SYMPOSIUM CC
CC: Microbattery and Micropower Systems
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*Invited paper
8:30 AM *CC1.1
Micro Fuel Cell Fabrication using Thick Film Printing Techniques, Andrew Swan, Jesse S. Wainwright and Laurende Dickie,
Chemical Engineering, Case Western Reserve University, Cleveland, Ohio; *Electronics Design Center, Case Western Reserve University, Cleveland, Ohio.

Thick film printing can be utilized in the production of fuel cells by microfabrication techniques. Thick film printing, which does not require clean room conditions, can handle the 'unclean' nature of the catalyzed ink. In this study, we experimentally produced layers of appropriate thickness, ca. 10 micron. By using the proper formulations, a fuel cell can be produced by thick film printing that operates under ambient conditions. Due to the nature of the fuel cell, the ink for thick film printing was severely limited, including ink layers and porous current collectors. The challenge was devising inks that were specifically designed to give the proper function in the fuel cell, and that were compatible with each other and the printing process. Polarity curves will be presented for individual cells and for stacks of three series connected cells fueled from on-chip metal hydride storage. The effects of the various factors contributing to the overall cell and stack performance, including kinetic, mass transfer and re-oxidation losses within a cell and within the stack, will be considered.

9:00 AM *CC1.2

Formic acid fuel cells have been proposed for small portable power applications. In this paper the characteristics of a series of small formic acid fuel cells built are discussed. Formic acid is a liquid fuel. It has a lower energy content than for example methanol, but it offers a higher theoretical potential, few crossover issues, and easier water management. The UIUC fuel cell is a pumpless design with silicon current collectors, Nafion membranes, and a mixed catalyst. The device originally operated at 0.1mF/cm² of silicon die. So far the device has been able to produce 25 mV of power with a total energy content of over 400 wh/kg based on fuel. A variety of catalysts have been tested in the devices. Palladium shows the highest initial activity, but the activity degrades over 10 hours. Platinum-palladium has a lower activity but the activity is stable. Platinum-ruthenium shows the highest currents at lower fuel cell potentials. These results show formic acid MEMS are attractive fuel for portable power applications.

9:30 AM *CC1.3
High Performance Direct Methanol Fuel Cell Electrodes using Solid-phase Synthesized Carbon Nanocomposites. Hong Jin Han, Youngkwon Yun, Young Eun Sung, Kyung-Won Park and Cheechoo Hyeong, School of Chemical Engineering, Seoul National University, Seoul, South Korea; *Engineering and Research Center for Energy Conversion and Storage, Kwangju Institute of Science & Technology, Kwangju, South Korea.

We report on the synthesis of carbon nanocomposites composed of nanometer-thickness graphitic fibers by the catalytic pyrolysis of polymeric carbon precursor. The carbon nanocomposites were successfully applied as electrode materials for direct methanol fuel cells. We synthesized carbon nanocomposites by simply heat-treating nanocomposites composed of carbon precursor, silic, and transition metal salt, followed by the removal of silic and metal. The XRD pattern of carbon nanocomposites exhibits that these carbon materials are well-graphitized. The carbon material exhibited high surface area of 318 m²/g. The SEM image reveals that the carbon materials were consisted of ~ 100 nm sized particles. The TEM image shows that the individual particle was composed of ~ 5 - 10 nm thick coils. The high-resolution transmission electron microscopic image of a single nanocomposite shows well-aligned graphitic layers. It is well known that it is extremely difficult to synthesize carbon materials with both surface area and good graphitization. Accordingly, in terms of the design and application for a support in fuel cells, the carbon nanocomposites, which possess high surface area, well-defined porosity and excellent crystallinity, is considered as a very attractive choice. The electronic and electrochemical properties of the carbon nanocomposites were compared with those of Vulcan XC-72 carbon that is the most widely used electrode material for DMFC. The specific oxidation currents of the carbon nanocomposites at 0.1 V were also examined. At a higher potential of 0.6 V, CNIL-C17 has six times (20 A/g) the current of Vulcan-XC72 (40 A/g). The remarkably higher oxidation current of the supported catalyst is directly related to the high surface area and the superior dispersion of catalysts on the carbon nanocomposites that possess both excellent crystallinity and high surface area.

9:45 AM *CC1.4

Portable scale Direct Methanol Fuel Cell (DMFC) has great potential to come into early applications due to its higher tolerance of power and the fact that system integration has been relatively easy. A major issue is the development of micro-fluidics, which includes the micro pump for anode liquid recirculation and for recycling the excess water from the cathode back to the anode, and the passive CO2 gas bubble separation from the anode side liquids. In addition, the seamless integration of various micro-fluidic components and the electronic control system has been an essential concern for system reliability and cost reduction. Micro pumps and valves are in development at Carnegie Mellon University utilizing flexible diaphragms fabricated on silicon wafers. This technology has been successfully demonstrated on applications of micro-speakers and microphones, but not yet on pumps. Molds are formed on silicon and then suspended with isotropic etching. The openings are then sealed with polymer deposition. For its operation, the diaphragm is actuated with electrostatic forces. The micro pumps are used to send the excess water from the cathode back to the anode side. As a result, very small water storage is needed and most of the space is left for storage of pure methanol. High power density per unit volume is therefore achievable for the micro fuel cell. A passive CO2 gas separator has been developed, which is compatible with the silicon wafer manufacturing and integration. When the bubbly flow comes into a chamber formed by two pieces of silicon wafer at 350 micron distance, bubbles agglomerate and coalesce. One surface of the chamber contains an array of 30 micron holes etched through the silicon. Since the surface property of the silicon is hydrophilic, water flows through the holes whereas bubbles are blocked due to their surface tension. The other surface has an array of 20 micron holes etched through, but is hydrophobically coated with Teflon. Bubbles attach and dry the non-wetting surface, and gas escapes from the holes. This system has been successfully fabricated and tested. The micro pumps, valves, channels and gas separator could be fabricated on the same set of silicon wafers with a common fabrication process. The need for post-fabrication integration is eliminated. Furthermore, the CMOS electronics control system is also fabricated on the same wafer before the MEMS fabrication is conducted. This CMU-CMOS-MEMS process shall further reduce the interconnections between electronic and mechanical components, resulting in a fully integrated low-cost, high-performance micro-fluidics for DMFC.

10:30 AM *CC1.5
Laminar Flow-Based Microfuel Cells, Paul J.A. Kinsel, Eric Choban, Piotr Waszkuc, Markoski Larry and Andzej Wieskowski, Chemistry and Biological Engineering, UIUC, Urbana, Illinois; *Beckman Institute, UIUC, Urbana, Illinois; *Chemistry, UIUC, Urbana, Illinois.

Current efforts to develop micro fuel cells have mostly focused on polymer electrolyte membrane-based designs. However, several technological challenges have prevented widespread introduction of these fuel cells into commercial applications. Two of these technological challenges are fuel crossover and membrane dry out, whereas the majority of these systems employ metallic mesh to separate the anode and the cathode. Here we describe a novel concept: a membrane-less microfluidic fuel cell that exploits a unique characteristic of fluid flow at the microscale, laminar flow, to keep the two streams containing fuel and oxidant separated while still in diffusional contact. The fuel and oxidant streams are brought together in a common microfluidic channel and continue to flow in parallel without turbulent mixing over catalyst-covered opposing channel walls. The two physicochemical phenomena that govern the chemical conversion and accompanied energy and mass transport in these laminar flow-based fuel cells will be examined: depletion of reactants at the electrode walls and diffusion across the mutual liquid-liquid interface. Integration of an external reference electrode has enabled the assessment of the performance of the anode and cathode separately and simultaneously in a single experiment. This allows for the determination of the limiting factor of the membrane-less fuel cell and also makes possible the use of the membrane-less fuel cell as a tool for the optimization of catalyst under true fuel cell conditions. At current, multiple changes in the design are being explored to overcome some of the limitations, such as concentration boundary layer formation, in order to increase the performance characteristics of these conceptually novel micro fuel cells. Finally, an assessment whether this type of membrane-less fuel cell in a system is expected to be superior over existing PEM-based microfuel cell technology will be presented.
Thin-film Membrane Materials for Use in Microfluidic Devices: Methanol Cells
Christopher W. Moore, Jun Li and Paul A. Kohl, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Portable electronic devices, including those for mobile communications, computations, microsensors, micro-electromechanical systems (MEMS), and microfluidic devices all require advances in energy storage. The availability of power sources with higher energy density and longer range of operation is a function of this research. One possible source of higher energy power is the use of fuel cells. The availability of high energy density storage is expected to have significant impact on commercial, industrial, individual, and military applications. The goal of this research is to investigate a number of materials that could be suitable for use as proton exchange membrane in direct methanol fuel cells (DMFCs). DMFCs are considered low temperature fuel cells because their typical operating temperatures are 60-100°C. They usually employ a solid polymer electrolyte membrane (PEM). A methanol-water mixture is fed to the anode in either liquid or vapor form. Methanol is an attractive fuel option because it can be stored as a liquid, is inexpensive, and has a high specific energy (1-3). Microfabricated fuel cells based on using a sacrificial polymer to form microchannel structures (4-5) are being investigated at Georgia Tech. The sacrificial polymer is deposited, patterned, and covered with an encapsulating material. It is then heated and decomposed, with the decomposition products diffusing through the overcoat material. The encapsulating material for the micro fuel cells is the PEM. The fuel flows through these channels and comes in contact with the catalyst and PEM at the anode. The top of the PEM is considered for the cathode. A number of materials are being investigated for their use as the overcoat/membrane. The material properties that are of importance include the proton conductivity, methanol permeability, and dimensional stability. The materials must also withstand processing conditions which includes relative high temperatures during the decomposition of the sacrificial polymer. Protons generated on the anode side of the cell must pass through the membrane for reaction at the cathode. The membranes are tested for ionic conductivity in an electrochemical cell and with impedence spectroscopy. The ionic conductivity and methanol permeability measurements for different materials over a range of temperatures and relative humidity will be presented.

systems generates over 50 Wt. in a reactor device with a total volume of less than 25 cm^3, weighing less than 15 gm, and a thermal efficiency of greater than 40%.

2000 PM *CC2.2
Solid Oxide Fuel Cells for Portable Applications.
Sung-Mo Kim*1, Chau V. Kwan1, Jeongmin Ahn2, Craig Eastwood2, and Paul Rooney2.
1Materials Science, Calif. Inst. of Technology, Pasadena, California, 2Aerospace & Mech Engineering, U of Southern California, Los Angeles, California.

Technologies which take advantage of the inherently high energy densities of liquid hydrocarbon fuels are ideal for meeting the increasing energy demands of the microelectronics industry. Indeed, the power generating device were to be used on, for example, propellant and consist of 50 vol % fuel, one would require only a 5 % fuel-to-electricity conversion efficiency in order to meet existing battery technology benchmarks. Such efficiencies are easily achieved in solid oxide fuel cells, however, fabrication and thermal management at such small length scales become extremely challenging. To simultaneously address the issues of energy density, ease of fabrication and thermal management, we have developed an integrated microgenerator that features a single chamber fuel cell in its center and utilizes a unique "Swiss roll" design for thermal management. The single chamber fuel cell uses mixed fuel/oxidant as the single inlet, simplifying device design, and relies on the selective activity of anode and cathode materials to generate a potential across the electrolyte. In particular, the anode, in this case a nickel-electrolyte cermet (ceramic-metal composite), is active towards both partial oxidation of propylene to DME and H2, and the electrolyte (La_{2}Ti_{2}O_{7}) to affect fuel component towards electrochemical reduction of oxygen. The cathode, here a mixture of Sm_{0.2}Sr_{0.8}Co_{0.15}O_{3} and Ni-doped ceria is, ideally, active towards electrochemical reduction of oxygen but inactive towards propylene oxidation. For optimized gas compositions and flow conditions, power densities of 100 - 120 mW/cm^2 at 475 - 550°C were obtained from anode-supported, ceria-based cells placed in an externally heated furnace. The performance of the cells was then reproduced in the "Swiss roll" thermal recirculator, in which heat was generated via internal, flameless combustion and the temperature was controlled by control of the gas flow rate.

230 PM CC2.3
Design Considerations for Microscale Solid-Oxide Fuel Cells.
N. T. Turner*, V. T. Sikri², A. I.², and S. M. Sprouse².
²Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, ²Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Microfabricated solid oxide fuel cells (SOFCs) are one class of devices that are actively being developed as alternatives to batteries. SOFCs are attractive because they offer the potential for high conversion efficiency and high power densities compared to other fuel cell technologies. However, significant engineering challenges, including maintaining structural and electrical stability and managing heat losses, have prevented reliable, efficient, smallscale solid oxide fuel cells from being realized. The current work describes the development of a set of first-order design rules that can be used to design micro fuel cells.

245 PM CC2.4
Microstructured Thin Film Noble Metal Cathodes for Microscale Solid-Oxide Fuel Cells.
Joseph Hetts, Arnie Barcheck and Harry L. Tuller, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Micro-solid oxide fuel cells hold promise as portable power sources with energy densities considerably above that exhibited by batteries. At these scale sizes (sub-micron thick films), ohmic electrode losses are expected to be very low, even at reduced temperatures (≤850°C). Electrodes of noble metals are often utilized in design solid oxide fuel cells, e.g. lithographically prepared, are possible at these temperatures. However, one of the key issues for the success of these devices concerns the reaction pathways at the electrodes. It is not yet clear what electrodes of this size and operating parameter values will perform optimally. In particular, cathode performance is expected to be limiting and so this work concerns the characterization of noble metal cathodes for thin film solid oxide fuel cells. In this work, thin film yttria-stabilized zirconia (YSZ) solid electrolytes were deposited onto silicon substrates by sputtering or pulsed laser deposition. Platinum and gold electrodes were then deposited on top and lithographically patterned to give interdigitated electrodes with well-controlled geometry. Sixteen different electrode patterns, with independent variations in interdigitation distances and triple phase boundary lengths, were used. Impedance spectroscopy was carried out on these samples in controlled temperatures and oxygen partial pressures. Comparison of measured impedance data with the electrode geometry, composition, and measurement environment provided insight into the reaction pathways. A rational means for electrode optimization was thus gained. This work was supported by the DoD Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Grant DAAD19-01-L-0665.

3:30 PM CC2.5
Electrode Development for Micro Solid Oxide Fuel Cells.
Steven E. Weiss and Jackie Y. Ying, Chemical Engineering, MIT, Cambridge, Massachusetts.

Conventional ceramic processing techniques have produced yttria-stabilized zirconia (YSZ) electrolytes of 10-20 microm thick. Deposition techniques available to the semiconductor processing industry, such as sputtering, physical vapor deposition, or sol-gel deposition have allowed the deposition of self-supporting electrolytes of YSZ with thicknesses of 100-400 nm. Such a dramatic decrease in electrolyte thickness would allow for lower temperature operation and reduce the system's thermal mass, greatly reducing startup and shutdown times of the device. Sputtering techniques, however, are very poorly suited to the deposition of active solid oxide fuel cell electrodes. Electrode performance is optimized by utilizing films with large quantities of fine-scale porosity. We have developed wet-chemical deposition techniques that show adhesion to silicon and allow for tailoring of the active microstructure. The synthesis technique is also applicable towards the deposition of catalysts for micro-reformer applications. Specifically, novel wet-chemical deposition techniques have been developed to allow for thick-film deposition of various cathode materials. These films are porous, 5-15 microm thick, and can adhere to substrates with heat treatment at a low temperature of 400°C. This is in contrast to traditional ceramic processing techniques, which require temperatures in excess of 900°C to promote film adhesion via sintering and chemical reaction. The synthesis technique has focused on hydroxide gel suspensions and sol-gels that can be used to build the desired complex oxides onto silicon surfaces with superior adhesion compared to traditional binder systems. Finally, wet-chemical techniques have been utilized to deposit porous Pt thin-film electrodes. These films have better adhesion and improved porosity compared to commercial thick-film Pt inks.

3:45 PM CC2.6
Pt/AO3, Thin Film Catalysts for Preferential Oxidation of CO in a Microkinetic Array.

Preferential oxidation of carbon monoxide in a H2-rich mixture (PrOx) is a crucial chemical step in PEM fuel cell applications for miniature portable power devices. This paper seeks to address the question of whether a thin-film catalyst immobilized on the walls of a microchannel reactor is sufficient to satisfy the catalytic activity requirements of PrOx for portable fuel processing applications. Microreactors were designed and fabricated based on state-of-the-art silicon micromachining techniques, and Pt/AO3 thin-film catalysts were deposited on the inner walls of Si microchannel reactors with sol-gel processing procedures. Physical characterization of the catalysts was accomplished with BET, CO chemisorption, XRD, TEM and SEM/EDS. A parallel microreactor system (microkinetic array) for fast catalyst screening was deployed for reaction analysis because of its high efficiency with minimal chemical and lab space requirements. Reaction conditions (feed rate, feed composition, temperature, and pressure) were automated and individualized for each reactor in the array for fast experimental turn-around and less human intervention. A number of catalyst samples with different preparation or initial catalyst samples with different pretreatment procedures for reaction conditions were able to be tested simultaneously. Product sampling was multiplexed by use of multiple-port gas sampling valves feeding common GC and MS analytical units. We sought to understand the kinetic mechanism of the catalytic PrOx reaction with an advanced reaction modeling solver, CHEMKIN™ M, which provides flexible and powerful tools for incorporating complex chemical kinetics.
4:00 PM CC2.7
Sequential and Simultaneous Electrodeposition of Pt-Ru Electrocatalsyst on HOPG Substrate: A surface morphology and electrocatalytic study. Carlos B. Callejas, Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico.

Sequential and simultaneous linear sweep potential deposition of Pt and Pt/Ru has been studied on previously activated HOPG substrates. RuCl3 and K2PtCl6 have been used as sources of Ru and Pt, respectively. The concentration of 1mM, K2PtCl6 was constant in all the experiments, and RuCl3 concentration was changed from 0.05 to 1 mM. Sequential voltametric results allowed the determination of Pt and Ru loading and a complete catalytic evaluation, which is difficult to determine via simultaneous deposition. Morphological characteristics through scanning electron microscopy (SEM) and atomic force microscopy (AFM) have shown that the deposits are composed by aggregates of different shape and size forming clusters. Scanning tunneling Microscopy (STM) demonstrate that the tops of these clusters are nano-clusters from 5 to 10 nm. The distribution of these clusters on the HOPG surfaces is heterogeneous and dispersive. The presence of Ru on the surface produce changes in diameter and height of clusters as compared with pure Pt clusters. XPS results show that Ru and RuOx or Ru(OH)x are the chemical species present on the electrode surface before methanol oxidation. The Ru amount increase remarkably after methanol oxidation experiments. The ratio of Pt/Ru surface concentration obtained via XPS and the electrochemical ratio follow the tendency of molar concentrations.

4:15 PM CC2.8
Proton conductivity in solids by first principles calculations. N. Kwon1,2 and Tomon Hanks2,4, Fukushima Institute for Fundamental Chemistry, Kyushu University, Fukuoka, Japan; 2Department of Materials Science and Engineering, Kyushu University, Fukuoka, Japan.

At the normal pressure, CaH2SO4 (CHS) has three phases. Below the temperature 340 K, CHS is in phase I with monoclinic structure. At the temperature 349 K, the phase III of CHS transforms into phase II with monoclinic structure. At a higher temperature 414 K, the phase II transforms into phase I with tetragonal structure. Among these phases, the structure in phase I shows an extremely high proton conductivity [1] and has been demonstrated a promising application in fuel cell [2]. Theoretically, atomic mechanism of proton conductivity in these phases are still not clear. For example, it is still open why phase II shows quite lower conductivity then that of phase I. In our study, we have performed first-principles calculations to investigate the proton conductivity in the phases (in particular, phase I and II). The difference factors and barriers for proton jumps have been searched by transition state theory. The mechanism of proton conductivity has been discussed by analyzing these transition states. Meanwhile, proton conductivity in other kind of materials such as ice was investigated using the same procedure. Similarities and differences in proton diffusion mechanism among them will be discussed in some detail.


4:30 PM CC2.9
Anhydrous Proton Conducting Polymer Electrolytes Based on Biological Nanostructured Materials. Hiroya Hoshina and Masaomi Yamada; EIEI, AIST, Tsukuba, Ibaraki, Japan.

Proton conducting polymer electrolyte membrane without a presence of incorporated water has been attracted much attention in recent years because a proton transport irrespective of water is more suitable for intermediate temperature above 100°C. PEFCEs have been widely recognized that intermediate temperature operation of PEFC has been recently pointed to overcome most of the technological problems such as CO poisoning onto the Pt electrode surfaces, a thermal compensation potential and complicated water management. In this presentation, new class of water-free proton conducting membranes has been synthesized by the hybridization of acidic polymer containing the phosphate groups and organic base of heterocyclic macrocycle. Inorganic acid-hybrid membranes based on the biological nanostructures showed high proton conductivity without the presence of water molecules. The proton conductivity and thermal stability of membranes with acid-base complex increased with the doping ratio of organic base. Maximum proton conductivity of the membrane was found to be 1X10^-4 S.cm^-1 at 150°C under water-free (non-humified) condition. The membrane was proved to be amenable to rapid proton transfer between the protonated basic molecules. Non-hydric proton conducting membranes may have technological potential not only for the polymer electrolyte membrane fuel cell (PEFC) but also for electrochemical devices including electrochromic displays, chemical sensors, separation and other.

4:45 PM CC2.10
Effect of monomeric sequence of Nafion on its nanostucture and transport properties. Tikhar Cagin, Seong Jang, Yale Moliner and William A. Goddard, Caltech, Pasadena, California.

Nafion is a hydrophilic polyether electrolyte consisting of nonpolar Na+-CF2-CF2- and polaroizible PF2- and CF3-CF2=CF2-SO3H segment. Hydrated Nafion 117 with an average of 6.5 hydrophilic tetrafluoroethylene units per vinyl ether sulfonate unit is widely used for membranes in fuel cell operations due to its relatively high proton conductivity, and mechanical and electrochemical stability. Although the ratio of hydrophobic to hydrophilic monomers is well known, to the best of our knowledge, the monomeric sequence in the Nafion polymer has not been characterized and taken into account as a design variable to improve the performance of fuel cells. There is a general consensus supported by experiments and simulations that hydrated Nafion has a ninosegmented structure consisting of hydrophobic and hydrophilic domains. Notwithstanding, the details of the segregated polymer remain unclear and highly debated. We studied the effect of polar/non-polar sequences on the structure and water transport of Nafion 117 with 20% wet water by molecular dynamics simulations. Although the systems show both hydrophobic/hydrophilic segregation in all the studied conditions, we observe that the more blocky sequence has better phase segregation and their miscibility is unevenly distributed in the interface leading big hydrophobic patches of polymer/water contact. The vehicular diffusion of water and hydronium was not affected by the blockiness of the polymer.
power supply provides the capability and flexibility needed to address the power needs of a variety of autonomous microsystems. Microelectronics that are powered by the array of photovoltaic cells and microbatteries are being developed. These batteries must have a high power and energy density (per area) in order to meet the size and power requirements of microsystem applications. The development and performance of batteries with the required characteristics will be presented. A Prototype cell of 140 mW/cm^2 has been observed, these power levels are sufficient to meet the project needs of many autonomous microsystems, including remote microsensors. In addition to the development of a suitable microbattery, and integration with other electrical components, the multi-functional design will be presented.

There is also a need for suitable switches. This session will describe our efforts to address these challenges.

9:30 AM CC3.3
Miniature Hybrid Battery-Photovoltaic Power Systems

Power sources are a prerequisite to the deployment of autonomous microelectronic devices. Systems that derive fuel from ambient sources are particularly attractive for miniature and/or remote applications, making photovoltaics an obvious choice. Our ultimate goal is the development of a hybrid micro-power system composed of microsolar cells and microbatteries to provide energy harvesting, energy storage, and high power levels to microelectronic devices. Current hybrid power systems highlight recent progress toward this broad objective, especially issues of packaging and interconnect materials and strategies. For the demonstration of microphotovoltaic components, we have chosen silicon nitride doped photodiodes. These solar cells have a number of advantages over silicon-based devices. Because they are made without the stringent processing requirements of semiconductor photodiodes, the films can be tailored to the needs of an application using a variety of microfabrication techniques. Secondary lithium-ion batteries are an obvious choice for power storage due to their high cycle life and operating voltage (~3.6 V).

The active materials for both the microsolar cells and batteries can be successfully and non-destructively transferred via a laser-direct write method but many obstacles remain to the direct integration of power sources into microelectronic devices. For example, the direct deposition of metals for current collectors, electrodes, and interconnects is a major area to explore. We have looked at some trials of packaging options for lithium-ion batteries. Also, metals and glasses are potential candidates for packaging micro-power systems, and appropriate materials and deposition methods must be devised. Progress on several of these components for total system design will be presented.

9:45 AM CC3.4
Design and Testing of an All-Solid State Polymer Nanoscale Battery, Renen E. Bullock2 and Peter Kofinas1,2, 1Chemical Engineering, University of Maryland, College Park, Maryland; 2Environmental Science and Engineering, University of Maryland, College Park, Maryland.

Solid polymer electrolytes have provided a promising route to an all-solid-state polymer- segmented A/B block copolymer. Current hybrid power systems typically involve a metal anode, a solvent-plasticized polyethylene, and a composite cathode. We have synthesized an A/B diblock copolymer for use in all-solid-state self-assembled nanoscale polymer lithium batteries. Self-assembly of block copolymers provides nanoscale domains whose morphology can be controlled. These domains can then act as templates for the formation of nanochannels containing inorganic moieties. The polymeric all-solid-state battery consists of a lanthanum intercalated microporous-silica-segmented A/B block copolymer, which is derived using Grubbs's catalyst for ring-opening metathesis polymerization (ROMP). The "A" block polyethylene is a ROMP derivative of PE0 and the "B" block polyethylene is a spinodal phase lithium permanganate. The diblock copolymer can act as a composite polyethylene or a composite cathode against lithium metal. In 13C NMR and FTIR we employed to determine the composition and structure of all monomers and polymers. Gel Permeation Chromatograms indicate a diblock copolymer with Intragranular aromatic structure, which was characterized by XPS and Wide Angle X-ray diffraction. Transmission electron microscopy was used to visualize the lamellae structure in the diblock copolymer. A current density of 64nmA/cm^2 was measured with cyclic voltammetry and charge/discharge curves were obtained.

10:30 AM CC3.5
Rapid Transport Paths for Li Diffusion in Nanosstructured Vanadia Cathodes, Stephen H. Garofalini and Weiqun Li, Ceramic and Materials Eng, Rutgers University, Piscataway, New Jersey.

Molecular dynamics (MD) computer simulations have been used to study Li migration in a nanocrystalline vanadium cathode in a solid state oxide thin film battery. Previous simulations have shown that Li transport into the cathode crystal is affected by the orientation of the layered crystal at the interface, with the largest activation barriers to diffusion in the (001) direction. Experiments show that these smallest diffusion direction is perpendicular to the interface, thus inhibiting diffusion. Molecular dynamics simulations show possible rapid diffusion paths in nanocrystalline vanadium that would effectively enhance the natural orientation of these crystals at the cathode/electrolyte interface. However, the width of these diffusion paths affect Li diffusion and the optimum width will be discussed based on the simulation results.

10:45 AM CC3.6
A Enhanced Interfacial Material for Lithium Micro-Batteries, Yuming Song, Peter Y. Zawil and Stanley M. Whittingham; Chemistry Department, SUNY-Binghamton, Binghamton, New York.

c-VOPO4 from two different precursors (vanadium-rich tetragonal phase and stoichiometric monoclinic phase) was synthesized by combustion and electrochemical recharge. The crystal structure has been determined and was refined in space group P41_2_1_2. It consists of chains of corner-sharing VO6 octahedra separated by PO4 groups. The c-VOPO4 formed from the vanadium-rich tetragonal hydroxide precursor has much better electrochemical behavior than that synthesized according to the literature from monoclinic VOPO4.H2O. The capacity exceeds 200 mA/cm2 at low cycling rates and even at a current density of 2mA/cm2 exceeds 90mAh/g, thus making this compound a viable candidate for a high rate cathode for secondary lithium batteries. The close relationship between the structures of the precursor materials, the c-VOPO4 phase and the lithium products will be described. This close relationship makes these materials particularly attractive for thin film and other micro-batteries. This was supported through the Batt program of DOE through LBNL.

11:00 AM CC3.7
Nanostructured Lithium Manganese Thin Film Cathodes For Rechargeable Micro-Batteries, N. Santander, M. Bonner, S. B. Mjumdar and R. S. Katiyar; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

In the present work we have investigated the electrochemical characteristics of nanostructured LiMn0.5O2 (LMO) thin films for lithium ion rechargeable micro-batteries. LMO cathode has a serious capacity-fading problem, especially show the room temperature operation. The origin of capacity fading has so far been poorly understood, however, the possible reasons for fading could be dissolution of manganese spinel into the electrolyte, decomposition of electrolyte on the surface of the cathode. In the present work by controlling the heat treatment schedule we have controlled the grain size and grain size distribution of LMO thin films deposited on photonic silicon substrates. The electrochemical behavior of these films were characterized by cyclic voltammetry and charge/discharge measurements. The grain size and crystallinity of the films increased with the increase in annealing temperature. The best CV and charge/discharge capacity was observed in films annealed at 780°C for 2h. The electrochemical properties of these films were correlated with the phase formation behavior and microstructure evolution of these films.

11:15 AM CC3.8
Carbon-Coated Layered LiNi0.5Mn0.5Co1-2yO2 (y=0.4) For Lithium Batteries, Makoto Mi, Kyung Ngn, Peter Zawil and M. Stanley Whittingham; Chemistry, Binghamton University, Binghamton, New York.

Layered LiNi0.5Mn0.5Co1-2yO2 (y=0.4) is attracting much interest as a possible alternative to LiCoO2 as the cathode for lithium batteries. It exhibits a reversible capacity of 180mAh/g at room temperature between 2.5 to 4.5 volts at rates as high as 2mA/cm2 and shows good cyclability. Chemical characterization showed that the electronic conductivity of the cobalt-doped layered compound is one order higher than that without cobalt. In addition, cobalt addition stabilizes the migration of nickel ions in the diblock copolymer. A current density of 64nmA/cm^2 was measured with cyclic voltammetry and charge/discharge curves were obtained.
11:30 AM **CC3.9**
The structure around oxygen and metal atoms in LiI, NIO, and A: A soft X-ray study
Faisal M Alsharqi1, 2, Mahalingam Balasubramanian3, Jay Whitacre3, Martin den Boer3, Chi-Chang Kuo1, James McBreen1 and Steven Greenbaum1; 1Brookhaven National Laboratory, Upton, New York; 2Physics, Hunter College of the City University of New York; New York, New York; 3Jet Propulsion Laboratories, Pasadena, California.

There has been a recent drive towards the miniaturization of rechargeable batteries to support the growing need for local power sources for microelectronics devices. This miniaturization has begun even while the physics of charge compensation (and the resulting structural changes) is not fully understood in the most common rechargeable batteries. One such system is the popular LiCoO2/II2O3-based battery. A proposed mechanism for the redox reaction of this battery is based on the de-intercalation of Li+ ions in the transition metal. The direct X-ray absorption spectroscopy (XAS) studies on the metal edges appear capable of this. Alternatively, it is proposed that the oxidation state of the O atoms change. This has the back of some ab initio calculations and energy band spectroscopy (EELS), although the EELS results require a redox assembly of a functional cell and exposing it to high vacuum conditions and a fast electron beam. We have designed a spectro-electrochemical cell which used for XAS in the soft X-ray region, thereby allowing us to examine dynamic structural changes around the O K-edge as well as the metal L2,3 edges. The initial results of a more holistic approach to the problem are presented here. We present the local electronic structure around both the metal as well as the oxygen atoms in fully assembled and functional thin-film batteries.

11:45 AM **CC3.10**

In the present work, we report the progress optimization to synthesize spinel type lithium manganese (LiMn2O4) and layered structured lithium nickel oxide (LiNiO2) ceramic powders to prepare composite cathodes for Li-ion rechargeable batteries. Two approaches were pursued to improve the capacity and cyclability of these materials. In the first approach, a part of the Mn or Co ions were substituted by the other reactive ions (e.g. Al, Ta, etc.) to raise the stability of the oxidation states of Mn/Co ions, as well as O2 ions in the respective layers. In the second approach, the individual cathode particles were mixed with the inert oxide particles (e.g. ZrO2, TiO2, Al2O3) in order to improve their electrochemical properties. Some of our recent findings pertinent to these two approaches will be presented.

SESSION CC4: Microbattery and Micropower Systems IV

Chairs: B.V.R. Chowdri and Jesee Winwright
Wednesday Afternoon, December 3, 2003
Independence East (Sheraton)

1:30 PM **CC4.1**
New Strategies for Li-Ion Batteries and Electrochemical Capacitors as Autonomous Microsource Sources.
Karen Swider Lyons, Ryan C. Wartena, Aimee E. Curtright and Arnold M. Skol; Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia.

Autonomous microelectronic devices for remote sensing and transmission require power sources that operate with little or no attendance. The micropower sources must be compact, have high energy density, and have low weight and volume to a means to refuel from the ambient. We are investigating two rechargeable microsource sources: Li-ion microbatteries and asymmetric ultracapacitors. First-generation Li-ion microbatteries were prepared from conventional lithium-ion battery materials, including LiCoO2, carbon, Celgard and an ethylene-carbonate-based LiPF6 electrolyte. These microbatteries have excellent cyclability and can be operated in ambient conditions when packed using a metal foil/plastic composite. The next generation of Li-ion batteries in development will be all solid state, because elimination of the liquid electrolyte will simplify packaging strategies and significantly improve specific energy. Fabrication methods are being developed to integrate the Li-ion microbatteries into the devices directly to define the cell. A new type of asymmetric electrochemical capacitor is being demonstrated because it can be used as a hybrid power source that operates both at -1 μA/cm2 in faradic mode for continuous energy (for sensing) and to 1 mA/cm2 in capacitive mode to produce high power (for transmission). The hydrous RuO2 and Pt electrodes recharge autonomously through the catalytic consumption of hydrogen and oxygen harvested from the ambient environment. From our research, we find that there are numerous new opportunities available for creating energy and power at the microscale, and potentially at the nanoscale.

2:00 PM **CC4.2**
New Solid Electrolyte, Thio-LiScO - Its Property And Application To All Solid-State Battery, Ryoji Kanno1, Masahiro Murayama1, Kyoji Kazahokom1, Taro Inoue1, Noriyuki Sonoyama2, Atsuo Yamada1 and Shigeo Kondo2, 1Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; 2Ion Engineering Research Institute Corporation, Hitachinaka, Ibaraki, Japan.

This-LiScO (Lithium Superionic Conducting Electrolyte) is one of the best lithium-ion conductive solids ever found in inorganic materials. The room-temperature conductivity exceeds 10-3 S/cm with negligibly small electronic conductivity and a high decomposition potential. It is of great interest to investigate the ion transport mechanism as well as an application to solid-state batteries. The material would be placed in place of flammable liquid electrolytes in conventional lithium-ion rechargeable batteries. Based on the structures and electrochemical properties of this-LiScO family, Li4+x, Li+M-x, M=Sn, Ge, and M=P, Al, Zn, Ga, As, we discuss the ion transport mechanism and its material design concept. We applied the thio-LiScO as solid electrolytes; all-solid-state cells using the most conductive composite, Li4+x, Ge, O, P, M=Sn, Ge, P, with the Chevrel phase cathode and Li anode showed excellent cycling characteristics. The cell design concept of all-solid-state batteries with the thio-LiScO electrolyte will be discussed.

2:30 PM **CC4.3**
Microscale Solid State Lithium Batteries, William C. West, Jay F. Whitacre and Ramakumar V. Bugnay; Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Lithium thin film batteries with sizes on the order of 1 sq. cm are readily fabricated via sputter deposition and thermal evaporation of thin-film cathode, anode, and electrolyte. The absence of liquid electrolytes and their components. Fabrication of cells with dimensions below 100 microns square requires more sophisticated methods to define the cell components, e.g., photolithography. However, these procedures must not compromise the highly reactive cell components such as the solid electrolyte and lithium metal anode. To this end, we have demonstrated micro-scale lithium batteries using a variety of cell fabrication techniques and cell materials. These microbatteries are capable of thousands of deep charge/discharge cycles, tolerate high charging/discharging rates in excess of 100 C, and are easily fabricated in series and parallel arrangement to yield batteries with higher voltage and/or capacity. In this report, we will discuss the microfabrication approaches developed; materials characterization and electrochemical performance results will be related and discussed. Also addressed will be individual cell performance in various multi-cell battery configurations.

3:30 PM **CC4.4**
Investigation Of Carbon Dioxide Bubble Detachment Conditions In Micro Pdu Cells, Ching Ching Wee, Sheung On Chin, Xiushen Chen and Peter J. Haddad; Georgia Institute of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The generation of carbon dioxide bubbles at anode in the micro DMFC poses a great challenge in the fuel delivery system to maintain steady fuel cell performance. The removal rate of carbon dioxide bubbles must exceed its generation rate so that the PEM is kept hydrated with electrolyte most of the time. This work investigates the detachment condition of carbon dioxide bubble in the micro channel through modeling and experimentation. The bubble detachment conditions are studied in a two dimensional computational model with given bubble sizes, contact angle and flow conditions, such as pressure and velocity. Micron channels fabricated by stereolithography are embedded with electrodes to simulate a bubble generation by electrolysis. Specific bubble sizes are controlled by gas injection to test the detachment conditions for single bubble. The feasibility of arranging flow patterns in fuel streams to flush off carbon dioxide bubbles and control their motion is explored.

3:45 PM **CC4.5**
Hybrid micropower systems using direct-write processing, Craig B Arnold, 1, Heungsoo Kim1, Thomas E Satt0 and Alberto Pique1, 1Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; 2Materials Science and Technology, Naval Research Laboratory, Washington, District of Columbia; 3Naval Surface Warfare Center, Dahlgren, Virginia.

The development of micropower systems, on the mm size scale, is
necessary for the smaller and more portable micro-electronic device applications that are currently being advanced by many research teams. We demonstrate the use of direct-write processes to produce the high-power, low-power, and recharging elements of such a microscale micro-power system. We have successfully fabricated anode and inter electrode bicarbonate microvolts, microwatts, micro-units, and doped-doped micro-solar cells on various low-processing substrates using direct-write as well as direct-write dispensing. The laser direct-write process has enabled the deposition of layers 30-40 μm thick while maintaining patterns as small as 5 μm for pinpoint. Our primary alkali microvolts exhibit open-circuit potentials of 1.5 V with high capacities and discharge currents up to 1 mA. Preliminary secondary LiCoO2 and LiNi0.44 μm microvolts exhibit open-circuit potentials of 3.95 V. We have shown multiple recharging cycles without loss of capacity. In this presentation, we will emphasize our recent results on these microvolts with particular focus on device fabrication and packaging for improved shelf-life performance.

4:00 PM CC4.6

Incorporating piezoelectric materials into MEMS allows a user to tailor the material to meet the requirements of the device rather than changing the structure of the device to work within the constraints of the selected material. A piezoelectric microgenerator based on lead zirconate titanate (PZT) thin films, the power output can be increased by decreasing the dielectric constant while increasing the effective transverse piezoelectric coefficient. Alternatively, reducing the stress in the thin film will increase the mechanical compliance and strain to failure, which will increase the total strain possible for a given pressure pulse. PZT films of both rhombohedral and tetragonal orientations have been deposited via solution methods. The effective piezoelectric coefficient is moderately insensitive to changes across the phase boundary, however the relative dielectric constant decreases in the tetragonal films from approximately 1000 to 850. Similarly, residual stresses decrease from 400 to 200 MPa across the phase boundary. Since reported values of non-doped PZT films have shown to alter internal stresses, dielectric properties, and piezoelectric coefficients, this paper will present a method of developing doped and graded PZT films to optimize the electrical power output during mechanical to electrical conversion. Films were grown using a sol-gel-based chemistry and processed with both conventional and rapid thermal annealing. Grain size was measured as a function of annealing time to track the evolution of structure from the amorphous to crystalline state using atomic force and scanning electron microscopy. Characterization of electrical output was carried out to measure the effectiveness of Nd-doped PZT for improving micro-power generation.

4:15 PM CC4.7

Integrated circuit evolution creates increased functionality and performance with lower cost and higher reliability. Advances in the integration of new materials with Si CMOS and SiGe for further improvements in circuit speed, power use, and even the integration of photonic devices. With the increasing use of portable electronic devices, the next generation of integration will focus on integrating the power system into Si CMOS. Such integration introduces great synergy in power control via Si CMOS circuitry as well as potentially lower overall system cost. The relatively low power required for microelectronics applications and the thin film fabrication available in microelectronics opens the door for conceiving of new materials and processes to create fully integrated on-chip solid-state thin film batteries. To fully integrate a battery technology into Si circuits, we have begun to scale processes and materials and fabrication processes to the Si CMOS process for solid-state battery formation. In the context of a rechargeable lithium battery, we have begun to explore the use of SiO2, i.e., thermal oxide used in Si CMOS technology as the critical gate insulator, as a solid-state electrolyte, as well as the use of Si itself as an electrode. Interestingly, ion transport through SiO2 was an early obstacle for MOS devices in the electronics industry, but in a battery fast transport of alkali ions through SiO2 is an attribute that is critical for the construction of ultra-thin, ultrahigh capacity solid-state electrolytes for fully integrated nanobatteries. Various Li2O2/SiO2/n+Poly-Si structures were fabricated on Si wafers in a clean room facility, using existing CMOS processing technology. The thickness of the LiO2 layer varied between 500 nm and the total thickness of the LiCo2O4/SiO2/n+Poly-Si stack was less than 600 nm. The microstructures of the stacks were characterized using Transmission Electronic Microscopy (TEM). Current-Voltage (LV) measurements were performed to study the transport of lithium ions through the oxide and the electrical properties of the different structures. The Si-compatible processes used to create the LiCo2O4/SiO2/n+Poly-Si structures will be described. We have been able to show that lithium ions, as charge carriers, can be controllably transported back and forth through the ultra-thin SiO2 with minimal bias, and thus introduce SiO2 as an interesting new candidate as a solid state electrolyte in an on-chip thin film battery.

4:30 PM CC4.8
Ni-Cu/MgO Nanocomposite for Reforming Catalysts. Seichi Suemura, Takayuki Kikawasa, Tomohiro Sueyama, Koichi Inada and Tadashi Goto, R&D Center, Toshiba Corporation, Kawasaki, Japan.

A new nanocomposite for monolith catalyst is proposed. Dispersion and fixing technology for Ni-based alloy catalysts using partial reduction of oxide solid solution has been newly developed. In this study, Ni-Cu/MgO nanocomposite was applied to honeycomb structure monolith catalysts. The experimental process was as follows; a Ni, Cu, MgO sintering body prepared for the catalyst precursor by reaction sintering was partially reduced so as to segregate the Ni-Cu particle diameters from 10 nm to 20 nm. The Ni-Cu particle composition was able to control the addition and reduction temperature with varying CuO. Compared to the Ni/MgO system, the Ni-Cu/MgO system metal particles were smaller. Steam reforming of methanol over a honeycomb structure monolith of the Ni-Cu/MgO composite was performed. This material was found to show high activity at high space velocities. This technology allowed small amounts of catalyst particles to be used efficiently, and shows promise as a new manufacturing process for high performance catalysts. Research supported by NEDO, under the Synergy Ceramics Project promoted by METI, Japan.

SESSION CC5: Poster Session: Microbattery and Micropower Systems

Chairs: B.V.R. Chowdury and Jesse Wainright
Wednesday Evening, December 3, 2003
8:00 PM

Exhibition Hall D (Hynes)

CC5.1
Abstract Withdrawn

CC5.2

Thin-film fuel cells (TFFCs) are of interest as power sources ranging from small portable microdevices to microelectronics, primarily due to availability of on-chip integration as well as their capability to operate the devices. In general, the electrodes in fuel cells consist of more than two phases such as a nanosized noble metal or alloy such as Pt/Ru, along with a porous material as a support for the metal. In addition, the Pt-based anode nanostructure, especially those formed by alloying Pt and Ru, is required for highly efficient fuel cells, in terms of adjusting proper composition of Pt/Ru in the electrodes. Accordingly, for an excellent performance, electrodes in TFFCs should contain Pt/Ru alloy nanoparticles in the porous material. Typically, however, sputtering methods are used for preparing thin-film electrodes and, as a result, materials prepared by the Pt/Ru alloy target have a fixed composition and no nanostructure. However, such conventional sputtering techniques with one sputtering target for a mixed two-phase material cannot be used to prepare nanostructured alloy electrodes having alloy catalysts with a controlled composition in porous oxides. Thus, in this study, nanostructured alloy electrodes for TFFCs were fabricated using multilayer sputtering system consisting of Pt and Ru targets for alloy formation and a WOS target for support of the nanoparticles. We designed an alloy nanostructured electrode [Pt(10)/WOS(90)] for use in high efficient TFFCs using multilayer sputtering system and compared its performance with Pt/Ru alloy thin-film electrode prepared without tungsten oxide. The nanostructured alloy electrode showed excellent current density for the TFFC, due to the alloy formation of Pt-Ru and nanoparticles in the tungsten oxides.

CC5.3
Electrochemical Characteristic of Nano-Coated Silicon-Metal on the Surface of Synthetic Graphite for Anodic Active Material of Lithium Secondary Battery. Jong-Kee Lee, Wonchul Choi, Myungro Lee, Dongjin Byun and Kyung Won Cho, Eco-Nano Research Center, Korea Institute of Science and
Technology, Seoul, South Korea; 2Dept of Materials Science, Korea University, Seoul, South Korea.

For an alternative anode material, the reversible insertion of Li in metal/alkalis has been studied extensively due to their higher specific capacities. However, Li alloys as negative electrode leads the rapid degradation of their mechanical structure that is caused by large volume change of the alloy during repeated charge-discharge cycling in Li cells. In order to stabilize the structure, small particles of Li alloys were embedded in a matrix or a second metal was incorporated in the structure [1]. In the present study, the effects of nano-coating of synthetic graphite surface with various metals and silicon in lithium alloy on electrochemical characteristics were investigated. We expect that the graphite matrix acts as not only a lithium intercalation site but also preventing rapid structure change of the coating alloy. Besides, the metals on the carbon surface play a role to form artificial precipitation films as conducting agent in the electrode. Commercial synthetic graphite with average particle diameter of 0.3-0.8 μm (MCMB 10018, Octagon) was used as raw material. Coating solutions were prepared by mixing of metal salts and methanol. Incase of silicon precursor, non-polar solutions such as benzene and benzene were used as a dispersing agent. Spray coating was carried out by gas suspension method: fluidized graphite powder were coated and dried simultaneously inside the chamber, and then calcined in the furnace under inert atmosphere. Electrostatic sprayer was employed to produce a uniform layer of a thin sol. The working DC voltage range was from 5000 to 10000 V. The values of specific charge capacities, discharge capacities and initial efficiencies were dependent on combination of metal species and 30-50 nano-sized Si coated. Acknowledgment: Research was supported by Center for Nanostructured Materials.

CC5.4


Future portable power requirements will demand greater specific energy and power from lithium batteries. To meet these goals, new battery technology needs to be developed that delivers increased performance in addition to high peak or pulse power. We wish to report on a novel carbon nanotube based, lithium-ion battery with remarkable performance. Through the correct combination of derived carbon nanotube materials either a 3 or 4.5 volt rechargeable battery with specific energy of over 400 Wh/kg and a peak pulse power capability of >4 kW/kg @ 100 Wh/kg was developed. Initial testing was performed with a standard two electrode polypyrrole test cell fitted with two stainless steel piston-cylinder electrodes for very fast power testing using this device, and a standard nonwoven glass separator, test electrodes were tested at a constant current. The electrode for these tests was 1M lithium trifluoromethanesulfonimide ([LiDM, 3 M Co] in a 50:50 mixture of ethylene carbonate and methylcarnitine. All measurements were conducted in an Ar-filled dry box. The electrochemical measurements were obtained using a Radiometer model PGZ 301 Voltablab electrochemical test instrument. Coin cells of the most promising materials were then fabricated using a Rollin coin cell press and were tested with an Arbin BT-2000 battery analysis system. The complete characterization of the derived carbon nanotube materials along with the battery design and the specifics of the testing/performance will be presented.

CC5.5

Application of Doped Lanthanum Gallate Electrolyte Films Prepared by Pulsed Laser Deposition for Solid Oxide Fuel Cell, Fumiki Mitsui 1, Seiji Kitamura 2, Tatsukuni Okubo 2, Yukihari Nomoto 3, Shinya Tsuuma 3 and Yusuke Takita 1; 1Venture Business Laboratory, Oita University, Oita, Japan; 2Electrical and Electronic Engineering, Oita University, Oita, Japan; 3Applied Chemistry, Oita University, Oita, Japan.

Doped Lanthanum Gallate of Ln₂Al₂O₆ + Sm₂O₃ + CeO₂ (2% mol) [LiMgO₂] in CECl₄ has been reported to be an electrolyte for solid oxide fuel cell (SOFC) but it remains high oxygen ion conductivity than that of conventional solid oxygen ion conductors such as YSZ. We prepared the LSFCG films on porous NiO-YSZ, which is used as an anode of the SOFC, by ECP electrochemical deposition technique with the slower electrolyte of 0.3 M LiCl solution at 0.6 V of Pt counter and a Pt wire as a reference. The oxygen partial pressure of the deposition temperature was kept at 1000°C. The LSFCG films were amorphous. The electric conductivity of the LSFCG film measured by the two terminal method was higher (0.7 S/cm at 800°C) than that of YSZ (0.025 S/cm at 800°C). The activation energies of the film is high temperature (600-800°C) and low temperature (400-600°C) regions were 0.72 and 1.05 eV, respectively. Electromotive force was obtained from a tube type solid oxide fuel cell with diameter of 20 mm composed by this LSFCG electrolyte film.

CC5.6

Fabrication Of Composite Of Amorphous Titania And Carbon And Its Electrode Performance For Rapid Discharge, Hirohisa Furukawa, Mitsurou Hibino and Ito Kunio, Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.

These days the need for new battery systems that can keep high-rate discharge for a long time has emerged with a view to popularization of electric vehicles and actualization of compact electric power plants. Our purpose was to obtain high-rate-dischargeable lithium ion batteries and to develop electrode materials for those. For the high-rate discharge, in other words, for operating under large current density, one of the effecting factors is shortening of diffusion length of lithium in active matteric anode or increase in the surface area of metal lithium. In accordance with the above views we synthesized composite of titania and carbon by sol-gel method and evaluated as electrodes for lithium batteries. Amorphous titanium oxide was prepared by a solgel route emplying TIV(IV) alkoxide as a starting agent. The average size of the primary particles was found to be about 4 nm from TEM observation. The BET specific surface area was 97.8 m² g⁻¹. The composite material was then discharged and charged around 2 V vs. Li/Li⁺. The TiO₂/AL composite test-treated at 150 °C exhibited 260 mAh g⁻¹ of specific capacity under 1 A g⁻¹ of current density in the initial discharge. However, the specific capacity that is the actual capacity goes down fast during initial cycles. This capacity loss could be decreased with increasing in the thermal treatment temperature. The TiO₂/AL composite test-treated at 330 °C showed the specific capacity above 125 mAh g⁻¹ even under large discharge current over 10 A g⁻¹. By the help of the relationship between the specific capacity and the current density, the chemical diffusion coefficient for lithium ion was estimated to be 6 × 10⁻⁷ cm² s⁻¹, when the diameter of the observed secondary particles (400 nm) was used as a diameter in the calculation.

CC5.7

Preparation And Properties Of Fine Particulate Li₂MnO₃· Li₂O, LiCoO₂, Batteries, Byo Yoko Nishizawa 1, Kenji Hamada 1, Sunashiro Nagase 1, Yuichi Abe 2 and Mouno Senn 2; 1Nara Machinery Co., Ltd., Tokyo, Japan; 2Faculty of Science and Technology, Keio University, Yokohama, Japan.

By virtue of solid mechanochemical effects, we prepared fine-grained, phase pure LiMn₂O₄ with and without partial substitution of Mn by Ni and/or Co. In order to acquire better mechanochemical effects, we compared various oxides and hydrides as starting materials. A stoichiometric mixture was milled under relatively mild condition in a specially developed multi-rotor type mill in N₂ for various periods. As we calcined the co-milled mixture without Ni or Co in N₂-2%H₂ mixture, we obtained phase pure manganese (Li₂MnO₃) at low temperature as low as 500°C. Merits of low temperature calcinations in view of smaller grain size without sacrificing the crystallinity were discussed in terms of incipient solid state reaction during milling. By substituting a part of Mn by Ni and/or Co, crystallite size was shifted to that of hexagonal or monoclinic regime, which are more beneficial for application to the cathode materials of rechargeable, small size Li-ion battery.

CC5.8

Characterization of Oxide-Coated LiMn₂O₄ Films for Microbatteries, Heo-Soo Moon, Jin-Hee Lee, Ki-Jong Lee, Jas-Pil Lee, Young Gyu Ro and Jong-Wan Park, Division of Materials Science and Engineering, Hanyang University, Seoul, South Korea.

There have been increasing interests in lithium rechargeable batteries, especially micro-batteries, with rapid development of portable electronic equipments and MEMS (Microelectromechanical systems) technology. Lithium manganese oxide (LiMn₂O₄), which is more abundant, stable in ambient state and less toxic than the other oxides such as lithium nickel oxides and lithium cobalt oxides, was a strong candidate for the thin-film cathode materials. In previous our work, the effect of thermal treatment on the microstructure and electrode characteristics of lithium manganese oxide cathode was reported. In operation of alkaline-lithium batteries, battery failure would be caused by electrode/electrolyte interface reaction, internal short-circuit due to electrolyte decomposition and/or electrode materials during charging/discharging processes. In the last point, we focus on interface reaction problem such as increasing internal resistance that would affect the cyclability and lifetime of microbatteries. In order to improve the electrochemical properties of LiMn₂O₄, transition-metal substitution method has been performed. However, this method
induced discharge capacity reduction, because of diminution of Mn$^{3+}$ ions, which was reacted with Li$^+$ ions when intercalation process. To improve this problem without capacity reduction, anion doping and surface treatment, such as oxide coating, was introduced. In this work, thin film cathode was deposited by rf magnetron sputtering with 3-inch-diameter of stoichiometric LiMn$_2$O$_4$ target. Pt deposited Si (100) substrate was used. To make spinel film, this solution was annealed at 750℃ in 2h. The film thickness was about 200 nm. To coat SnO$_2$ on the spinel film, stoichiometric SnO$_2$ target was used as sputtering target. The SnO$_2$ film thickness on the spinel film was less than that of the bulk due to roughness and morphologies of the film was measured by AFM and FE-SEM. The chemical bonding was analyzed by XPS. For electrochemical analysis, half-cells were made with the deposited film as cathode, the lithium metal as anode, and 1M solution of LiPF$_6$ in EC-DMC (1:1) as electrolyte. The spinel film was totally covered with SnO$_2$. The particle size of the SnO$_2$ was less than 10 nm. In the cyclic voltammetry text, the redox peak sharpness of the SnO$_2$-coated film was higher than that of uncoated film. The cycle retention of the spinel coated cell was higher than that of SnO$_2$ coated film. These results mean that SnO$_2$ film on the spinel film prevent the spinel film from the reaction with liquid electrolyte such as the Mn dissolution. The more results will be presented in the meeting.

**CC5.9**
**Post-Processing of LPEI/PAA Poly electrolyte MultiLayer Solid State Electrolytes, Jodie L Luckenbach, Dean M Delongchamp and Paula T Hammond, Chemical Engineering, MIT, Cambridge, Massachusetts.**

We have recently demonstrated that the intelligent design of poly electrolyte layer-by-layer (LbL) assembled films can result in thin films with ionic conductivity appropriate for consideration as solid or gel electrolyte components for batteries. The LbL polymer electrolytes are assembled by exposure of a charged substrate alternately to dilute aqueous solutions of species with opposite attractive affinities. Following drying of the film to remove residual solvent, the one remaining obstacle to battery applications is the persistence of protons within LbL films after assembly, an effect especially notable when considering LbL systems composed of weak [pH-sensitive] poly electrolytes. This work focuses on enhancing the compatibility of LbL films composed of the weak polyelectrolytes linear polyethyleneimine (LPEI) and polyacrylic acid (PAA) for potential use in this important application area. The first step in enhancing compatibility was the application of heat-induced amimation to permanently crosslink the electrostatically assembled films. This crosslinking step was followed by an ion exchange to replace remaining protons with lithium ions. The effects of these post-assembly treatment steps on the ionic conductivity and mechanical integrity of the films were assessed. These results provide knowledge for direct tailoring of new systems to realize commercial-level performance in both large-scale energy storage and future microbattery applications.

**CC5.10**
**Recent Progress on A Stabilized Membrane for HTMEAs, Xing Song, Lenin Borovile, H. Russell Kung, James M Henson, Michael Trankler, Andrew T Wei and Jane L Li, University of Connecticut, Connecticut; IonMem Corporation, Marlborough, Connecticut.**

Proton exchange membrane (PEM) fuel cells are being considered for both automotive and stationary power applications because of their cleanliness and high efficiency. As one of the most promising types of PEM fuel cells, high temperature PEM fuel cell is currently being aggressively researched and developed. Operating PEM fuel cells at higher temperatures (>1000℃) and atmospheric pressure has significant advantages over low temperature PEM fuel cells as CO poisoning at the anode is effectively alleviated. Higher temperature operation also enhances the energy efficiency, improves heat rejection, provides higher quality waste heat and permits easier water management. However, operating at high temperature and low relative humidity has a negative effect on performance of PEM fuel cells due to loss of ion conductivity in both the membrane and the electrode catalyst layer. The fuel cell lab at the University of Connecticut has successfully developed a type of Nafion®-Teflon-Phosphotungstic-Acid (NTPA) membrane with very good conductivity while operated at higher temperatures. The membrane technology has been improved and the cell performance increased to 0.61 volts with lower resistance at 120℃ and lower humidity being achieved. In order to further impart durability to the ionomer in the catalyst layer for long-term performance, it is necessary to get the special treatment done during fabrication by the catalyst layer onto the membrane. In this work, a stabilized membrane has been prepared by modifying the fabrication procedure to reduce potential dissolution of phosphotungstic acid that is being frequently used as a membrane additive to Nafion®. The fabricated in the tetraethyl ammonium form in the catalyst layer also was tested in the cells. All of these approaches are showing promise. And performance and conductivity data will be presented.

**CC5.11**
**Standard Porosimetry, Y M Volkovich, V S Bagotsky and I A Binov, POROTECH, Ltd; Vaughan, Ontario, Canada.**

The Method of Standard Porosimetry(MSP) offers the possibility of measurements in widest range of pore sizes for any sample including solid, fluid and materials integrated by mercury. The method is based on the laws of capillary equilibrium. If two (or more) porous bodies in contact with one another and partially filled with a wetting liquid. For the state of the capillary equilibrium the pressure P of the liquid in these bodies is equal. The capillary pressure is a function of the maximum radius of pores filled with the liquid. If the pore size distribution for one of the porous bodies (the standard) is known, and the equilibrium correlation of the liquid contents in the sample on the liquid content in the standard is determined, the pore size distribution for the sample can be calculated. The amount of liquid in both sample and standard is determined by weighing. Any wetting liquid can be used as working liquid. Based on the MSP, an Automated Standard Porosimetry (ASP) was developed. Utilizing MSP, ASP can test any porous and powdered material e.g., electrodes, membranes, separators, filters, geological strata, catalysts, adsorbents, ceramics, metallic ceramics, textiles, pharmaceuticals, construction materials, and polymers. MSP/ASP Provides 11 Points of Information -Integral and differential distribution of pore volume as a function of the pore radius within range from ~1 nm to 10^3 μm; -Average pore radius; -Specific pore volume (porosity); -Specific surface area (in the range from 10^-3 to 10^3 m^2/m^3); -Distribution of pore surface as a function of the pore radius; -Liquid distribution as a function of the sizes of the capillary pressure; -Differential characteristics of swelling; -Different structural properties of multiple component hydrophilic-hydrophobic bodies; -Adsorption isotherms; -Wetting angle and its dependence on pore radius. References 1. Yu, M. S. Volkovich, V. S. Bagotsky, V.E. Senkin, I.A. Binov, In: Collidos and Surfaces A: Physicochemical and Engineering Aspects, 187 – 188 (2001) 349. 2. J. Divisek, M. Ekerler, V. M. Masin, H. Schˆfer-Steinberg, U. Stimming, Yu. M. Volkovich, V. S. Bagotsky (1998) 2677. 4. Yu. M. Volkovich, V. S. Bagotsky, T. K. Zolotov and E. Yu. Pahreeskaya, Electrochemistry Acta, 41 (1996) 1995.

**SESSION CC6: Microbattery and Micropower Systems**

**Chair: Paul Kiloh and Jesse Wainwright**

**Thursday Morning, December 4, 2003**

**8:30 AM CC6.1**
**Electrochemical performance of the a-Si,Sn, binary system, Timothy D Hatchard, Mike D Flietherman and Jeff R Dahn, 1,2 Physics, Dalhousie University, Halifax, Nova Scotia, Canada; 2Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada.**

Micro-electronic technologies are continually advancing, and as a result greater demands are being made of the batteries that power them. New materials are needed which can be used in smaller, lighter, yet more energetic batteries. Recent work has shown that alloy materials are promising candidates for use as anodes in Li-ion batteries [1]. Much attention is given to alloys of materials like silicon, tin, aluminum and others because of their extremely high gravimetric and volumetric capacities when compared to graphite. The best is silicon with a capacity of 4200 mAh/g (900 mAh/cc). A lot of work has been done on many alloy systems, but there are many problems to be addressed. Many of the materials tried so far suffer from very poor capacity retention [2]. Also, many systems suffer from huge irreversible capacity on the first cycle [3-5]. Recent work has shown that amorphous materials cycle far better than crystalline materials with the same composition [6, 7]. In addition, there have been reports of excellent behavior for both a-Si and a-Si$_{1-x}$Sn$_x$ as [6]. Using the apparatus described in [8], we decided to investigate the electrochemical properties of the a-Si$_{1-x}$Sn$_x$ (0 < x < 0.45) system. A combinatorial binary film of a-Si$_{1-x}$Sn$_x$ was deposited on a number of substrates, including 6x6-chip glass, a 8x8 grid glass with electrical contacts, and copper foil. A combinatorial electrochemical cell with 61 individual channels was used to test the electrochemical properties of this system. As the cell was filled out on an 8 x 8 grid, and the variation in composition is in only one direction, there are eight sets of nearly identical data. This talk will describe the results found, including capacities of up to 3500 mAh/g, and virtually no irreversible capacity. We will carefully consider the advantages and disadvantages of
singly bridged (N or O) species, and species containing up to four phosphorus atoms, in both linear and ring structures, as well as structures such as NPO. The results of the model calculations are revealing as to what we might and might not expect to see in the vibrational spectra of the oxide glasses. The P-N and P-O stretching vibrations show extensive mixing and overlap of their frequency regions. Consequently, the C-S, C=C, N=C, and C=O vibrations are not clearly resolved from the P-O vibrations. The assignment of bands to the phosphate glasses and in comparable phosphorus oxide molecules. We included simple

8:45 AM C6C6.2
Deposition and Properties of Lithium Phosphorus Oxynitride (Lipon) Films, Nancy J. Dudney and Young-II Jung, Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Vapor deposited lithium phosphorus oxynitride (Lipon) films have been used for over a decade as the lithium electrode material in a high density, thin film rechargeable lithium microbatteries. Since first reported by J.B. Bates in 1992, researchers at ORNL have been investigating the synthesis of Lipon films to further understand the deposition-property relationship. Films continue to be grown by rf magnetron sputtering processes from a Li$_3$PO$_4$ ceramic source with a nitrogen mixture, though now films are deposited at far higher rates. Typical films are amorphous with a composition near Li$_3$PO$_4$N$_x$. New impedance and spectroscopic results will be presented indicating results of deposition conditions, concentrations, and the effects of thermal annealing and surface reactions. Solute variations in the composition may occur when Lipon is deposited on a substrate that reacts with lithium, or over a thin film of another lithium anode or cathode material. These variations can be controlled by applying a dc bias to the substrate during the Lipon film deposition. Research supported by the DOE Office of Science Laboratory Technology Research Program and the DOE Division of Materials Sciences under contract numbers DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

9:00 AM C6C6.3
IBAD Lipon: A Solid Electrolyte with High Electrochemical Stability, Fernando Vereda, Ronald B. Goldner, Terry E. Hans, Jeremy Leung and Peter Zergin; Tufts University, Medford, Massachusetts.

We previously reported the fabrication of lithium phosphorus oxynitride (Lipon) electrolyte films that exhibited high Li-ion conductivity and a high decomposition voltage (> 6 V) [1]. These films were fabricated using ion-beam assisted deposition (IBAD) of thermally evaporated Li$_3$PO$_4$. Recent evidence indicates that the electrochemical stability is higher than 8 V, which significantly exceeds the 5.5V reported for magnetron sputtered films [2]. We shall present the results of a study which strongly suggests that the improved stability is a consequence of a considerably lower concentration (by more than two orders of magnitude) of reduced phosphorus (oxidation state ≤ 5) in IBAD Lipon compared to sputtered deposited Lipon. F. Vereda et al, Electrochem. Solid-State Lett., 5 (11), A289 (2002). 2. X. Yu et al., J. Electrochem. Soc. 144, 524 (1997).

9:15 AM C6C6.4
Vibrational Characterization of Lipon Glasses by Ab Initio Calculations on Model Compounds, Terry E. Hans, Fernando Vereda, and Ronald B. Goldner; Dept. of Chemistry, Tufts University, Medford, Massachusetts. 2Electro-Optics Technology Center, Tufts University, Medford, Massachusetts.

Lithium phosphorus oxynitride (Lipon) glasses have become a favored electrolyte material for lithium micro-battery applications, because of its good lithium ion conductivity and excellent electrochemical stability window against both strong oxidizing cations such as LiCoO$_2$ and strong reducing anions, including lithium metal. As a glassy material its structural characterization, especially in the amorphous form, is difficult and there is a fairly broad consensus in the literature that the introduced oxygen modifies the typical phosphate glass structure by introducing triglycine N=P3 and P-N=P units [3]. Of particular interest in the context of the electron optical calculations is a vibrational spectroscopy, both infrared and Raman. We performed ab initio electronic structure optimizations and vibrational frequency calculations on a number of model compounds containing the structural units of Lipon to be present in the phosphate glasses and in comparable phosphorus oxide molecules. We included simple
10:30 AM CC6.7
Ultrathin polymer electrolytes for 3-D solid-state nanostructured energy storage architectures.

Christopher P. Rhodes, Jeffrey W. Long, Michael S. Dresscher and Debra R. Rollison, Naval Research Laboratory, Washington, District of Columbia.

Mesoporous nanoarchitectures, such as aerogels and ambipole, provide an interconnected network of nanoscale particles and porosity and have shown improved electrochemical properties for energy storage applications due to their combination of high surface area, thinness, low electrical contact resistance, and short Brownian transport distances within the nanoscale solid domains [1]. Electrically conductive metal oxide nanoarchitectures coated with an ultrathin polymer separator and filled with an anode create an integrated interpenetrating energy storage architecture in which all functional components are within nanometers of one another therefore offering high rate capabilities. Electropolymerization provides a route to synthesize thin pinhole-free polymer films directly at the electrode surface. The electrodeposited polymers can be both electronically insulating and ionically conducting and therefore function as the electrolyte/separatior in solid-state devices including batteries and electrochemical capacitors. The electro-oxidation of phenol derivatives has been used to deposit ultrathin conductive polymer coatings onto mesoporous manganese oxide nanoarchitectures and plane ITO substrates. The thickness of the PPO films on ITO is determined using AFM profilometry and shown to be between 5 and 10 nm. Scanning electron and X-ray absorption measurements of PPO and other polymers on ITO are made using a two-electrode configuration using soft anodic contacts such as Au or slowly evaporated Al at the top electrode [1]. D.R. Rollison, B. Dunn, J. Mater. Chem., 11, 963 (2001).

10:45 AM CC6.8
Degradation Studies of Microporous Separator Membranes in Lithium-ion Batteries, Giosuè Nunnangelo, Energy Systems Group, Motorola, Lawrenceville, Georgia.

Microporous separator membranes are a critical component of rechargeable lithium-ion (L-ion) batteries that power many of today's portable electronic devices. The general trend in L-ion batteries is to utilize thinner separators in order to create more space in the cell for the active anode and cathode materials that contribute to increasing the energy density. In parallel with the trend, L-ion batteries are also increasingly used in devices that operate at higher power and higher temperature. Furthermore, separators in multi-cell systems (e.g. laptop battery packs) may often experience voltages higher than the 4.2 V that is typically recommended as the upper voltage limit for L-ion cells. In this study, the effect of higher temperature and higher voltage on the performance of separator membranes with thickness values of 20 microns or less was investigated. Tests on several commercial L-ion cells indicated that separators based on polyethylene and polypropylene laminates were more resistant to failure during constant voltage trickle charging, than cells with single layer polyethylene separators. The failure times could generally be accelerated by increasing temperature or voltage of the tests. Preliminary Fourier Transform Infrared (FT-IR) spectroscopic studies suggest that the degradation mechanism may be associated with an oxidation of the polyolefin separators. This is evident from the observation of an additional infrared absorption peak that appears in the carbonyl region of the polyolefin spectra. Degradation studies of separators in L-ion cells that have undergone hundreds of charge-discharge cycles will also be reported. Possible mechanisms for separator oxidation will be discussed.

11:00 AM CC6.9

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An Eulerian [microscopic] model, aimed at incorporating solid-state physics of particulate electrodes coupled with their multiphase hydrodynamics has been developed. Multiphase conservation equations for each phase are derived using the volume averaging technique and are shown to contain interfacial terms which allow for the incorporation of microscopic physical phenomena, such as diffusion and Ohmic drop, as well as interfacial phenomena such as concentration polarization. Convective relations for these interfacial terms are derived and linked to the macroscopic conservation equation and charge transfer. The results include the potential distribution in electrolyte and particulate phase, intensity of electrolyte chemical reaction coefficient and the formation of solution/particle phase conductivity, hydrodynamic parameters and the operating potential.

11:15 AM CC6.10
Titania PEOMS: High Proton Conductivity in Porous Titania Nanodioxide Prepared by the Silicon Gel Route.

Elismer Maron Vidu1, Maris Isabel Tejedor Tejedor2 and Marc Anderson2.1 Institute of Nanotechnology, University of Stuttgart - USP, Sono Paulo, Sono Paulo, Brazil; 2 Environmental Chemistry and Technology Program, University of Wisconsin - Madison, Wisconsin, Wisconsin.

Porous Oxide Electrolyte Materials (PEOMS), obtained as nanometric ceramics via the sol-gel route, are interesting materials, because they have a proton conductivity which is similar to that of Nafion [2], the material used presently in most Proton Exchange Membrane Fuel Cells (PEMFC). Inorganic oxides have the advantage of being less costly, and have the potential to operate at higher temperatures, since they are hydrophilic, in contrast to their polymeric counterparts. In this presentation we describe the preparation and some interesting properties of TiO2 ceramic materials which can be easily slipcast on porous supports to form PEOMS. Monolithic chips of the ceramic material were obtained by the controlled drying of the precursor sol, followed by a heat treatment of the resulting aerogel at 1500°C. Samples of these aerogels were submitted to a further treatment with acidic solutions of different pH values in order to increase the number of surface acidic sites. The protonic conductivity was determined by impedance spectroscopy at temperatures ranging from 10 to 40°C and relative humidities (RH) ranging from 33 to 81%, and from these results, activation energies for proton conduction were obtained. The conductivity of these ceramics increases from 0.0013 S/cm to 0.035 S/cm at 25°C and 81% RH for modification of the surface acidity by a treatment at 150°C. Conversely, the activation energy for proton conduction decreases from 40.4 to 15.8 kJ/mol, respectively, under the same conditions. The modification of the surface acidity with a solution of pH 2.5 yields a material with a conductivity of 0.0088 S/cm at 25°C. Water adsorption isotherms were obtained to determine the water content in these materials, and a pore-filling model was established, in which water clusters rather than monolayers are formed at the surface of the pore walls. The activation energy shows a sharp increase at the onset of the capillary condensation which follows the formation of these water clusters, and starts at approximately 65% RH.

11:30 AM CC6.11
Abstract Withdrawn

11:45 AM CC6.12
Understanding the effect of composition on amorphous alloy Li-ion electrochemical performance, Michael D. Fleischauer, J M Topple1, T D Harchett and J R Dahn1.1Physics, Dalhousie University, Halifax, Nova Scotia, Canada; Physics and Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada.

The electrochemical characteristics of Li-ion alloys could be dramatically increased if the volume changes during charge/discharge cycling could be reduced. The high quality of the collected data will also aid modeling efforts. A thin film of Li-Si-Al-B (Li 2Si3Al3B4) was simultaneously deposited on a variety of substrates using the multi-target sputtering machine described in [2]. Combustion electrochemical measurements were used to determine the charge capacity of the deposited thin film. All electrochemical measurements were performed with a multi-channel potentiostat and the combinatorial electrochemical cell described in [3]. This talk will describe the effect of B content on the electrochemical performance of the amorphous alloys under investigation, present a phenomenological model to explain them and issue a challenge to theorists to fully explain these results from first principles. [1] L. Beaufils et al. Accepted by Journal of The Electrochemical Society (2002). [2] J. Dahn et. al Chemistry of Materials 14, 3519 (2002). [3] M. Fleischauer et. al Submitted to Journal Of The Electrochemical Society (2001).