

SYMPOSIUM CC

CC: Microbattery and Micropower Systems

December 2 - 4, 2003

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* Invited paper

8:30 AM *CC1.1

Micro Fuel Cell Fabrication using Thick Film Printing Techniques. Andrew Swann¹, Jesse S. Wainright¹ and Laurie

Dudik²; ¹Chemical Engineering, Case Western Reserve University, Cleveland, Ohio; ²Electronics 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 catalyst, as well as readily produce 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, inks for thick film printing of several components had to be created, including catalyst 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. Polarization 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 resistive losses within a cell and within the stack, will be considered.

9:00 AM *CC1.2

Formic Acid Fuel Cells for Micro Power Generation.

Rich Masel, Su Ha, Brian Adams, Mark Shannon and Wieckowski Andrzej; Box C-# RAL, University Of Illinois, Urbana, Illinois.

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 occupies 1cm² on a 6cm² silicon die. So far the device has been able to produce 35 mw of power with a total energy content of over 400 w-hr/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 Nanocoils. Sangjin Han¹,

Youngkwang Yun¹, Yung Eun Sung², Kyung-Won Park² and Taeghwan Hyeon¹; ¹School of Chemical Engineering, Seoul National University, Seoul, South Korea; ²Engineering and Research Center for Energy Conversion and Storage, Kwangju Institute of Science & Technology, Kwangju, South Korea.

We report on the synthesis of carbon nanocoils composed of nanometer-thick graphitic fibers by the catalytic graphitization of polymeric carbon precursor. The carbon nanocoils were successfully applied as electrode materials for direct methanol fuel cells. We synthesized carbon nanocoils by simply heat-treating nanocomposites composed of carbon precursor, silica, and transition metal salt, followed by the removal of silica and metal. The XRD pattern of carbon nanocoils 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 nanocoil exhibits well-aligned graphitic layers. It is well known that it is extremely difficult to synthesize carbon materials with both surface area and good crystallinity. Accordingly, in terms of the design and application for a support in fuel cells, the carbon nanocoils, which possesses high surface area, well-defined porosity and an excellent crystallinity, is considered as a very attractive choice. The electrochemical properties of the carbon nanocoils 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 nanocoils and Vulcan-XC72 at 0.4 V are 80 and 21 A/g, respectively. At a higher potential of 0.6 V, CNR-CL7 has six times (240 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 nanocoils

that possess both excellent crystallinity and high surface area.

9:45 AM CC1.4

Micro-Fluidic Development for Portable Scale Direct Methanol Fuel Cells. S.C. Yao, G. Fedder, C. Amon, C. Hsieh, X. Tang, M. Vladimer and Y. Alyousef; Carnegie Mellon Univ., Pittsburgh, Pennsylvania.

Portable scale Direct Methanol Fuel Cell (DMFC) has great potential to come into early applications due to its higher tolerance of power cost. However, obstacle on system integration has to be overcome. A major issue is the development of micro-fluidics, which includes the micro pump for anode liquid re-circulation 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. Meshes 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 250 micron distance, bubbles agglomerate and coalesce. One surface of the chamber contains an array of 30 micron holes etched through the thickness. 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. Therefore, 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. Kenis^{1,2}, Eric Choban^{1,2}, Piotr Waszczuk¹, Markoski Larry² and Andrzej Wieckowski³; ¹Chemical and Biomolecular Engineering, UIUC, Urbana, Illinois; ²Beckman Institute, UIUC, Urbana, Illinois; ³Chemistry, UIUC, Urbana, Illinois.

Current efforts to develop micro fuel cells have mostly focused on polymer electrolyte membrane (PEM)-based designs. However, several technological challenges have prevented wide scale introduction of these fuel cells into commercial applications. Two of these technological challenges are fuel crossover and membrane dry out, where the majority of these systems employ methanol as the fuel. 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 membraneless fuel cell and also makes possible the use of the membraneless 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 microfuel cells. Finally an assessment whether this type of membrane-less fuel cell as a system is expected to be superior over existing PEM-based microfuel cell technology will be presented.

11:00 AM CC1.6

Thin-film Membrane Materials for Use in Microfabricated Direct Methanol Fuel 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 will enable a wider range of usage and functionality for such devices. 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 membranes in direct methanol fuel cells (DMFCs). DMFCs are considered low temperature fuel cells because their typical operating temperatures are 60-120°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 contains catalyst for the air cathode. A number of materials are being investigated for their use as the overcoat/membrane. The material features that are of importance include the proton conductivity, methanol permeability, and dimensional stability. The material must also withstand processing conditions, which includes relatively 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 impedance spectroscopy. The ionic conductivity and methanol permeability measurements for different materials over a range of temperatures and relative humidity will be presented. Acknowledgement: This work is performed under DARPA grant #F33615-01-1-2173. References: 1. Carrette, L. et al. Fuel Cells, 1, no. 1, 5-39 (2001) 2. Wasmus, S. and A. Kuver, Journal of Electro-analytical Chemistry, 461, 14-31 (1999) 3. Arico, A.S. et al. Fuel Cells, 1, no.2, 133-161 (2001) 4. Bhusari, D. et al. Journal of Microelectromechanical Systems, 10, no. 3, 400-408 (2001) 5. Moore, C. and P. Kohl, ECS Proceedings Volume 2002-6: Microfabricated Systems and MEMS VI, 183-189 (2002)

11:15 AM CC1.7

Platinum-Based Nanostructure Electrodes for Small Sized Fuel Cells. Kyung-Won Park and Yung-Eun Sung; Materials Sci. & Eng., Kwangju Institute of Sci. & Tech., Gwangju, South Korea.

Catalytic, physical, (electro)chemical, electronic and optical properties of nanostructure materials are extremely different from those of bulk materials. Because the size and structure of nanoparticles have a significant effect on catalytic reactions, well-controlled nanostructures are essential for achieving efficient catalysts and in the preparation of catalysts for use in fuel cells. In particular, direct methanol fuel cells (DMFCs) have attracted considerable interest because of a variety of merits. The excellent catalytic activity of platinum for methanol oxidation, especially, at low temperatures makes this metal electrocatalyst ideal for use as an anode in DMFCs. However, since pure platinum is readily poisoned by intermediates produced during methanol electrooxidation, at low temperatures, Pt-based alloy or nanocomposite catalysts by alloying or mixing platinum with 2nd elements need to be designed and synthesized. Accordingly, structural and (electro)chemical understandings of Pt-based alloy or nanocomposite structure is essential for methanol electrooxidation study. The Pt-based alloy and nanocomposite structure were prepared by chemical synthesis and thin-film technology. The methanol oxidation in the Pt-based alloy nanoparticles were investigated and compared with alloy thin-film electrodes fabricated by means of thin-film techniques such as e-beam evaporation, rapid thermal annealing, and co-sputtering system.

11:30 AM CC1.8

Miniaturised Proton Exchange Fuel Cell in micromachined Silicon surface. Giuseppe D'Arrigo¹, Corrado Spinella¹, Giuseppe Arena² and Simona Lorenti²; ¹CNR-IMM, Catania, Italy; ²ST-Microelectronics, Catania, Italy.

The fabrication of porous electrocatalytic membranes with a wide surface plays an important role in the electrochemical technology for

energy storage and bio-catalytic processes. One of the most promising systems for energy storage is the fuel cell: the miniaturisation of catalytic membranes and the development of materials with a high H₂ content represent new challenges. The electrocatalytic reactions are generated in proximity of the surface where the catalyst elements are localised. For this reason it is necessary the use of porous material with a wide surface. Porous Si is characterised by a surface as wide as 200 m² for cm³. Aim of this work is to show the feasibility to fabricate a suspended and auto-supporting electrocatalytic sector, by using only surface micromachining processes compatible with the standard Si-based ULSI technology. This sector can be used for the realisation of miniaturised and Si-based proton exchange membrane fuel cell (PEMFC). The structures are formed by two symmetric semicell fabricated on a silicon wafer. A patterned Au structure is used to define the permeable porous sector areas and to collect the energy produced during the cell operation. Miniaturised rhomboidal microchannels localised below the porous sectors, at several microns from the surface, are formed by using an innovative surface micromachining process. The microchannel allows the injection of comburent and fuel from the tank towards the reactor sector. The catalyst element (Pt or Ru) is deposited inside the porous Si skeleton by electro deposition. The proton exchange membrane is deposited on the patterned porous membrane by a spinning process. The compatibility with the ULSI processes allows the integration of the power consumption circuit on the fuel cell.

11:45 AM CC1.9

Functionalized Porous Semiconductors: Active Proton Exchange Membranes for Micro Fuel Cells. Chang Lu¹, Scott Gold², Kuan-Lun Chu² and Richard Masel²; ¹Applied and Engineering Physics, Cornell University, Ithaca, New York; ²Chemical and Biomolecular Engineering, University of Illinois, Urbana, Illinois.

Small proton exchange membrane (PEM) fuel cells are likely to displace batteries in many portable power applications. Presently, many investigators have been trying to incorporate fuel cells into small silicon devices, but so far there has been some difficulty in identifying proton-conducting membranes that bond well to silicon and are compatible with standard semiconductor processing. This paper demonstrates that functionalized nanoporous silicon membranes are promising proton-conducting electrolytes for micro fuel cells. The membranes can be fabricated using standard micromachining techniques. 30~50 micron thick nanoporous silicon membranes, with an average pore size of 10~15 nm exhibit proton conductivities comparable to those of Nafion. The membranes are easy to bond to silicon substrates and thermally stable to at least 160 C. There is no significant expansion and contraction upon exposure to water. A non-optimised prototype micro fuel cell, running on formic acid at 20 C and atmospheric pressure, gave an open circuit voltage of 0.73 V and a current density of 13.3 mA/cm². These novel silicon electrolyte membranes provide unique opportunities for elegant and efficient micro fuel cell designs. The membranes will also be useful in sensors and other devices where proton conductivity is important to device operation.

SESSION CC2: Microbattery and Micropower Systems II

Chairs: Paul Kohl and Jesse Wainright
Tuesday Afternoon, December 2, 2003
Independence East (Sheraton)

1:30 PM *CC2.1

Micro-Power Systems Using Small Reforming Reactors and Fuel Cells. Evan Jones, Jamie Holladay and Dan Palo; Process Science & Engineering, Battelle MS#K6-24, Richland, Washington.

Micro-reforming systems integrated with meso-scale fuel cells combine the high energy density of liquid fuels with the simple, quiet power of fuel cells to create miniature and small power supplies for the next generation of personal electronics, micro-sensors, and the soldier of the future. This paper will discuss the results from testing of two different scales of micro-scale power systems. Battelle, Pacific Northwest Division (Battelle), under a program for the Defense Advanced Research Projects Agency (DARPA) and other military agencies has designed, built, and tested integrated micro-power systems to produce a hydrogen rich stream for fuel cells. All of the reforming reactor systems integrate a catalytic combustor, methanol reformer, vaporizers, and heat exchangers into one device. Miniature systems have been operated over a wide range of power levels and have produced hydrogen sufficient to supply 100 mWt to over 700 mWt of power, based on the LHV, at efficiencies ranging from 8% to over 25%. The total volume of the miniature reactor system is less than 0.25 cm³. The miniature system is thermally independent meaning that no heat source other than the integrated combustor is needed, and it can be started without electric heating. Small power

systems generates over 50 Wt in a reactor device with a total volume of less than 25 cm³, weighing less than 150 gm, and a thermal efficiency of greater than 60%.

2:00 PM *CC2.2

Solid Oxide Fuel Cells for Portable Applications.

Sossina M. Haile¹, Chan Kwak¹, Jeongmin Ahn², Craig Eastwood² and Paul Ronney²; ¹Materials Science, Calif. Inst. of Technology, Pasadena, California; ²Aerospace & Mech Engineering, U of Souther 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, if the power generating device were to operate on, for example, propane 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 of micro-SOFCs 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 micropower generator 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 propane to generate CO and H₂, and electrochemical oxidation to generate CO₂ and H₂O, but is inactive towards electrochemical reduction of oxygen. The cathode, here a mixture of SmSr_{0.5}Co_{0.5}O₃ and samaria-doped ceria, is, ideally, active towards electrochemical reduction of oxygen but inactive towards propane oxidation. For optimized gas compositions and flow conditions, power densities of 100 - 120 mW/cm² 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 rates.

2:30 PM CC2.3

Design Considerations for Microscale Solid-Oxide Fuel Cells.

K. T. Turner¹, V. T. Srikar², A. Ie² and S. M. Spearing²;

¹Mechanical 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 have high power densities compared to other fuel cell technologies. However, significant engineering challenges, including maintaining structural stability and managing heat losses, have prevented reliable, efficient, small-scale solid oxide fuel cells from being realized. The current work describes the development of a set of first-order, scale dependent, models that can be used to examine the competing requirements in fuel cell design. Analytical models which describe the electrochemical performance, structural stability, and thermal losses for small-scale planar SOFCs have been developed. The results of the structural modeling are summarized in design diagrams, which include the effect of intrinsic residual stress and thermal stress on membrane failure via buckling or fracture. The diagrams show the tradeoff between material properties, fuel cell geometry, and operation temperature. Thermal losses due to conduction through the structure have been analyzed and the results clearly demonstrate that unique thermal isolation schemes will be required for efficient microscale SOFCs. Finally, coupled design charts that incorporate multiple considerations such as structural stability and thermal losses, have been developed to highlight the non-intuitive scaling that sometimes occurs. These models, along with results and their implications for selection of materials and geometry for microscale fuel cells, are discussed in detail.

2:45 PM CC2.4

Microstructured Thin Film Noble Metal Cathodes for Micro-Solid Oxide Fuel Cells. Joshua Hertz, Anja Bieberle 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 size scales (sub-micron thick films), ohmic electrolyte losses are expected to be very low, even at reduced temperatures (<600°C). Electrode materials and structures not normally utilized in 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 how electrodes of this size scale affect device performance. 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 independently variable separation distances and triple phase boundary lengths, were used. Impedance spectroscopy was carried out on these samples in controlled temperatures and oxygen partial pressures. Correlating the 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 DAAD19-01-1-0566.

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 micron thick. Deposition techniques available to the semiconductor processing industry such as sputtering, pulsed laser deposition and e-beam 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 the start-up time 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 oxide 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 micron 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 techniques have focused on hydroxide gel suspensions and sol-gels that can be used to bind 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/Al₂O₃ Thin Film Catalysts for Preferential Oxidation of CO in a Microkinetic Array.

Xun Ouyang, Lucie Bednarova, Haibiao Chen, Woocheol Shin and Ronald S Besser; Chemical, Biochemical and Materials Engineering, Stevens Institute of Technology, Hoboken, New Jersey.

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. Pt/Al₂O₃ thin-film catalyst was deposited on the inner walls of Si microchannel reactors with sol-gel processing procedures. Physical characterization of the catalyst 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 turnaround and less human intervention. A number of catalyst samples with different preparation or identical catalyst samples with different pretreatment procedures and/or 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, CHEMKINTM, which provides flexible and powerful tools for incorporating complex chemical kinetics

into simulations of reacting flow. Initial simulation results yielded temperature dependencies of conversion and selectivity which agreed well with our experiments. In addition, a mechanism for observed deactivation of the Pt/Al₂O₃ thin-film catalyst was inferred from the simulation results. The film under study was shown to be an effective catalyst for PrOx in portable systems as <1 mg of catalyst was found sufficient to treat a reformat flow corresponding to 0.5 W of electrical energy.

4:00 PM **CC2.7**

Sequential and Simultaneous Electrodeposition of Pt-Ru Electrocatalysts on HOPG Substrate: A surface morphology and electrocatalytic study. Carlos R. Cabrera, Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico.

Sequential and simultaneous lineal 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 10mM. Sequential voltammetric results allowed the determination of Pt and Ru loading and a complete catalytic evaluation, which is difficult to determine via simultaneous deposition. Morphological characterizations through scanning electron microscopy (SEM) and atomic force microscopy (AFM) have shown that the deposits are composed by aggregates particles of different shape and size forming clusters. Scanning tunneling Microscopy (STM) demonstrate that the tops of these clusters are nanoclusters from 5 to 10 nm. The distribution of these clusters on the HOPG surfaces is heterogeneous and disperses. 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 amounts decrease 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 solid acids by first principles calculations. X. Ke¹ and Isao Tanaka²; ¹Fukui Institute for fundamental Chemistry, Kyoto University, Kyoto, Japan; ²Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan.

At the normal pressure, CsHSO₄ (CHS) has three phases. Below the temperature 340 K, CHS is in phase III 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 the phase I shows an extremely high proton conductivity [1] and has been demonstrated a promising application in fuel cell [2]. Theoretically, atomistic mechanism of proton conductivity in these phases are still not clear. For example, it is still left open why phase II shows quite lower conductivity than that of phase I. In our study, we have performed first-principle calculations to investigate proton conductivity in these phases (in particular, phase I and II). The diffusion paths 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 kinds 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. [1] A.I. Baranov, L.A. Shuvalov and N.M. Shchagina, JETP Lett. 36(1982) 459 [2]S.M. Haile, D.A. Boysen, C.R.I. Chisholm and R.B. Merle, "Solid Acid as Fuel Cell Electrolytes," Nature 410 (2001) 910-913.

4:30 PM **CC2.9**

Anhydrous Proton Conducting Polymer Electrolytes Based on Biological Nanostructured Materials. Itaru Honma and Masanori Yamada; EEL, 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 PEFC operation above 100C. It has been widely recognized that intermediate temperature operation of PEFC has been recently pointed out to overcome most of the technological problems such as CO poisoning onto the Pt electrode surfaces, a large activation overpotential and complicated water management. In this presentation, new class of water-free proton conducting membranes have been synthesized by the hybridization of acidic polymer containing the phosphate groups and organic base of heterocycles at nanophase scale. The acid/base 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 7x10⁻³ S cm⁻¹ at 150C under water-free (non-humidified) condition. The membrane fast ionic transport without water has been possibly ascribed to rapid proton transfer between the protonated basic molecules. Non-hydrous proton conducting membranes may have technological potential not only for the polymer electrolyte membrane fuel cells (PEFC or DMFC) but also electrochemical devices including electrochromic displays, chemical sensors, separation and others.

4:45 PM **CC2.10**

Effect of monomeric sequence of Nafion on its nanostructure and transport properties. Tahir Cagin, Seong Soon Jang, Vale Molinero and William A Goddard; Caltech, Pasadena, California.

Nafion is a hydrophobic polyelectrolyte consisting of nonpolar N=(CF₂-CF₂) and polar-ionizable P=(O-CF₂-CF(CF₃))₂-CF₂-CF₂-SO₃H) segment. Hydrated Nafion 117 with an average of 6.5 hydrophobic 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 nanosegregated structure consisting of hydrophobic and hydrophilic domains. Notwithstanding, the details of the segregated morphology 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%wt water by molecular dynamics simulations. Although the systems show clear hydrophilic/hydrophobic segregation in all the studied conditions, we observe that the more blocky sequence has better phase segregation and their anionic moieties are unevenly distributed in the interface leaving big hydrophobic patches of polymer/water contact. The vehicular diffusion of water and hydronium was not affected by the blockiness of the polymer.

SESSION CC3: Microbattery and Micropower Systems III

Chairs: B.V.R. Chowdari and Paul Kohl
Wednesday Morning, December 3, 2003
Independence East (Sheraton)

8:30 AM ***CC3.1**

Thin Film Solid State Batteries: Commercialization Status Report. John B. Bates, Oak Ridge Micro-Energy, Oak Ridge, Tennessee.

Several U.S. companies are striving to commercialize thin film solid state batteries under a license with UT-Battelle, LLC. The license grants the use of a portfolio of patents originating from a decade of research at the Oak Ridge National Laboratory. The batteries are fabricated by standard physical vapor deposition techniques of sputtering (current collectors, cathode, electrolyte, inorganic anodes) and evaporation (metallic lithium anode). In addition to requirements of composition and structure of the active thin film materials, minimizing the production of micron and sub-micron particles in the plasma that occurs under some circumstances during sputtering of LiCoO₂ and Li₃PO₄ targets is one of the keys to achieving good yield and high performance. Packaging is another important consideration. Because of the small mass of active materials, stringent requirements are demanded of a protective coating in order to prevent significant deterioration of the battery over 10 to 20 years of exposure to air. There are several broadly based and numerous niche markets for this technology, but large scale volume production of lithium or lithium-ion thin film batteries in the U.S. has not yet been achieved as of June 2003.

9:00 AM ***CC3.2**

Development of a Microbattery-Based Hybrid Micropower Supply. John N. Harb¹, Larry L Howell² and Craig S Petrie³; ¹Chemical Engineering, Brigham Young University, Provo, Utah; ²Mechanical Engineering, Brigham Young University, Provo, Utah; ³Electrical and Computer Engineering, Brigham Young University, Provo, Utah.

This presentation describes our efforts to develop a self-sustained hybrid micropower supply that utilizes both microbatteries and energy harvesting. Such a power supply is ideally suited for autonomous microsystems, and can be customized in order to minimize size, optimize performance and provide reserve power for times when energy harvesting is not possible. Consequently, a hybrid

power supply provides the capability and flexibility needed to address the power needs of a variety of autonomous microsystems. Microbatteries represent a critical element of the hybrid power supply. 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. Power densities of 140 mW/cm² have been observed; these power levels are sufficient to meet the projected needs of many autonomous microsystems, including remote microsensors. In addition to the development of a suitable microbattery, several other challenges must be met before a hybrid power supply can be demonstrated. A strategy for use of microbatteries and an energy conversion device (e.g. solar cell) in tandem to meet power requirements is needed. Methods for fabricating and integrating system components must be developed. There is also a need for suitable switches. This presentation will describe our efforts to address these challenges.

9:30 AM CC3.3

Miniature hybrid battery-photovoltaic power systems.

Aimee E. Curtright, Ryan C. Wartena, Arnold M. Stux and Karen E. Swider-Lyons; Code 6171, Naval Research Lab, Washington, District of Columbia.

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 micropower system composed of microsolar cells and microbatteries to provide energy harvesting, energy storage, and high power capabilities to microelectronic devices. This paper will highlight recent progress toward this broad objective, especially issues of packaging and interconnect materials and strategies. For the demonstration of micro-photovoltaic components, we have chosen dye-sensitized photoelectrochemical cells. These solar cells have a number of advantages over silicon-based devices. Because they are made without the stringent processing requirements of semiconductor materials, dye-sensitized photovoltaics 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-deleteriously 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 one area to explore. We have looked at several film packaging options for lithium-ion batteries. Also, metals and glasses are potential candidates for packaging micropower 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. Steven E. Bullock² and Peter Kofinas^{1,2}; ¹Chemical Engineering, University of Maryland, College Park, Maryland; ²Materials Science and Engineering, University of Maryland, College Park, Maryland.

Solid polymer electrolytes have provided a promising route to an all-solid-state polymer battery. Current battery configurations typically involve a metal anode, a solvent-plasticized polyelectrolyte, 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 nanoclusters containing inorganic moieties. The polymeric all-solid state battery consists of a lamellar microphase separated A/B block copolymer, which is derived using Grubbs's catalyst for ring-opening metathesis polymerization (ROMP). The "A" block solid electrolyte is a ROMP derivative of PEO and the "B" block cathode is a spinel phase lithium permanganate. The diblock can act as a composite polyelectrolyte or a composite cathode against lithium metal. ¹H and ¹³C NMR and FTIR was employed to determine the composition and structure of all monomers and polymers. Gel Permeation Chromatograms indicate a diblock polymer with a molecular weight of 123,000. The metal oxide nanoclusters were characterized by XPS and Wide Angle X-ray diffraction. Transmission electron microscopy was used to visualize the lamellar microstructure in the diblock copolymer. A current density of 64mAh/g was measured with cyclic voltammetry and charge/discharge curves were obtained.

10:30 AM CC3.5

Rapid Transport Paths for Li Diffusion in Nanostructured 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 vanadia cathode in a solid state oxide thin film battery. Previous simulations have shown that Li transport into the cathode crystal is effected by the orientation of this layered crystal at the interface, with the largest activation barriers to diffusion in the <001> direction. Experiments show that this slowest diffusion direction is perpendicular to the interface, thus inhibiting diffusion. Molecular dynamics simulations show possible rapid diffusion paths in nanocrystalline vanadia that would offset the natural orientation of these crystals at the cathode/electrolyte interface. However, the width of these diffusion paths affect Li diffusion and an optimum width will be discussed based on the simulation results.

10:45 AM CC3.6

ϵ -VOPO₄: An Enhanced Intercalation Material for Lithium Micro-Batteries. Yanning Song, Peter Y. Zavalij and Stanley M. Whittingham; Chemistry Department, SUNY-Binghamton, Binghamton, New York.

ϵ -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 P2₁/n. It consists of chains of corner-sharing VO₆ octahedra separated by PO₄ groups. The ϵ -VOPO₄ formed from the vanadium-rich tetragonal hydroxide precursor has much better electrochemical behavior than that synthesized according to the literature from monoclinic VPO₄·H₂O. The capacity exceeds 130 mAh/g at low cycling rates and even at a current density of 2 mA/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 ϵ -VOPO₄ phase and the lithiated products will be described. This close-relationship makes these materials particularly attractive for thin-film and other micro-batteries. This work was supported through the BATT program of DOE through LBNL.

11:00 AM CC3.7

Nano-Structured Lithium Manganate Thin Film Cathodes For Rechargeable Micro-Batteries. N. Santander, M. Bonner, S. B. Majumder 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 nano-structured LiMn₂O₄ (LMO) cathode thin films for lithium ion rechargeable micro-batteries. LMO cathode has a serious capacity-fading problem, especially above the room temperature operation. The origin of capacity fading has so far been poorly understood, however, the probable reasons for fading could be dissolution of manganese spinel into the electrolyte, decomposition of electrolyte on the surface of the cathode, Jahn-Teller distortions etc. From the studies of bulk LMO ceramics, it is known that the particle size and the surface morphology have immense influence on the charge-discharge rate capabilities of the batteries. 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 platinumized 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 discharge capacity was observed in films annealed at ~ 700°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 LiNi_yMn_yCo_{1-2y}O₂ (y=0.4) For Lithium Batteries. Miaomiao Ma, Katana Ngala, Peter Zavalij and M. Stanley Whittingham; Chemistry, Binghamton University, Binghamton, New York.

Layered LiNi_yMn_yCo_{1-2y}O₂ (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 4.3 volts at rates as high as 2 mA/cm² and shows good cyclability. Electrochemical characterization showed that the electronic conductivity of the cobalt doped layered compound is one order higher than that without cobalt. In addition, cobalt addition suppresses the migration of nickel ions into the lithium layers, enhancing the layer-like behavior of the compound. Carbon-coating was performed on LiNi_yMn_yCo_{1-2y}O₂ (y=0.4) by using gelatin as the bonding material. Comparison will be made between the carbon-coated and the bare compound. This work is supported by the BATT project of DOE through LBNL.

11:30 AM CC3.9

The structure around oxygen and metal atoms in Li(Co,Ni)O₂ microbatteries: A soft X-ray study.

Faisal M Alamgir^{1,2}, Mahalingum Balasubramanian¹, Jay Whitacre³, Marten denBoer², Chi-Chang Kao¹, James McBreen¹ and Steven Greenbaum²; 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 microelectronic 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 Li(Co,Ni)O₂-based battery. A proposed mechanism for the redistribution of upon the de-intercalation of Li⁺ ions is the corresponding change in the oxidation state of the transition metal. X-ray absorption spectroscopy (XAS) studies at the metal edges appear to bear this out. Alternatively, it is proposed that the oxidation state of the O atoms change. This has the backing of some ab-initio calculations and electron energy-loss spectroscopy (EELS), although the EELS studies require a disassembly of a functional cell and exposing it to high vacuum conditions and a fast electron beam. We have designed a spectro-electrochemical 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 L_{III,II}-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 and the oxygen atoms in fully assembled and functional thin-film batteries.

11:45 AM CC3.10

Modified Cathode Materials for Li Ion Based Rechargeable Batteries. S. R. Das, S. B. Majumder and R. S. Katiyar; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

In the present work, we report the process optimization to synthesize spinel type lithium manganate (LiMn₂O₄) and the layered structured lithium cobalt oxide (LiCoO₂) ceramic particles to prepare composite cathodes for Li-ion rechargeable batteries. Two approaches were pursued to improve the capacity and cycleability of these materials. In the first approach, a part of the Mn or Co ions were substituted by electrochemically inert cations (eg. Al³⁺, Cu²⁺, etc.) to impart stability of the oxidation states of Mn/Co ions, as well as O₂ ions in the respective lattices. In the second approach, the individual cathode particles were located with the inert oxide particles (e.g. ZrO₂, TiO₂, Cr₂O₃) 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. Chowdari and Jesse Wainright
Wednesday Afternoon, December 3, 2003
Independence East (Sheraton)

1:30 PM *CC4.1

New Strategies for Li-Ion Batteries and Electrochemical Capacitors as Autonomous Micropower Sources.

Karen Swider Lyons, Ryan C. Wartena, Aimee E. Curtright and Arnold M. Stux; 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 specific energy, and have a means to refuel from the ambient. We are investigating two rechargeable micropower sources: Li-ion microbatteries and asymmetric ultracapacitors. First-generation Li-ion microbatteries have been prepared from conventional battery materials, including LiCoO₂, carbon, Celgard and an ethylene-carbonate-based LiPF₆ electrolyte. These microbatteries have excellent cycleability and can be operated in ambient conditions when packaged 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 with solar cells directly into a microelectronic device. 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 *fuelcellmode* for continuous energy (for sensing) and to 1 mA/cm² in *capacitormode* 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-Lisicon - Its Property And Application To All Solid-State Battery. Ryoji Kanno¹, Masahiro Murayama¹, Kazuyuki Sakamoto¹, Taro Inada¹, Noriyuki Sonoyama¹, 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, Hirakata, Osaka, Japan.

Thio-LISICON (Lithium SuperIonic CONductor) is one of the best lithium ion conductive solids ever found in inorganic materials. The room-temperature conductivity exceeds 10⁻³ S/cm-1 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 all solid-state batteries; the material would be installed in place of flammable liquid electrolytes in conventional lithium-ion rechargeable batteries. Based on the relationships between the structures and ionic conduction of the thio-LISICON family, Li_{4-x}M_{1-y}M'_yS₄ with M = Si, Ge, and M' = P, Al, Zn, Ga, Sb, we discuss the conduction mechanism and its material-design concept. We applied the thio-LISICON as solid electrolytes; all solid-state cells using the most conductive composition, Li_{3.25}Ge_{0.25}P_{0.75}S₄, with the Chevrel phase cathode and Li anode showed excellent cycling characteristics. The cell-design concept of all solid-state batteries with the thio-LISICON electrolyte will be discussed.

2:30 PM *CC4.3

Microscale Solid State Lithium Batteries. William C. West, Jay F. Whitacre and Ratnakumar V. Bugga; 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 films, using shadow-masking techniques to define the cell 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 accommodate the highly moisture 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 100C, 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 Fuel Cells. Chi-fu Wu, Seungwon Shin, Xiaowan Chen and Peter J. Hesketh; George W. Woodruff School 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. Microchannels fabricated by stereolithography are embedded with electrodes to simulate bubble generation by electrolysis. Specific bubble size is 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 Arnold¹, Heungsoo Kim², Thomas E Sutto³ and Alberto

Pique²; 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 mesoscale micropower system. We have successfully fabricated alkaline and lithium based microbatteries, micro-ultracapacitors, and dye-sensitized micro-solar cells on various low processing temperature and flexible substrates using laser direct-write as well as direct-write dispensing. The laser direct-write process has enabled the deposition of layers 10-50 μm thick while maintaining patterns as small as 5 mm^2 footprint. Our primary alkaline microbatteries exhibit open circuit potentials of 1.5 V with high capacities and discharge currents up to 1 mA. Preliminary secondary LiCoO_2 and LiMn_2O_4 microbatteries exhibit open circuit potentials of 3.95 V and have shown multiple recharging cycles without loss of capacity. In this presentation, we will emphasize our recent results on these microbattery systems with particular focus on device fabrication and packaging for improved shelf-life performance.

4:00 PM CC4.6

Design and Selection of Thin Film Piezoelectric Materials for Micro-Power Generation. J. V. Martinez, L. M.R. Eakins, J. Cho, C. D. Richards, R. F. Richards and D. F. Bahr; Mechanical and Materials Engineering, Washington State University, Pullman, Washington.

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. For a piezoelectric-membrane power generator 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 tensile stress in the thin film will increase the mechanical compliance and strain to failure, which will increase the total strain possible for a give 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 Nb-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 an acetic acid-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 assess the effectiveness of Nb-doped PZT for improving micro-power generation.

4:15 PM CC4.7

A Study of Lithium Ion Transport in Ultra-Thin SiO_2 for On-Chip Battery Applications. Nava Ariel, Gerbrand Ceder, Donald R. Sadoway and Eugene A. Fitzgerald; Materials Science and Engineering, M.I.T, Cambridge, Massachusetts.

Integrated circuit evolution creates increased functionality and performance with lower cost and higher reliability. Advances in the integration of new materials with Si CMOS have opened a path 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 consider materials and processes already available in 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 SiO_2 , 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. Ironically, ion transport through SiO_2 was an early obstacle for MOS devices in the electronics industry, but in a battery fast transport of alkali ions through SiO_2 is an attribute that enables the construction of ultra-thin, uniform solid-state electrolytes for fully integrated nanobatteries. Various $\text{LiCoO}_2/\text{SiO}_2/n+\text{Poly-Si}$ structures were fabricated on Si wafers in a clean room facility, using existing CMOS processing technology. The thickness of the Si oxide varied between 5-50nm and the total thickness of the $\text{LiCoO}_2/\text{SiO}_2/n+\text{Poly-Si}$ stack was less than 600nm. The microstructures of the stacks were characterized using

Transmission Electron Microscopy (TEM). Current-Voltage (I-V) 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 $\text{LiCoO}_2/\text{SiO}_2/n+\text{Poly-Si}$ 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 SiO_2 with applied bias, and thus introduce SiO_2 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. Seiichi Suenaga, Takayuki Fukasawa, Tomohiro Suetsuna, Koichi Harada and Yasuhiro 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, Mg) O sintering body prepared for the catalyst precursor by reaction sintering was partially reduced so as to segregate the Ni-Cu nanoparticles over the surface of the sintering body. Ni-Cu particle diameters ranged 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 V

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

Exhibition Hall D (Hynes)

CC5.1

Abstract Withdrawn

CC5.2

Alloy Nanocomposite Electrode Structure for Thin-Film Fuel Cells. Kyung-Won Park, Jong-Ho Choi and Yung-Eun Sung; Materials Sci. & Eng., Kwangju Institute of Sci. & Tech., Gwangju, South Korea.

Thin-film fuel cells (TFFCs) are of interest as power sources ranging from small digital devices to micro-electromechanical systems because of availability of on-chip or 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 or PtRu, along with a porous material as a support for the metals. In addition, the Pt-based an alloy nanostructure, especially, those formed by alloying Pt and Ru, is required for highly efficient fuel cells, in terms of adjusting proper composition of Pt and Ru in the electrodes. Accordingly, for an excellent performance, electrodes in TFFCs should contain PtRu alloy nanophases in the porous material. Typically, however, sputtering methods are used for preparing thin-film electrodes and, as a result, materials prepared by the PtRu 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 multigun sputtering system consisting of Pt and Ru targets for alloy formation and a WO_3 target for support of the nanophases. We designed an alloy nanostructured electrode (PtRu- WO_3) for use in high efficient TFFCs using multigun sputtering system and compared its performance with PtRu 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 nanophases 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. Joong-Kee Lee¹, Wonchang Choi¹, Myungro Lee², Dongjin Byun² and Byung Won Cho¹; ¹Eco-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/alloys has been studied extensively due to their higher specific capacities. However, Li alloys as negative electrode leads the rapid disintegration 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 with Li alloy. In the present study, the effects of nano-coating of synthetic graphite surface with various metals and silicon as 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 passivation films as conducting agent in the electrode. Commercial synthetic graphite with average particle diameter of about 10 μ m (MCMB1028, Osaka Gas) was used as raw material. Coating solutions were prepared by mixing of metal salts and methanol. In case of silicon precursor, non-polar solutions such as hexane and benzene were used as a dispersive agent. Spray coating was carried out by gas suspension method: fluidized graphite powder were coated and dried simultaneously inside the column, and then calcined in the furnace under inert atmosphere. Electrostatic sprayer was employed to increase the dispersion of coating solution. Working DC voltage range was from 5000 to 1000V. 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. Acknowledgement Research was supported by Center for Nanostructured Materials.

CC5.4

Novel Carbon Nanotube Electrodes for High Energy Lithium Batteries. R. Scott Morris¹, Brian G. Dixon¹, Ryne P. Raffaele² and Thomas Gennett², ¹Phoenix Innovation Inc., West Wareham, Massachusetts; ²NanoPower Research Laboratory, Rochester Institute of Technology, Rochester, New York.

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 derivatized carbon nanotube materials either a 3 or 4.2 volt rechargeable battery with sustained specific energies of > 400Wh/kg and a peak pulse power capability of > 4kW/kg @ 100Wh/kg was developed. Initial testing was performed with a standard two electrode polypropylene test cell fitted with two stainless steel piston-type electrodes (~1cm² area). Using this device, and a standard nonwoven glass separator, test electrodes were tested at a constant pressure. The electrolyte for these tests was 1M lithium trifluoromethanesulfonimide (LiIm, 3M Co.) in a 50:50 mixture of ethylene carbonate:ethylmethylcarbonate. All measurements were conducted in an Argon-filled dry box. The electrochemical measurements were obtained using a Radiometer model PGZ 301 Voltalab electrochemical test instrument. Coin cells of the most promising materials were fabricated using a Hohsen coin cell press and were tested with an Arbin BT-2000 battery analysis system. The complete characterization of the derivatized 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. Fumiaki Mitsugi¹, Seiji Kanazawa², Toshikazu Ohkubo²,

Yukiharu Nomoto², Ishihara Tatsumi³ and Yusaku Takita³, 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 La_{0.8}Sm_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{2.8} (LSGMCO) is useable as an electrolyte of solid oxide fuel cell (SOFC) because it has higher oxygen ion conductivity than that of conventional solid oxygen ion conductor such as YSZ. We prepared the LSGMCO films on porous NiO+Ce_{0.8}Sm_{0.2}O_{1.9} substrates, which is used as an anode electrode of the SOFC, by KrF excimer pulsed laser deposition technique with the laser energy of 300 mJ and repetition rate of 20Hz. The LSGMCO film deposited on the porous substrate at 800°C and oxygen pressure of 20 Pa was polycrystallized with the same stoichiometry as the bulk target. In the case of the deposition temperature less than 700°C the films were amorphous. The electric conductivity of the LSGMCO film measured by 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 at 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 tube-type solid oxide fuel cell with diameter of 20 mm composed by this LSGMCO electrolyte film.

CC5.6

Fabrication Of Composite Of Amorphous Titania And Carbon And Its Electrode Performance For Rapid Discharge.

Hiroyasu Furukawa, Mitsuhiro Hibino and Itaru Honma; 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 effective strategies is shortening of diffusion length of lithium in active materials or increase in the surface area of electrode materials. 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 sol-gel route employing Ti(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 390 m² g⁻¹. The composite materials could be galvanostatically discharged and charged around 2 V vs. Li/Li⁺. The TiO₂/AB composite heat-treated at 150 °C exhibited 260 mA h g⁻¹ of specific capacity under 1 A g⁻¹ of current density in the initial discharge. However, the specific capacity goes down fast during initial 10 cycles. This capacity loss could be decreased with increasing in the thermal treatment temperature. The TiO₂/AB composite treated at 330 °C showed the specific capacity above 125 mA h g⁻¹ even under large discharge current of 10 A g⁻¹ after 10th cycle. Based on the relationship between the specific capacity and the current density, the chemical diffusion coefficient for lithium ion was estimated to be 6 × 10⁻¹² cm² s⁻¹, when the diameter of the observed secondary particles (400 nm) was used as a diameter on the calculation.

CC5.7

Preparation And Properties Of Fine Particulate Li(Mn_{1-x-y}Ni_xCo_y)O₂ For Lithium Ion Battery.

Yuko Nakahara¹, Kenji Hamada¹, Sanshiro Nagare¹, Yuichi Abe² and Mamoru Senna²; ¹Nara Machinery Co., Ltd., Tokyo, Japan; ²Faculty of Science and Technology, Keio University, Yokohama, Japan.

By virtue of soft mechanochemical effects, we prepared fine-grained, phase pure LiMnO₂ with and without partial substitution of Mn by Ni and/or Co. In order to acquire better mechanochemical effects, we compared various oxides and hydroxides as starting materials. A stoichiometric mixture was mechanically activated prior to calcination under relatively mild condition in a specially developed multi-ring type mill in N₂ for various periods. As we calcined the co-milled mixture without Ni or Co in N₂-4%H₂ mixture, we obtained phase pure orthorhombic (o)-LiMnO₂ at temperatures 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 Co, crystallographical properties shifted toward those 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. Hee-Soo Moon, Jae-Ho Lee, Ki Lyung Lee, Jae-Pil Lee, Myoung Gyun Ko 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 microbatteries, with rapid development of portable electronic equipments and MEMS(Micro electromechanical 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 all-solid-state microbatteries, battery failure would be caused by electrode/electrolyte interface reaction, internal stress, degradation of electrode and electrolyte materials during charging/discharging process and so on. In this research we focus on interface reaction problem such as increasing internal resistance that would affect the cyclability and lifetime of microbattery. 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 the properties 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 2-inch-diameter of stoichiometric $LiMn_2O_4$ target. Pt deposited Si (100) wafer used as substrate. To make spinel phase, the deposited film was annealed at $750^\circ C$ in 2h. The film thickness was about 200 nm. To coat SnO_x on the spinel film, stoichiometric SnO_2 target was used as sputtering target. The SnO_x film thickness on the spinel film was less than 100 nm. Surface 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 1 M solution of $LiPF_6$ in EC-DMC(1:1) as electrolyte. The spinel film was totally covered with SnO_x . The particle size of the SnO_x was less than 10 nm. In the cyclic voltammetry test, the redox peak sharpness of the SnO_x -coated film was higher than that of uncoated film. The cycle retention and the reversible capacity of the SnO_x -coated film were better than those of the undoped film. These results mean that SnO_x 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 Polyelectrolyte Multilayer

Solid State Electrolytes. Jodie L Lutkenhaus, Dean M Delongchamp and Paula T Hammond; Chemical Engineering, MIT, Cambridge, Massachusetts.

We have recently demonstrated that the intelligent design of polyelectrolyte layer-by-layer (LBL) assembled films can result in thin films with ionic conductivity appropriate for consideration as solid or gel electrolyte layers in lithium polymer 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 water, 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) polyelectrolytes. 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 amidation 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 directed 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.

Ying Song¹, Lenard Bonville², H. Russell Kunz², James M Fenton¹, Michael Trahiotis¹, Yu Wei¹ and Jane Li¹; ¹University of Connecticut, Storrs, Connecticut; ²Ionomem 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 (>100°C) 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 increases 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 ionic 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°C 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 of 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

Nafion[®] fabricated in the tetrabutyl 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 Bagotzky and I A Blinov; 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 soft, frail and materials amalgamated 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 are in the state of capillary equilibrium then the capillary 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 content 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 Porosimeter (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 functions of the pore radius within range from ~ 1 nm to 3×10^5 nm; -Average pore radius; -Specific pore volume (porosity); -Specific surface area (in the range from 10^{-3} to 10^3 m²/cm³); -Distribution of pore surface as a function of the pore radius; -Liquid distribution as a function of the values of the free binding energy between sample and liquid (in the range from 10^{-3} to 10^4 J/mole); -Liquid distribution as a function of the values of the capillary pressure; -Differential characteristics of swelling; -Different structural properties of multi-component hydrophilic-hydrophobic bodies; -Adsorption isotherms; -Wetting angle and its dependence on pore radius. **References** 1. Yu. M. Volkovich, V. S. Bagotzky, J. Power Sources, **48** (1994) 327, 348. 2. Yu. M. Volkovich, V.S. Bagotzky, V.E. Sosenkin, I.A. Blinov, In: Colloids and Surfaces A: Physicochemical and Engineering Aspects, **187 – 188** (2001) 349. 3. J. Divisek, M. Eikerling, V. M. Mazin, H. Schmitz, U. Stimming, Yu. M. Volkovich, J. Electrochem. Soc., **145** (1998) 2677. 4. Yu. M. Volkovich, V. S. Bagotzky, T. K. Zolotova and E. Yu. Pisarevskaya, Electrochimica Acta, **41** (1996) 1905.

SESSION CC6: Microbattery and Micropower Systems

VI

Chairs: Paul Kohl and Jesse Wainright
Thursday Morning, December 4, 2003
Independence East (Sheraton)

8:30 AM CC6.1

Electrochemical performance of the a-Si_{1-x}Sn_x binary

system. Timothy D Hatchard¹, Mike D Fleischauer¹ and Jeff R Dahn^{1,2}; ¹Physics, 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 (9800 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 studied to date experience 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 behaviour for both a-Si [7] and a-Si_{0.64}Sn_{0.36} [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 64-channel combinatorial electrochemical cell plates, and copper foil. A combinatorial electrochemical cell with 64 individual channels was used to test the electrochemical properties of this system. As the cell is laid out in 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

materials with $x \neq 0$. [1] M. Winter, J.O. Besenhard, M.E. Spahr and P. Novak, *Adv. Mater.*, 10 (10): 725-763 JUL 9 1998. [2] Good review articles: M. Winter and J.O. Besenhard, *Electrochimica Acta*, 45, 31-50, 1999. R.A. Huggins in: J.O. Besenhard (Ed.) *Handbook of Battery Materials*, Wiley-VCH, Weinheim, 1999, Part III, ch. 5. [3] M. Wachtler, M. Winter and J.O. Besenhard, *J Power Sources*, 105(2), 151-160, 2002. [4] M.M. Thackeray, J.T. Vaughey, C.S. Johnson, A.J. Kropf, R. Benedek, L.M.L. Fransson and K. Edstrom, *J. Power Sources*, 113(1), 124-130, 2003. [5] I. Rom, M. Wachtler, I. Papst, M. Schied, J.O. Besenhard, F. Hofer, M. Winter, *Solid State Ionics*, 143(3-4), 329-336, 2001. [6] L.Y. Beaulieu, T.D. Hatchard, A. Bonakdarpour, M.D. Fleischauer and J.R. Dahn, submitted to *J. Electrochem. Soc.* [7] S. Ohara, J. Suzuki, K. Sekine and T. Takamura, *J. Power Sources*, in press. [8] J.R. Dahn, S. Trussler, T.D. Hatchard, A. Bonakdarpour, J.R. Mueller-Neuhaus, K.C. Hewitt and M. Fleischauer, *Chemistry of Materials*, 14 (8), 3519 -3527, 2002.

8:45 AM CC6.2

Deposition and Properties of Lithium Phosphorus Oxynitride (LiPON) Films. Nancy J Dudney and Young-Il Jang; 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 electrolyte material in a variety of 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_3PO_4 ceramic source with a nitrogen plasma, though now films are deposited at far higher rates. Typical films are amorphous with a composition near $\text{Li}_3\text{PO}_{3.3}\text{N}_{0.46}$. New impedance and spectroscopic results will be presented including results of expanded deposition conditions, increased Li and N concentrations, and the effects of thermal annealing and surface reactions. Subtle variations in the composition may occur when LiPON is deposited over a substrate that reacts with lithium, or over a thin film of either a 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 no. DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

9:00 AM CC6.3

IBAD LiPON: A Solid Electrolyte with High Electrochemical Stability. Fernando Vereda, Ronald B Goldner, Terry E Haas, Jeremy Leung and Peter Zerigian; 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 ($> 6 \text{ V}$) [1]. These films were prepared by a nitrogen ion beam assisted deposition (IBAD) of thermally evaporated Li_3PO_4 . Recent evidence indicates that the electrochemical stability is higher than 8 V, which significantly exceeds the 5.5 V 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 sputter-deposited LiPON. 1 F. Vereda et al., *Electrochem. Solid-State Lett.*, 5 (11), A239 (2002). 2 X. Yu et al., *J. Electrochem. Soc.* 144, 524 (1995).

9:15 AM CC6.4

Vibrational Characterization of LiPON Glasses by Ab Initio Calculations on Model Compounds. Terry E. Haas^{1,2}, Fernando Vereda² and Ronald B. Goldner²; ¹Dept. 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 strongly oxidizing cathodes such as LiCoO_2 and strongly reducing anodes, including lithium metal. As a glassy material its structural characterization, especially in thin film form, is difficult. There is a fairly broad consensus in the literature that the introduced nitrogen modifies the typical phosphate glass structure by introducing triply linked N-(P)3 and P-N=P linkages. An important tool for examining such materials is 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 expected to be present in phosphate glasses and in comparable phosphorus oxynitride molecules. We included simple

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 $\text{N}[\text{PO}(\text{OH})_2]_3$. The results of these calculations are revealing as to what we might and might not expect to see in the vibrational spectra of the oxynitride glasses. The P-N and P-O stretching vibrations show extensive mixing and overlap of their frequency regions. Consequently we can not expect to identify a characteristic frequency for the N-(P)3 structural unit in these materials, or use vibrational spectroscopy to demonstrate the presence of this structural unit. In contrast, the isolated P-N=P linkage seems to have a fairly narrow vibrational frequency range, and shows little tendency to mix with other vibrational modes of the $\text{PO}_2\text{-X-PO}_2$ structural units. A comparison of the results on different molecules in the calculations, and to experimental data on some of our own LiPON films and to data from the literature, will be presented.

9:30 AM CC6.5

Dielectric and Conductivity Studies of PVA- LiClO_4 Polymer Electrolytes. R. Baskaran and S. Selvasekarapandian; Physics, Bharathiar University, Coimbatore, Tamilnadu, India.

Solid polymer electrolyte films based on Poly (vinyl alcohol) (PVA) complexed with lithium perchlorate (LiClO_4) have been prepared in different stoichiometric ratio by solution casting technique. The complexation of LiClO_4 salt with the polymer PVA has been confirmed by FT-IR spectroscopy technique. The complex impedance and dielectric studies are carried out on the polymer electrolyte samples with aluminium blocking electrodes in the frequency range 42Hz- 5MHz. From the complex impedance spectrum, observed high frequency depressed semicircle indicates that the conductivity is mainly dominated by the bulk effect of the material. The plots of log conductivity vs $1000/T$ are found to be linear over a temperature range 303-358K, which indicates the samples fit well with Arrhenius type relation. The conductivity is found to increase with an increase in the concentration of the salt in the polymer and also with an increase of temperature. The activation energy decreases with the increase of salt concentration. The maximum conductivity for PVA (80) - LiClO_4 (20) sample is found to be $3.16 \times 10^{-3} \text{ Scm}^{-1}$ at 358K. The modulus spectrum of the samples shows the distribution of relaxation time and non-Debye behaviour of the polymer- salt complex. The low- frequency dispersion of the dielectric constant implies the space charge effects arising from the electrodes.

9:45 AM CC6.6

Polymer/Fumed Silica Composite Separators for Lithium-Ion Batteries. Brett L Lucht¹, Rafael Rodriguez^{2,1}, Joe DiCarlo² and K. M. Abraham²; ¹Chemistry, University of Rhode Island, Kingston, Rhode Island; ²Lithion Inc., Pawcatuck, Connecticut.

Lithium-ion batteries have been under intense investigation over the last decade. Much of this research has involved the use of polymer electrolytes but there has been recent interest in the development of polymer/inorganic composites as solid electrolytes(1,2). This investigation reports on the preparation and investigation of PVDF/fumed silica and PEO/fumed silica composites as solid electrolytes for lithium ion batteries. A suspension of a polymer (PVDF or PEO), fumed silica, NMP, and ethanol is prepared via the dissolution of the polymer in NMP followed by the sequential addition of ethanol and fumed silica. The suspension was then deposited on the surface of the electrodes by an ultrasonic spraying system. During the coating process the solvents are vaporized allowing deposition of a thin layer of the composite material on the surface of the electrodes. The polymer provides adhesion of the composite to the surface of the electrodes. After preparation of the thin films, the surface is wetted with 1.0 M LiPF_6 in 1:1:1 EC/DEC/DMC to prepare the gel electrolyte. The thin films of polymer/ silica composites were characterized by a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), conductivity measurements, and cycling performance of Li-ion cells. SEM analyses suggest that the composite is mostly uniform with some small ($10 \mu\text{m}$) polymer rich particles. The thickness of the films is dependent upon the number of coatings of the composite. Film of up to $60 \mu\text{m}$ have been prepared with relatively uniform thickness. However, a thickness of at least $25 \mu\text{m}$ is needed to prevent pinholes and shorting of coin cells. TEM analyses provide evidence for the formation of aggregates of fumed silica particles with approximately 20 nm diameter surrounded by networks of polymer. Conductivity of the composites gelled with 1.0 M LiPF_6 in 1:1:1 EC/DMC/DEC varies with both polymer structure and polymer/ SiO_2 content. The optimized composititons containing 17 % polymer and 83 % SiO (wt), conductivity varies from 5.0-3 to 6.0-3 S/cm. The cycling performance of coin cells prepared with $\text{LiNi}_{(1-x)}\text{Co}_x\text{O}_2$ cathode, MCMB anode, a composite polymer/fumed silica separator gelled with 1.0 M LiPF_6 in 1:1:1 EC/DMC/DEC was comparable to that of cells utilizing the standard porous polymer separator. The coin cells had an irreversible capacity loss between 21 and 26 % in the first charge cycle, but retained the same capacity for over 50 additional cycles.

Acknowledgements We would like to thank the National Aeronautics and Space Administration for financial support of this research under contract No. NAS-01195. References 1.K.M.Abraham, V.R.Koch and T.J. Blakely, J. Electrochem. Soc., 147,1251 (2000) 2. J.DiCarlo, R. Rodriguez and K.M.Abraham, in Proc. Of the 40th Power Sources Conference, Cherry Hill, NJ, 2002.

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 Doescher and Debra R Rolison; Naval Research Laboratory, Washington, District of Columbia.

Mesoporous nanoarchitectures, such as aerogels and ambigels, provide an inter-connected network of nanoscale particles and porosity and have shown improved electrochemical properties for energy storage applications due to their combination of high surface area, through-connected porosity, and short solid-state 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/separator in solid-state devices including batteries and electrochemical capacitors. The electro-oxidation of phenol derivatives has been used to deposit ultrathin conformal polymer coatings onto mesoporous manganese oxide nanoarchitectures and planar ITO substrates. The thickness of the PPO films on ITO is determined using AFM profilometry and shown to be on the order of 10 nm. Solid-state electrical measurements of PPO and other polymers on ITO are made using a two-electrode configuration using soft ohmic contacts such as Hg or slowly evaporated Au or Al as the top electrode [1]. D.R. Rolison, B. Dunn, J. Mater. Chem., 11, 963 (2001).

10:45 AM CC6.8

Degradation Studies of Microporous Separator Membranes in Lithium-ion Batteries. Ganesh Venugopal, Energy Systems Group, Motorola, Lawrenceville, Georgia.

Micro-porous separator membranes are a critical component of rechargeable Lithium-ion (Li-ion) batteries that power many of today's portable electronic devices. The general trend in Li-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 this trend, Li-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 4.20V that is typically recommended as the upper voltage limit for Li-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 Li-ion cells indicated that cells with tri-layer 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 Li-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

An Eulerian Formulation for the Physicochemical Hydrodynamics of Spouted Bed Electrolytic/ Fuel Cell System. Pezhman Alireza Shirvanian¹ and Joseph Manuel Calo¹;

¹Chemical Engineering, Brown University, Providence, Rhode Island; ²Chemical Engineering, Brown University, Providence, Rhode Island.

An Eulerian(micro-macroscopic) 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 separately 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 electrochemical reactions. Constitutive 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 electrochemical reactions and mass transfer coefficient as a function of solution/particulate phase conductivity, hydrodynamic parameters and the operating potential.

11:15 AM CC6.10

Titanium POEMS: High Proton Conductivity in Porous Titanium Dioxide Prepared by the Sol-Gel Route.

Flavio Maron Vichi¹, Maria Isabel Tejedor Tejedor² and Marc Anderson²; ¹Institute of Chemistry, University of Sao Paulo - USP, Sao Paulo, So Paulo, Brazil; ²Environmental Chemistry and Technology Program, University of Wisconsin - Madison, Madison, Wisconsin.

Porous Oxide Electrolyte Materials (POEMS), obtained as nanoporous ceramics via the sol-gel route, are interesting materials, because they have a proton conductivity which is similar to that of Nafion[®], 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 POEMS. Monolithic chips of the ceramic material were obtained by the controlled drying of the precursor sol, followed by a heat treatment of the resulting xerogel at 300°C for 3h. Samples of this material 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 0.063 S/cm at 25°C and 81% RH after modification of the surface acidity by a treatment at pH 1.5 for 24h. 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. Fleischauer¹, J

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Electrodes based on Si or Sn could dramatically increase the performance of Li-ion rechargeable batteries. However, large and uneven volume changes during charge / discharge cycling in crystalline high-capacity anode materials, such as the various phases of Li-Sn, can lead to cracking, loss of electrical contact and therefore reduced capacity. Uniform and reversible volume changes can be obtained by using amorphous electrode materials [1]. The reversible volume expansion and high Li storage capacity of some amorphous alloys make them promising candidates as anodes in Li-ion cells. However, the capacity of the alloys is sometimes significantly less than that of the individual components. Combinatorial materials science methods are well-suited to fabricate a large range of amorphous alloys. Sample to sample variability can also be eliminated by simultaneous testing. The high quality of the collected data will also aid modeling efforts. A thin film of Si-A-B (B ≠ boron) was simultaneously deposited on a variety of substrates using the multi-target sputtering machine described in [2]. Combinatorial electrochemical measurements were used to determine the charge storage 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. Beaulieu 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 (2003).