with the partial transformation to orthorhombic α-PbF₂ takes place, and the rate of this transformation increases for low values of x (x < 0.025). For x > 0.025, it decreases dramatically with increasing x such that for ca. x > 0.12, no α-PbF₂ is formed on milling, and no phase transition takes place on ball-milling; only a small decrease of the crystallite dimension is observed. For x > 0.30 the β-PbSnF₄ type tetragonal solid solution undergoes a transformation to a cubic fully disordered nanocrystalline β-PbF₂ type, with a rate increasing as x increases.

**BT-37**

**Preparation of Nanosuperionic Materials by Ball-Milling.**

George Dones, M. Cecilia Madumon, Abdulhadi Muntasir and Alem Perauciu. Chemistry and Biochemistry, Concordia University, Montreal, Quebec, Canada.

The best fluoride-ion conductors were, for a long time the MF₂ (M = Ca, Sr, Ba and Pb) compounds that have the fluoride-type structure, with β-PbF₂ having the highest performance from far. The superior performance of the fluoride-type materials has been explained by the presence of a large number of empty F₂ cubes (half of them, the other half being occupied in its center by a M⁴⁺ cation) that can be used as interstitial sites for a Frenkel defect type of conduction. However, Denès has shown that this mechanism does not explain why β-PbF₂ has a conductivity much higher than that of BaF₂, since the F₂ cubes of BaF₂ are large enough to take a fluoride ion without local strain, whereas the F₂ cube of β-PbF₂ requires local distortion and should therefore be less efficient. Furthermore, new materials, containing divalent cations, prepared in the last two decades, have fluoride ion conductivity much higher than any other fluoride known before, and can therefore be labeled superions. This is the case of the MSnF₄ materials (M = Ba and Pb), the conductivity of which is three orders of magnitude higher than that of the corresponding MF₂, and also of disordered systems such as PbSnF₄ and the Pb₁₋ₓSnₓF₂ solid solution. Furthermore, new materials, the conductivity of which has not been measured yet, have been prepared in our laboratories as PbSbF₄, CaSbF₄, SrSbF₄, and the CaF₂ and PbF₂ 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 min for all the PbSnF₄ phases, up to 40 min for BaSnF₄). The order-disorder transition has been studied by X-ray diffraction, and ¹²⁹Sn 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.

**BT-38**

**Studies on Dielectric Properties of Ionically Conducting Polymer Nanocomposite Films.** Dilip K. Pradhan, B. K. Sanantaray, R. N. P. Choudhury and Awangelka 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 behavior 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 arise from two processes, one by reorientational 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 sample. The high-frequency dielectric relaxation and the low-frequency dielectric 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 the relationship between dielectric analysis. The results of dielectric and conductivity analysis of a Na⁺-ion conducting polymer nanocomposite film containing general formula PEO₂₅-5NaClO₄ + x wt.% Na₄+ Montmorillonite. The freestanding polymer nanocomposite films have been prepared by tape casting technique using a self-designed tape caster. The dielectric properties of the materials have been carried out using impedance spectroscopy. Application of electric 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 dispersions (α = 0.5-0.6) 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 Chemistry**

**Chairs: Isabel Davidson and Clare Grey**

**Thursday Morning, December 1, 2005**

**Room 310 (Hynes)**

**8:00 AM** **PB-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 solid state chemistry, is often characterized of electrochemical 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 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 Li₄MnO₃, 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** **PB-2**

**Mechanical and Electromechanical Characterization of Rechargeable Lithium Ion Batteries.** Timothy Chin, Urs Rhyner, Yukinori Komaya 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 LiCoO₂ 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 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 kJ/m³, 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 number W911W6-05-C-0013.

**8:45 AM** **PB-3**

**InSitu Microprobe Studies of Local Detrimental Processes in Li-Ion Battery Composite Cathodes.** Robert Milosz Kostekci, Marie Kerlau, Jinglei Lei and Frank McMarnon; Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory.
Laboratory, Berkeley, California.

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 into and extraction from the composite electrode 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 nanoscale disorder, which 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 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.


9:15 AM B8.4 X-ray Absorption Spectroscopy study of lithium insertion mechanisms in γ-MnO2 materials. Emillie Machaufaux1, Stephanie Belin2, Dominique Guyomard1 and Guy Ouvrard1; 1 Institut des Matériaux Jean Rouxel, NANTES, France; 2 Soleil, Saint Aubin, France.

Due to low cost of raw material, and their non-toxicity, manganese oxides, and especially γ-MnO2 materials, present a strong interest as active material in the positive electrodes for Li metal primary and secondary batteries. The γ-MnO2 material is of interest to be seen as one of two types of structural defects in a Ramdelliste structure: intergrowth of rutile-type structural units (noted Pr) and microtwisting (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 γ-MnO2 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 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...)? γ-MnO2 compounds obtained in this study show a relatively high degree of crystallization compared to compounds synthesized by more traditional methods. The relative amounts of pyrolysis intergrowth, Pr, and microtwisting defects, Mt, can be determined from the position of the (110), (221) and (420) peaks. To characterize γ-MnO2 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 change of the XRD pattern at the manganese peaks of γ-MnO2 is visible in the 2θ range, while after the charge, the XRD patterns show strong similarities with that of the non lithiated γ-MnO2 compound. However, the complexity of the XRD patterns does not allow to determine if the transformation is a complete one, or if an insertion mechanism. The local structural environments and the electronic states of manganese in the lithiated and pure γ-MnO2 compounds have been investigated by X-ray absorption spectroscopy (XANES and EXAFS) at the Mn K edge. The data show a reduction 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 modified after discharge, and the results 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 in formation. 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 Li(Ni0.5Mn0.5Co1-y)2O4 via the Magnetic Properties. Natasha A. Chernova1, Xiaomiao Ma1, Jie Xiao1,2, Peter Y. Zavaliy1,1 and Stanley Whittington1; 1 Institute for Materials Research, SUNY-Binghamton, Binghamton, New York; 2 Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland.

Magnetic properties of the promising cathode material for the rechargeable lithium batteries Li(Ni0.5Mn0.5Co1-y)2O4 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 Ni, NiMnCo(O1-y)2O4 (y=0.2, y=0.5, 0.45, 0.4, 0.3) using a SQUID magnetometer. At high temperatures, the Curie-Weiss behavior is observed. The average magnetic moment changes from 3.2 μB per formula unit consistent with S=1, Mn3+ (S=3/2), Co3+ (S=0) oxidation states for x=1. For x<1, the magnetic moment increases as a fraction of Co3+ ions becomes Co2+ (S=3/2); for x<1, the magnetic moment decreases as part of Ni2+ becomes Ni3+ (S=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 Tc increases with increasing magnetic moment. Below Tc, 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 and Mn content. Above Tc, the hysteresis of magnetization is found below Tc, whose size increases with decreased Co and Li content. AC susceptibility shows pronounced frequency dependence around and below Tc for all the materials. In LiNi0.5Mn0.5O2 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 frequency. Based on these results, ferrimagnetic ordering is proposed for LiNi0.5Mn0.5O2, 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 and, as a result, the transition metal ions become magnetically ordered. The distribution of magnetic Mn3+ and Ni2+ ions provides a spin-glass behavior in LiNi0.5Mn0.5Co2O4. When Ni2+ ions occur on Li sites, magnetic clusters are formed that have net magnetic moment when ordered, therefore cluster-glass is observed in LiNi0.5Mn0.5Co2O4. When Ni2+ ions occur on Li sites, magnetic clusters are formed that have net magnetic moment when ordered, therefore cluster-glass is observed in LiNi0.5Mn0.5Co2O4.

10:15 AM B8.6 Lithium metal battery study by Electrochemical impedance spectroscopy. Renaud Bouchet1, Lucas Sannier2, Delphine Guy4, Bernard Lestriez5, Michel Rosso6, Dominique Guyomard1 and Jean-Marie Tarascon5; 1 MADREL, Marsouin codex 29, France; 2LRCUS UMR 6007, Amiens, France; 3LPMC 7643, Palaiseau, France; 4Institut des Matériaux 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 electric properties of the 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 the interface, are observed. Hence, EIS allows theoretically a complete
characterisation of an electrochemical system from the materials to
to their interface. The aim of this presentation is to show the ability of
EDS to reveal such a material battery. The analysis of the
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/IV-d-HFP based polymer. The
lithium-ion battery as the anode and the charge transfer reaction
across the electrolyte are determined. Then, the cathode composite
properties are analyzed in the framework of their texturing 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’Keeffe
and Tom O’Keeffe; 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, Zn2+ 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-1980s, Hg and Pb additions to the alloys inhibited Zn
corrosion. The development of next generation, environmentally friendly Zn anode 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 getters. 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 microscopy (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 spectrophotometry. 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 different Bi and 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 Tjiaan and Andrew Talk; C&RD, 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, cyclability, electrochemical stability, etc. These disparate
disciplines have not met. Energy storage devices make their way
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 disciplines of composites: on cathode, LiCoO2, 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 evaluated. The compositional ratio of electroactive
cell size, crystallinity of the binder, melt vs. solution processing, processing temperature, etc. The microstructure of the composites is
determined using electron microscopy (SEM), X-ray diffraction, DSC,
and surface analysis (atomic force microscopy, X-ray photoelectron
spectroscopy), the mechanical properties are evaluated via dynamical test equipment, 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 Morimoto1, Shunji Taniguchi2 and Masahiko
Takahashi3; 1Department of Environmental Systems Science, Doshisha
University, Kyoo-tanabe, Kyoto, Japan; 2Research 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
mixed with ORR catalysts and Pt/Fe particles. The air-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 catalysts, and Pt/Fe powders. The
obtained air electrode shows good polarizability behaviors for oxygen
evolution and oxygen reduction, although KOH is used, 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 series of rechargeable metal-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 one hand the
reversible H2NiO2 - HNiO2 (or Ni(OH)2 - NiOOH) reaction takes
place. This requires the transport ofprotons through an outer layer of
the H2NiO2 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 H2NiO2 /
HNiO2 boundary. This boundary is thus displaced as the reaction
proceeds. When the electrode is fully charged, or completely discharged,
the NiOOH is present. Upon discharge the interface moves toward the
current collector, and in the end its structure consists of only
H2NiO2. When the H2NiO2 solid electrolyte has disappeared and the
HNiO2 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
generation 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. H2 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
the cell is deeply discharged, it is possible to recharge, but it is
still possible to extract further hydrogen. This leads to a higher
plateau, and a new process takes place, resulting in the rapid
generation of gaseous oxygen and a modification of the solid phase. The
label gamma-NiOOH is often used in this connection. During

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 deposited 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 nanoparticle. The synthesized nanoparticles are then captured in a powder collection apparatus to maintain processing time and hold 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 2x10⁻⁵ S/cm, which is significantly larger than is observed for Ligeon 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 700 mAh/g Sn were achieved at 25 mA/g rates with powder-based composite materials and those attained at 100 mAh/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 nanomaterials of these compounds are attractive for their potential to deliver greater rate capability and reversibility, and because preparing nanodimensional layers of the correct phase is extremely difficult due to the potential for hard agglomeration to occur at the nanoscale. The possibility of layered structure decomposition to NiO and Li2O at elevated temperatures. In preliminary efforts, first cycle charge capacities exceeded 120 mAh/g which, with X-ray diffraction data suggest the presence of the layered LiCoO2-Ni1-xO2 phase. Additionally, SEM results indicate primary particle sizes ranging from 50 to 200 nm and larger agglomerates on the order of 300-500 nm.

2:15 PM B9.3

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 neck length, demonstrating that the fiber sidewalls are electronically active. Using simple aqueous and chemically functionalized VACNFs in both aqueous and non-aqueous electrolyte solutions, the electrical double-layer at the VACNF-aqueous electrolyte interface shows a high capacitance of ~1000 F/cm² macroscopic electrode area, which is weakly frequency-dependent; these measurements indicate the facile access of ions to the nanofiber sidewalls. Measurements using an 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 mechanical 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 BuOCH3, 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 other methods having the lowest percolation threshold (~0.01 vol%). It is to be noted that these values rive those reported for single walled carbon nanotube-polymer composites. Combining the two methods described above results in conductivities that fall in between the two methods of fabrication. At a given carbon black content, it is possible to vary the electrical conductivity by as much as 12 orders of magnitude.

SESSION B9: Electrolytes
Chairs: Gerbrand Ceder and Steven Greenbaum
Thursday Afternoon, December 1, 2005
Room 410 (Hyne

1:30 PM B9.1

Plastic crystal electrolytes which can combine the benefits of plastic-like workability 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. Comparison will be made of the electrochemical performance with various combinations of anodes and cathodes.

2:00 PM B9.2

Polyethylene oxide (PEO) has been a polymer electrolyte of interest because of its low glass transition temperature, its ability to coordinate with transition metals 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 crystallization in PEO and promote the conduction of a single ion, we introduce two different electrolytes 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 way to both 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.
Self-Filling Electrochemical Cells by Dual Laser Processing. Craig B. Arnold1 and Alberto Pique2; 1Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; 2Materials Science and Technology Division, Naval Research Laboratory, Washington, District of Columbia.

The fabrication of small-scale energy storage components for microelectronics to meet growing demands in these emerging technologies. Successful microfabrication 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 steps. We focus on the use of hydrous ruthenium oxide electrode material with liquid sulfuric acid electrolyte. Electrode and electrolyte material is deposited by laser direct writing. All cells are fabricated using 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/Li polymer batteries with acceptable Li+ 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+ 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+ 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+ through model SEI layers have revealed that while Li+ is readily transported through common SEI components at high temperature, with conductivity comparable to that found in liquid electrolytes, the mobility of Li+ in the SEI layer decreases much more dramatically with decreasing temperature that 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 interest 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, the benzene denoted as 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+ and then is reduced to S again. The chemical stability of the radical cation S+ greatly determines the overcharge protection capability of the redox shuttle. For instance, 1-brom-2,5-dimethylbenzene was claimed as a redox shuttle for lithium-ion batteries[1,2], and was finally reported unstable and impractical recharge protection capability by Chen et. al.[3]. At the same time, Chen et. al. also proposed 2,5-diterbutyl-1,4-dimethylbenzene as a super stable redox shuttle[3]. In order to understand the criteria of a good redox shuttle, the density functional theory study the improved calculation methods applied to the substitution groups on the benzene ring. Current effort was focused on the charge distribution of the oxidized redox shuttle (S+) 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 Contract 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(styrene Oxide). Larisa Gitelman1, Mohe Israeli2; Amir Averbeck3, Menachem Nathan4, Diana Golodnitsky5 and Zeev Schuss1; 1Faculty of Mathematics, Technion, Haifa, Israel; 2Faculty of Computer Science, Technion, Haifa, Israel; 3School of Computer Science, Tel Aviv University, Tel Aviv, Israel; 4Department of Physical Electronics, Tel Aviv University, Tel Aviv, Israel; 5School of Chemistry, Tel Aviv University, Tel Aviv, Israel; 4School 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. LiI) serves as a solid polymer electrolyte (SPE) candidate in 3-dimensional (3D) thin-film microbatteries (M. Nathan et al., MRS Proceedings, vol. 835, K10.10.1 - K10.10.6, 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., J. Phys. Rev. E, vol. 64(2-3) 025116, 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 helically-orientated helix polymer. Each helix forms a random angle α with a "stretching" axis perpendicularly to the electrodes. Upon mechanical stretching, α > 0. For this configuration, we assume that the main Li-ion 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 voltages across the channels. 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 at 60°C 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 surrounding by poorly conducting bounaries, 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 40°C, our simulations predict the much larger (order of magnitude) actually observed decrease.

4:15 PM B9.9

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 flexible polymer which can be filled with Li+ ions to improve the energy density. Commercial Li-ion batteries use liquid electrolytes, which are highly flammable, and further the volume of electrodes usually changes during the charge/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 such a house, so weight is saved. Polymer electrolytes 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 study the electrolyte in the form of nano fiber by electrosprinning 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 of PEO fibers formed by coating PEO and LICIO4 dissolved in acetonitrile solvent for different Li:O ratios. The
electrosyn 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 electrosyn fibers. The results of the investigations are discussed in detail.

4:30 PM B9.10

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.

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