

**SYMPOSIUM M**  
**Materials Aspects of Fuel Cells**

November 29 - December 2, 2004

**Chairs**

**Hector D. Abruña**

Dept. of Chemistry & Chemical Biology  
Cornell University  
Ithaca, NY 14853-1301  
607-255-4720

**Debra R. Rolison**

Surface Chemistry Branch  
Naval Research Laboratory  
Code 6170  
4555 Overlook Ave. SW  
Washington, DC 20375-5342  
202-767-3617

**Eugene Smotkin**

Dept. of Chemistry  
University of Puerto Rico  
Rio Piedras Campus  
P.O. Box 23346  
San Juan, PR 00931-3346  
787-764-0000 x-1-4796

**Hubert Gasteiger**

General Motors Corporation  
MC 144-001-101, (10 Carriage St.)  
P.O. Box 603  
Honeoye Falls, NY 14472-0603  
585-624-6725

\* Invited paper

**8:30 AM M1.1**

**A High Performance Cathode for the Next Generation of Solid-Oxide Fuel Cells.** Sossina M. Haile and Zongping Shao; Materials Science, Chemical Engineering, California Institute of Technology, Pasadena, California.

Perhaps the greatest technical obstacle to the widespread implementation of solid oxide fuel cells (SOFCs) is the lack of an active cathode that can enable operation at reduced temperatures (500-700 °C). While state-of-the-art SOFCs combine the benefits of fuel flexibility with environmentally power generation, their high operating temperatures (800-1000 °C) lead to high costs and materials compatibility challenges. Here we present  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) as an ideal cathode for operation at  $T < 600$  °C. Power densities of  $1010 \text{ mW}\cdot\text{cm}^{-2}$  and  $402 \text{ mW}\cdot\text{cm}^{-2}$  were achieved at 600 and 500 °C, respectively, using a 20  $\mu\text{m}$  doped ceria electrolyte, humidified hydrogen as the fuel, and air as the cathode gas. This remarkable performance results from the high oxygen diffusivity through BSCF, which eliminates oxygen diffusion as the rate-limiting step in the overall electroreduction process. Instead, surface exchange, a rapid process, is rate-limiting. We further demonstrate that BSCF is ideally suited to 'single-chamber' fuel cell operation, in which anode and cathode reactions take place within the same physical chamber. Under this configuration  $440 \text{ mW}\cdot\text{cm}^{-2}$  was achieved at a furnace set temperature of 500 °C (cell temperature 650 °C) using  $\text{C}_3\text{H}_8 + \text{O}_2 + \text{He}$  as the feed gas.

**8:45 AM M1.2**

**Evaluation of a Ruddlesden-Popper Phase for Cathode-Use in Intermediate Solid-oxide Fuel-Cells.** Gisele Amow<sup>1</sup> and Isobel Davidson<sup>2</sup>; <sup>1</sup>Air Vehicle Research Section, Defence Research and Development Canada, Ottawa, Ontario, Canada; <sup>2</sup>Institute for Chemical Process and Environmental Technology, National Research Council Canada, Ottawa, Ontario, Canada.

Previous work on the Ruddlesden-Popper (RP) phases have suggested this class of materials to be alternatives for the conventionally-used perovskites employed as solid-oxide fuel cell cathodes. In this study, an RP nickelate-phase has been synthesized and evaluated as a novel cathode material for intermediate-temperature solid-oxide fuel-cells (IT-SOFCs). Measurements in the intermediate-temperature range (600-700°C) show this material to possess reasonable electrical conductivity (90 S/cm). Furthermore, ASR studies have shown that the performance of this material as a cathode on LSGM electrolyte is significantly improved in comparison to the previously-studied RP phase,  $\text{La}_2\text{NiO}_{4+\delta}$ . This result suggests this material to be a more viable candidate for cathode-use in IT-SOFCs. A discussion of the synthesis, structural and physical-property measurements will be presented.

**9:00 AM M1.3**

**Performance Enhancement of SOFC Electrode Materials by Mechanical Particle Bonding Technique.** C. C. Huang<sup>1</sup>, Takehisa Fukui<sup>2</sup>, Kenji Murata<sup>2</sup>, Makio Naito<sup>3</sup> and Kiyoshi Nogi<sup>3</sup>; <sup>1</sup>Hosokawa Nano Particle Technology Center (USA), Summit, New Jersey; <sup>2</sup>Nano Particle Technology Center, Hosokawa Powder Technology Research Institute, Hirakata, Japan; <sup>3</sup>Joining and Welding Research Institute, Osaka University, Osaka, Japan.

Mechanical Particle Bonding Technique is an advanced dry particle coating method to create chemical bonds between particles without any liquid binder. It can produce multifunctional composite materials for various applications contributing to the development of advanced materials and devices for batteries, fuel cells, ceramics, metals, superconductors, and pharmaceuticals. In this study, the electrode material of solid oxide fuel cell, NiO-Y2O3 stabilized ZrO2 (YSZ), was processed by the Mechanical Particle Bonding Technique to form composite particles. The composite particles consisted of submicron sized NiO particles covered with finer YSZ particles. A Ni-YSZ cermet anode fabricated from the NiO-YSZ composite particles showed a uniformly dispersed micron-sized-porous structure having Ni and YSZ grains less than several hundred nano-meters. It was found that the mechanically treated cermet anode has the advantage of achieving high electrical conductivity at the low operating temperature (<800 degree C). It is believed that the mechanical particle bonding technique can also be applied to other material compositions to improve the performance of solid oxide fuel cells.

**9:15 AM M1.4**

**Effect of YSZ Particle Size and its Distribution on Sintering Behavior of Electrolyte for Anode-Supported Solid Oxide Fuel Cells.** Hailei Zhao<sup>1</sup>, Feng Ju<sup>1</sup>, Uday Pal<sup>1</sup>, Srikanth Gopalan<sup>1</sup>,

Guosheng Ye<sup>1</sup> and Donald Seccombe<sup>2</sup>; <sup>1</sup>Dept. of Manufacturing Engineering, Boston University, Brookline, Massachusetts; <sup>2</sup>BTU International, N. Billerica, Massachusetts.

The aim of this research is to employ co-firing below 1250 oC to fabricate anode-supported solid oxide fuel cells (SOFCs). The selection of the lower sintering temperature and the manufacturing technique is directed at reducing the cost of producing fuel-cell stacks and to prevent performance degradation due to component interaction that usually occurs at higher sintering temperatures. The challenge in this research is to densify the yttria-stabilized zirconia (YSZ) electrolyte at reduced temperatures. In the present work, two kinds of YSZ powders, nano-scale (50 nm) and sub-micron scale- (0.15  $\mu\text{m}$ ), were used in different proportions to prepare the green electrolyte specimens for sintering by uni-axial pressing, tape casting, and screen printing. The samples were then fired at temperatures between 1150-1250 oC, to determine the effect of particle size and its distribution and the method of preparation of the green sample on the sintering behavior of the electrolyte. The effect of adding other micron-size oxides as dopants and liquid-phase sintering aides to the YSZ-powder mixture to improve its sinterability were also investigated. In general four sample distributions containing submicron/nano-scale YSZ powder mixtures having ratios of 100/0, 50/50, 30/70 and 0/100 were prepared for this investigation. The experimental results indicated that at a given sintering temperature, in the range investigated, addition of nano-YSZ to submicron-YSZ generally enhanced the sinterability of the mixture and thus increased the relative density of the sintered sample. However, the microstructure of the sintered YSZ tended to be much coarser with larger grains when it contained all nano-YSZ powders. All nano-scale sintered YSZ powders can contain some amount of exceptionally large YSZ grains (20  $\mu\text{m}$ ) and penetrable pores dispersed among the small-sized grains. This is not desirable for the electrolyte since it would lower the conductivity and strength of the electrolyte, and also make it gas permeable. Due to the larger surface area, the nano-scale YSZ particles exhibit a greater tendency for grain growth in order to lower its surface energy. Therefore, depending on the sintering temperature there is an optimum distribution between the submicron-scale and the nano-scale YSZ powders that result in the densest sample with a uniform microstructure.

**9:30 AM M1.5**

**Patterned, Thin Film Cathodes for Micro-SOFC.** Anja Bieberle<sup>1</sup>, Martin Soegaard<sup>1,2</sup>, Joshua L. Hertz<sup>1</sup> and Harry L. Tuller<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Materials Research Department, Risoe National Laboratory, Roskilde, Denmark.

Thin film deposition of cathode materials is interesting for prospective micro-Solid Oxide Fuel Cell (SOFC) applications utilizing Si-based microfabrication technology. Aside from design considerations, thin films are ideal for studying reaction mechanisms, since well-defined geometries can be fabricated allowing for more straightforward investigation of the kinetics of the system. In support of both of the above objectives, we have deposited and microstructured a number of different cathode materials by RF sputtering, photolithography, lift-off, and etching. Si wafer substrates were prepared by first depositing a SixNy insulating layer followed by a thin solid electrolyte film. Pt and a number of lanthanum strontium cobalt oxide (LSCO) compositions with different La to Sr ratios were studied as electrode materials. LSCO cathodes are a favorable material for low temperature SOFCs due to their mixed ionic electronic conductivity and their good catalytic behavior towards oxygen reduction. The structure, the topography, and the chemistry of the cathodes were characterized by XRD, SEM, AFM, WDS, and RBS. Electrochemical characterization was performed by impedance spectroscopy and 4 probe conductivity measurements as functions of temperature, partial pressure of oxygen, and applied bias. A detailed picture of the electrochemical response of the thin film cathodes was obtained by comparing different electrode-electrolyte combinations, such as LSCO-YSZ, LSCO-CGO, Pt-YSZ, and Pt-CGO.

**10:15 AM M1.6**

**Design and Characterization of MIEC Nanocomposites Based upon Doped Lanthanum Manganite and Ceria.** Vladislav A. Sadykov<sup>1</sup>, Yulia V. Frolova<sup>1</sup>, Vladimir V. Zyryanov<sup>2</sup> and Stylianos Neophytides<sup>3</sup>; <sup>1</sup>Heterogeneous catalysis, Borekov Institute of Catalysis, Novosibirsk, Russian Federation; <sup>2</sup>Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russian Federation; <sup>3</sup>Institute of Chemical Engineering & High Temperature Processes, Patras, Greece.

Design of oxygen-separating membranes including those used in reactors for direct syngas generation from hydrocarbon feedstock is at present among the most important tasks of materials science. Nanocomposites comprised of particles possessing separately a high electronic or ionic conductivity could be a viable option. They are

also of a great interest as cathodes and/or anodes in SOFC. This work is devoted to synthesis of dense nanocomposites comprised of Gd or Pr doped ceria oxide as an ionic conductor and lanthanum manganite ( $\text{LaMnO}_3$ ) as an electronic conductor. For synthesis, polymerized complex ester precursor method (Pechini route) was chosen due to its ability to ensure molecular-scale homogeneity for the components mixing. In the course of green pressed samples sintering up to 1300 °C, density, structural parameters of constituting phases and features of interphase boundaries were followed by XRD and TEM. The effect of the fluorite-like phase composition and sintering additives ( $\text{Bi}_2\text{O}_3$ ,  $\text{CoO}$ ) on the dynamics of sintering was elucidated. Neither appearance of new compounds or destruction of starting phases was observed, though some redistribution of cations between phases occurred, being nearly absent for Gd-containing systems. Nanodomain sizes of perovskite and fluorite phase were retained even in dense ceramics, thus ensuring required percolation. This agrees with a high mixed conductivity of those composites and a high oxygen mobility in their bulk estimated by conductivity measurements,  $\text{CH}_4$  TPR and oxygen TPD/permeability studies. The oxygen mobility in nanocomposites was shown to greatly exceeds the values found for separate components thus proving efficient conjugation of ionic and electronic currents. A higher lattice/surface oxygen mobility and reactivity were observed for Pr-containing system due to the effect of  $\text{Pr}^{3+}/\text{Pr}^{4+}$  redox couple, while syngas selectivity was improved for Co-containing systems due to efficient activation of methane on the surface Co atoms. Supports of INTAS 01-2162 and Russian Ministry of Education #3N-292-03 Projects is gratefully acknowledged.

#### 10:30 AM M1.7

**Oxygen reduction reaction (ORR) studies of sol-gel derived  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$  (SG-LSCF).** Jingbo Louise Liu and Viola Birss; chemistry, University of Calgary, Calgary, Alberta, Canada.

A number of researchers have demonstrated that  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$  perovskite cathodes are more attractive than  $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$  because of their high catalytic activity for  $\text{O}_2$  reduction, and their very good ionic and electronic conductivity at intermediate temperatures. However, LSCF has poor compatibility with yttria stabilized zirconia (YSZ), and two non-electronically insulating products can form, resulting in the degradation of the electrode activity. Therefore, CeO<sub>2</sub>-based materials are typically used as the electrolyte with LSCF cathodes. Traditionally, SOFC materials have been synthesized using high temperature methods, which generally lead to large particle sizes and pore structures. The sol-gel (SG) method has become increasingly popular for the preparation of metal oxides, due to its advantages of producing materials with high porosity, high surface areas, and homogeneity on the molecular scale. In the present work, SG methods have been employed to synthesize LSCF (SG-LSCF). Precursor SG materials were synthesized from various mixtures of metal nitrate salts in refluxing ethanol, followed by removal of the solvent to form highly viscous products. The SDC electrolyte was formed by heating its sol-gel derived precursor, grinding it into a powder, pressing it to form a pellet, and then densifying it at 1450 Celsius for 4 hrs. Information regarding the phase, morphology, particle size and elemental composition of the SG-LSCF cathodes were obtained using XRD, HRTEM, SEM and WDS. Electrochemistry was carried out in a 3-electrode half-cell configuration, exposed to air. The counter and reference electrodes were also composed of LSCF, and Pt gauze attached to a Pt wire was press-contacted to the LSCF electrodes serving as current collectors. The exchange current densities and mechanism of the ORR were obtained at various temperatures using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The cathode is found to be primarily composed of the LSCF tetragonal phase. Based on XRD peak broadening, as well as on TEM analysis, the crystallite size of the LSCF ranges between 20-50 nm. SEM showed that the SG-LSCF cathode layer is uniform and has highly structured channels with thin walls and pores on the order of a micron or less in diameter. HRTEM images of a typical particle indicate the presence of a highly crystalline plane (101). In terms of electrochemical performance, the exchange current densities of the ORR at SG-LSCF cathodes were 250, 50, 4 and 0.25 mA/cm<sup>2</sup> at 700, 600, 500, and 400 Celsius, respectively, as obtained from the EIS results. These agree closely with the values obtained from low field CV analyses. It was also found that the impedance determined ORR reaction rates remained high even after the sample was polarized at increasingly more positive potentials and at longer times. Potentiostatic studies indicated that no short-term deterioration of LSCF performance was observed.

#### 10:45 AM M1.8

**Correlation between Microstructure and Degradation of Ionic Conductivity in  $\text{Y}_2\text{O}_3$ -Doped Zirconia.** Benjamin Butz<sup>1</sup>, Heike Stoermer<sup>1</sup>, Dagmar Gerthsen<sup>1</sup>, Axel Mueller<sup>2</sup> and Ellen Ivers-Tiffée<sup>2</sup>; <sup>1</sup>Laboratorium fuer Elektronenmikroskopie (LEM), Universitaet Karlsruhe (TH), Karlsruhe, Germany; <sup>2</sup>Institut fuer Werkstoffe der Elektrotechnik (IWE), Universitaet Karlsruhe (TH), Karlsruhe, Germany.

The application of Ytria-stabilized Zirconia as solid electrolyte in high-temperature solid oxide fuel cells (SOFC) is well established. However, the decrease of the ionic conductivity in cubic 8.5 mol% and 10 mol%  $\text{Y}_2\text{O}_3$ -doped  $\text{ZrO}_2$  ( $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-0.5x}$ ,  $x=17,20$ ) at high temperature has not yet been clarified completely. To contribute to the understanding of the degradation process, transmission electron microscopy was applied to analyse the microstructure of sintered YSZ electrolyte substrates before and after aging. The investigated samples were processed by tape casting and sintering of high-purity YSZ powder at about 1550 °C and heat treated at 950 °C for 1000-2500 h applying an electrical load (current density was varied between 150 and 600 mA/cm<sup>2</sup>). Selected-area electron diffraction along different zone axes and conventional TEM images yield information about the potential presence of different phases and their spatial distribution in the samples. Energy dispersive X-ray analysis (EDX) was applied to study segregation of impurities at grain boundaries which did not yield any indication of impurity concentration above the detection limit. Reflections corresponding to the tetragonal phase were observed in electron diffraction patterns despite  $\text{Y}_2\text{O}_3$  concentrations of 8.5 and 10 mol %. Dark-field images taken with reflections of the tetragonal phase show nanometer-scaled regions embedded in the cubic matrix. Two-beam bright-field images shows contrast fluctuations on a scale of 10 nm which can be associated with strain fluctuation induced by compositional modulations. We attribute the presence of the tetragonal phase to locally reduced  $\text{Y}_2\text{O}_3$  concentrations. Therefore,  $\text{ZrO}_2$  is not fully stabilised in the cubic phase in the investigated doping range. The tetragonal phase exists in the as-sintered and the heat-treated samples and does not disappear during the aging process. Selected-area electron diffraction patterns also show non-thermal diffuse scattering. The diffuse background can be explained by short-range order of oxygen vacancies which is well known. It exists in the as-sintered samples and becomes sharper and slightly more intensive during the aging process. Increased short-range order on the oxygen sublattice reduces the oxygen vacancy concentration available for diffusion, which has been considered up to now as main reason for the reduction of ionic conductivity. We have observed additional weak reflections which have not been described up to now. These reflections can be explained consistently in several zone-axis orientations by assuming ordering on the cation sublattice. The intensity of these reflections increases after the degradation process of sintered samples exposed to high temperatures which could be correlated with the reduction of ionic conductivity.

#### 11:00 AM M1.9

**Materials System for Intermediate Temperature Solid Oxide Fuel Cell.** Wenquan Gong, Srikanth Gopalan and Uday B. Pal; Manufacturing Eng., Boston University, Boston, Massachusetts.

The objective of this research is to investigate a materials system for intermediate temperature solid oxide fuel cell (SOFC) that is capable of operating between 500-700C. The electrolyte, anode, and cathode materials in the SOFC system being investigated are based on lanthanum gallate ( $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  or LSGM), nickel-ceria ((Ce<sub>0.85</sub>Gd<sub>0.15</sub>O<sub>2</sub> or GDC) cermet, and LSGM-lanthanum cobaltite ( $\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_3$ , or LSCF) composite, respectively. These material choices are based on their property information available in the literature. Interfacial polarizations of the candidate electrodes for the LSGM electrolyte have been investigated by impedance spectroscopy technique. Among the cathode materials (LSM ( $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ ) and LSCF), the pure LSM electrode had the worst polarization performance. The addition of LSGM electrolyte material to the LSM electrode increases the mixed-conducting boundary with the gas phase and lowers the overall polarization. Although LSM-LSGM composite electrodes are better than just pure LSM, the performance of the best LSM-LSGM (40:60) electrode was similar to that of platinum. Single-phase mixed-conducting LSCF electrode had three orders lower polarization resistance than the LSM-LSGM composite electrodes. Addition of LSGM to LSCF did not significantly alter (lower) the polarization resistance of the LSCF electrodes. However, a composite LSCF-LSGM electrode is preferred over plain LSCF electrode in order to match the coefficient of thermal expansion with the LSGM electrolyte. It is also observed that the interfacial polarization resistance of the LSCF electrode decreased asymptotically as the electrode thickness increased. An optimum thickness of 30 to 40 micron is required to minimize the cathodic polarization resistance. The anode material investigated was Ni-GDC. It was observed that the LSGM electrolyte reacts with the Ni during processing and also at the operating temperature and increased both the ohmic and the polarization resistances. A buffer layer of GDC between the LSGM electrolyte and the Ni-GDC composite anode could not completely prevent this interaction due to lanthanum diffusion, when sintering temperature was above 1200C. The la diffusion also resulted in increasing the ohmic resistance. It is possible to prevent the La diffusion from the LSGM electrolyte by changing the buffer layer from GDC to lanthanum doped Ceria (LDC). It is to be noted that the lanthanum in the LDC does not react with the Ni.

Since the ionic conductivity of the LDC is lower than that of GDC, it may be desirable to employ a Ni-GDC cermet anode above the LDC barrier layer to lower the polarization resistance. Effects of Ni-GDC anode composition, structure and thickness on interfacial polarization are investigated. After determining the optimum electrode composition, structure and thickness of the cathode and the anode, complete planar cells will be fabricated and evaluated in terms of its I-V characteristics and stability.

#### 11:15 AM M1.10

**Ferritic Stainless Steels for SOFC Interconnect Applications: Status and Challenges.** Z. Gary Yang<sup>1</sup>, Prabhakar Singh<sup>1</sup>, Steve P. Simmer<sup>1</sup>, Jeff W. Stevenson<sup>1</sup>, Matt S. Walker<sup>2</sup> and Guanguang Xia<sup>1</sup>; <sup>1</sup>Pacific Northwest National Lab, Richland, Washington; <sup>2</sup>GE Power, Torrance, California.

In recent years, progress in materials and fabrication techniques has allowed for a reduction in SOFC operating temperatures to an intermediate range (650-800°C) where high temperature oxidation resistant alloys can be considered as replacement materials for the traditional ceramics in high temperature (900-1,000°C) SOFC stacks. Chromia-forming ferritic stainless steels are among the most promising alloy candidates, due to the formation of electrically conducting oxide scale, appropriate thermal expansion behavior, and low cost. However, even at these temperatures, the SOFC interconnect application remains challenging for the traditional compositions as well as newly developed ones. PNNL has carried out a systematic work in investigation of these steels for this particular application. This paper will give an overview on the issues of traditional ferritic stainless steels and status of newly developed ones for the interconnect applications in intermediate temperature SOFC stacks.

#### 11:30 AM M1.11

**Finite Element Simulation for Camber During Co-Sintering of Solid Oxide Fuel Cells.** Guosheng Ye<sup>1</sup>, Donald Secombe<sup>2</sup>, Srikanth Gopalan<sup>1</sup> and Uday Pal<sup>1</sup>; <sup>1</sup>Manufacturing Engineering, Boston University, Brookline, Massachusetts; <sup>2</sup>BTU International, North Billerica, Massachusetts.

The anode-supported planar solid oxide fuel cell (SOFCs) is currently the preferred state-of-the-art design and a one-step co-sintering process is the desirable low-cost manufacturing technique. The multi-layer components of the planar SOFC can be fabricated in the green state by tape-casting and screen-printing techniques. However, a successful one-step co-firing of the multi-layer structure requires that we are able to minimize the distortion of the structure (camber) during the process. In order to do this we need to understand the relative importance of sintering shrinkage, thermal expansion coefficients (CTE), elastic properties of all the components, temperature uniformity that is required across the device structure during firing and the firing schedule. In this paper, the authors will apply finite element models to simulate camber formation during one-step co-sintering of the SOFC component layers. A two-step simulation which regards heating up and holding at sintering temperature as the first step and the subsequent cooling down to the ambient temperature as the second step is considered. In the first simulation step, a linear-viscous porous materials model developed by V. V. Skorohod[1] and E. A. Olevsky[2] is applied and in the second step, the materials are assumed to be in their elastic regimes. In both the first and the second steps, the simulations are run in the fully coupled temperature-displacement mode using the commercially available finite element code, ABAQUS. Through a parametric study, the model will show how the relative density of the initial green tape, heating and cooling rates during sintering, variation of electrolyte, electrodes and interconnection thicknesses, and Young's moduli and thermal expansion coefficients impact the camber. Manufacturing methods are analyzed and methods to reduce camber in the SOFC manufacturing process are recommended. 1. Skorohod, V. V., Rheological Basis of the Theory of Sintering, Naukova Dumka, Kiev, 1972. 2. Theory of Sintering: From Discrete to Continuum, Materials Science and Engineering, R23, pp. 41-100, 1998.

SESSION M2: Combinatorial Approaches and Characterization

Chairs: Hector D. Abruna and Andrew Hillier  
Monday Afternoon, November 29, 2004  
Fairfax A (Sheraton)

#### 1:30 PM M2.1

**A Systematic Stability Study of Pt-based Ternary Fuel Cell Catalysts Using EDS Integrated into a High Throughput Discovery Workflow.** Keith Cendak, Konstantinos Chondroudis, Martin Devenney, Qun Fan, Daniel Giaquinta, Sasha Gorer and Peter Strasser; Symyx Technologies, Inc., Santa Clara, California.

One of the most challenging aspects of fuel cell research is the development of a more active cathode catalyst with reduced Pt content. Conventional research has not yielded a suitable candidate despite decades of research. To accelerate the discovery process, high throughput experimentation techniques have been applied to cathode catalyst research; high throughput research holds the promise of materials discovery and optimization at an unprecedented rate. Most research in fuel cell cathode electrocatalysis concentrates on the optimization of Pt mass-based activity, while little emphasis is generally given to the chemical stability of the alloy catalyst. In this study, electron dispersive x-ray spectroscopy (EDS) was used to analyze the composition of a catalyst before and after rotating disk electrode (RDE) measurements. Integrated into a high throughput combinatorial workflow, stability, electrochemical activity and structure of a Pt-based ternary alloy system is rapidly mapped. Results from a carbon supported, high-surface-area catalyst alloy system will be discussed.

#### 1:45 PM \*M2.2

**Development of High Throughput and Combinatorial Approaches for the Discovery and Characterization of New Electrocatalytic Materials.** Andrew C. Hillier, Chemical Engineering and Chemistry, Iowa State University, Ames, Iowa.

The discovery of more active and poison-tolerant catalysts for anode and cathode reactions of low temperature fuel cells remains a major barrier to commercialization of this technology. The search for improved catalyst formulations is hindered by the massive parameter space available for their construction. Combinatorial and high throughput experimental methods are well suited to accelerate this discovery through the ability to generate and screen a multitude of compositions in a single experiment. In this work, we describe high throughput strategies to generate a wide variety of catalyst compositions (binary/ternary/quaternary) and interrogate their activity directly in an electrochemical environment. Several library fabrication tools based upon array and gradient deposition methods are used to prepare samples possessing a range of catalyst compositions including combinations of Pt, Ru, Rh, Mo, Pd and W. We have primarily employed electrochemical deposition for library design in which solution diffusion or local reagent delivery are used to create spatially-varied catalyst libraries. High throughput screening of catalytic activity is accomplished by scanning methods based upon microelectrodes and mass spectrometry as well as optical screening via pH-sensitive fluorescent probes and surface plasmon resonance. Results include scanning electrochemical screening of hydrogen oxidation in the presence of carbon monoxide on a variety of multicomponent catalysts, reaction pathway and reaction efficiency mapping of catalyst arrays with scanning differential electrochemical mass spectrometry, and optical screening of several anode reactions on multicomponent catalyst gradients.

#### 2:15 PM M2.3

**A High Throughput Method for Finding New Fuel Cell Electrocatalysts.** Mark David Prochaska<sup>1</sup>, Robert Bruce van Dover<sup>2</sup>, Francis J. DiSalvo<sup>3</sup>, Hector D. Abruna<sup>3</sup>, Jing Jin<sup>3</sup> and Dominic Rochefort<sup>3</sup>; <sup>1</sup>Applied and Engineering Physics, Cornell University, Ithaca, New York; <sup>2</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>3</sup>Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Recent studies on fuel cell electrocatalysts (1,2) show that some intermetallic compounds have improved oxidation onset potentials and current densities relative to pure platinum electrodes. To find other compounds, we have developed a high-throughput method for synthesizing, testing, and characterizing a large range of ternary compositions in a single sample. We use on-axis cosputtering of three metallic elements onto a three-inch substrate, creating a thin-film with a large composition spread. A scanning electrochemical microscope tests the sample for regions of electrocatalytic activity. We are also using differential thermographic imaging to measure the temperature rise associated with electrocatalytic activity, thereby obtaining an in-parallel evaluation of the entire composition spread. The regions with interesting properties are then characterized using x-ray diffraction, microprobe, and scanning electron microscopy. We have applied this method to prepare a Pt-Bi-Pb spread that covers the central 60% of the ternary phase diagram. Compositions that are rich in Pt show the best electrocatalytic activity, as expected (1,2). Other experimental results will be presented. (1) E. Casado-Rivera, Z. Gál, A.C.D. Angelo, C. Lind, F.J. DiSalvo, H.D. Abruna, ChemPhysChem 2003, 4, 193-199. (2) E. Casado-Rivera, D.J. Volpe, L. Alden, C. Lind, C. Downie, T. Vázquez-Alvarez, A.C.D. Angelo, F.J. DiSalvo, H.D. Abruna, J. Am. Chem. Soc. 2004, 126(12), 4043-4049

#### 2:30 PM M2.4

**In-situ X-ray Absorption and FTIR Analysis of PtRu Anodes in Fully Operating Direct Methanol Fuel Cells.** Eun-Hyuk Chung<sup>2</sup>, Stanislav Stoupin<sup>2</sup>, Soma Chattopadhyay<sup>2</sup>, LaSalle

Swenson<sup>4</sup>, Carlo Segre<sup>2</sup> and Eugene S. Smotkin<sup>1</sup>; <sup>1</sup>Chemistry, University of Puerto Rico, San Juan, Puerto Rico; <sup>2</sup>Physics, Illinois Institute of Technology, Chicago, Illinois; <sup>3</sup>Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois; <sup>4</sup>Chemistry, Penn State University, College Park, Pennsylvania.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) experiments were performed on an operating liquid feed direct methanol fuel cell (DMFC). The Pt LIII-edge and Ru K-edge of unsupported Pt-Ru (1:1) anode electrocatalysts were studied in the transmission mode to initiate elucidation of the role of oxides in methanol electrooxidation. Anode X-ray absorption spectra were obtained as a function of fuel cell potential and methanol concentration using a Pd cathode to avoid interference with the anode Pt edge. The Ru edge data of the as prepared catalysts show a substantial oxide component. Exposure to methanol rapidly reduces the catalysts to a primarily metallic core. However, least squares fitting of the Ru XANES data to a library of XANES data references including Ru metal, Ru oxide and Ru oxide hydrate required that about 15% of the Ru be fitted as oxides, at all potentials. The Ru radial distribution functions also could not be fit as pure metallic either. In contrast all of the XANES and EXAFS data of the Pt could be fit as purely metallic. The XRD pattern showed only a face centered cubic lattice. Other non crystalline phases are possible. The above and additional data obtained after the submission of this abstract will be discussed in terms of a model for nanostructured PtRu Johnson Matthey catalysts.

### 3:15 PM \*M2.5

**In Situ Nanoparticles Surface Analysis.** Juan M. Feliu, Rodriguez Paramaconi, Francisco J. Vidal, Jose Solla, Enrique Herrero and Antonio Aldaz; Institute of Electrochemistry, University of Alicante, Alicante, Spain.

Electrocatalytic reactions are structure sensitive. This means that adequate surface control could be used to improve the performance of fuel cell anodes. In order to achieve this purpose, it is necessary to control the surface properties of nanoparticles, such as those of platinum, dispersed on the substrate. It is proposed that structure sensitive surface reactions can be used as specific probes to identify the corresponding surface sites in nanoparticles. The comparison between the reactivity monitored on well defined stepped surfaces enables to prepare analytical calibration curves. These results may be used in to in situ monitor the different types of sites present on dispersed nanoparticles. In this way characteristic reactions as those undergone by irreversibly adsorbed adatoms, such as Bi on Pt(111) or Ge on Pt(100) terrace sites, together to more complex structure sensitive responses, such as hydrogen and anion adsorption, can be used to establish a detailed picture of the surface. The latter process enables to evaluate the whole surface area and also shows qualitatively the presence of the different surface sites. The specific information from the single site probe reactions can be used to rationalize and deconvolute the overall picture given by the electrochemical responses. Specific electrocatalytic reactions, such as those taking part in fuel cells, may be used to confirm the site assignment based in this purely electrochemical method. Among them, ammonia oxidation in alkaline electrolytes has been shown to be specific to Pt(100) terrace sites on the surface of nanoparticles.

### 3:45 PM M2.6

**Atomic Structure of Platinum-Iron Phosphate Electrocatalyst.** Wojciech Dmowski<sup>1</sup>, Peter J. Bouwman<sup>2</sup> and Karen E. Swider-Lyons<sup>2</sup>; <sup>1</sup>Univ. Tennessee, Dougherty Engr. Bldg., Tennessee; <sup>2</sup>Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia.

We use atomic pair distribution function (PDF) analysis and X-ray spectroscopy (XANES) to study the structure of Pt-iron phosphate (Pt-FePO), a new catalyst for oxygen reduction in proton exchange membrane fuel cells. The X-ray diffraction of hydrous Pt-FePO has a diffuse pattern characteristic of a glassy system, but the PDF analysis shows that the local atomic structure of the Pt-FePO is similar to that of  $\alpha$ -quartz (berlinite). The Fe<sup>2+</sup>, Fe<sup>3+</sup> and phosphorus are tetrahedrally coordinated in a corner linked tetrahedral network structure and facilitate an iron 2+/3+ redox couple. In the catalysts with the highest electrocatalytic activity there is no Pt metal, but rather the Pt is distributed atomically as 2+ and 4+ ions and adds a slight distortion to the FePO framework structure. The Pt ligand coordination and proximity to iron redox couples may influence the electrochemical activity of the catalysts. This detailed structural analysis of the Pt-FePO can be used to understand the high activity of the catalysts in the absence of Pt metal.

### 4:00 PM \*M2.7

**Influence of Interfacial Water Activity in the Electrocatalysis of Cathodic Oxygen Reduction and Anodic CO and Methanol Oxidation: Combination of Electrochemistry and Synchrotron**

**based In-situ XAS.** Sanjeev Mukerjee<sup>1</sup> and Vivek S. Murthi<sup>2</sup>;

<sup>1</sup>Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts; <sup>2</sup>Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts.

In a fully hydrated environment of a polymer electrolyte fuel cell (PEMFC), the anodic oxidation of water (water activation,  $\text{Pt-M} + \text{H}_2\text{O} \rightarrow \text{Pt(M)-OH} + \text{H}^+ + \text{e}^-$ ) plays a crucial role in determining the overpotential losses at both the cathode and anode (when using direct methanol or reformate feed). Wealth of recent data published by us has shown that it is possible to modify surface properties of Pt by alloying and surface pre-treatments which dramatically modify its selectivity and overall kinetics. This presentation will provide an overview of our experimental data which shed unique insight on the electrocatalysis in the PEM context. At the cathode, poisoning of the surface due to water activation (oxide formation above 0.7 V vs. RHE) on nano-crystalline Pt is now confirmed to be the principal source of overpotential losses. Alloying with first row transition elements and as a consequence modification of the electronic and short range atomic order around Pt has been shown to positively shift the onset of oxide formation. This is reflective of changes in the pre-exponential term in the Arrhenius context rather than any changes in the activation energy for cathodic oxygen reduction reaction (ORR). This presentation will provide a comprehensive picture of the electrocatalysis of ORR on Pt alloys including the effect of changes in water activity at the interface, thereby changing the effect of water activation. For this, results from RRDE investigation will be presented with use of varying concentrations of trifluoromethane sulfonic acid (TFMSA). From an anodic electrode perspective, previously, a 3-fold enhancement in activity for CO oxidation was shown on a PtMo/C relative to a PtRu/C in a PEMFC operating at 85°C under an anodic H<sub>2</sub> stream mixed with 100ppm CO. From kinetic studies of H<sub>2</sub> and CO oxidation, it was concluded that the oxidation states of the Mo surface atoms determine the electrocatalytic activity on these alloys. In-situ X-ray absorption data (XANES and EXAFS) at the Pt L and Ru and Mo K edges confirm an increase in Pt d-band vacancy concentration and a lower Pt-Pt bond distance on these type of alloys. It was concluded that, while there is a competition between oxide species and CO adsorption for Ru surface sites on a PtRu/C, the Mo surface on a PtMo/C was shown to have no affinity for CO and as a result was available for efficient CO oxidation. However, a more complicated interaction was envisaged for methanol oxidation which results in a build up of C1 oxide species on a PtMo/C in contrast to a PtRu/C. This presentation will provide a comprehensive view of both cathodic and anodic electrode processes in the PEM context using experimental data from steady state fuel cell tests, RRDE measurements with varying concentrations of TFMSA correlated with in situ synchrotron x-ray absorption measurements under actual cell operating conditions.

### 4:30 PM \*M2.8

**Probing Stability and Activity of Nanometer-Scale, Bimetallic Catalysts.** Carol Korzeniewski, Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas.

Bimetallic, Pt-based catalysts have been of central importance in the development of low temperature (< 120 °C) H<sub>2</sub>-air and direct methanol fuel cells. The primary role of Pt has been to serve as an effective catalyst for H<sub>2</sub> oxidation and C-H bond cleavage in CH<sub>3</sub>OH, while the second component activates H<sub>2</sub>O at low potentials creating oxides that convert carbon containing fragments derived from CH<sub>3</sub>OH, or impurities such as CO in H<sub>2</sub> feeds, to CO<sub>2</sub>. Traditionally, bulk metal electrodes have been employed to investigate electrocatalytic reactions. However, fuel cell catalysts are high surface area particles, typically 2-10 nm diameter, and questions have been raised about the stability of bimetallic catalyst particles and the extent to which bulk metal electrodes represent conditions at catalyst surfaces. To investigate these questions, we have been employing a variety of analytical techniques. In particular, we have found CO stripping voltammetry to be a useful probe of phase separation in PtRu materials, since separate waves arise from CO oxidation in Pt-rich and Ru-rich regions of catalyst. This presentation will discuss these measurements and the correlation of phase separation properties to the rate of methanol oxidation (1.0 M - 0.1 M CH<sub>3</sub>OH in 0.1 M H<sub>2</sub>SO<sub>4</sub>). Comparisons are made between PtRu catalysts prepared through a sonochemical procedure that results in uniform alloy properties and nanometer-scale core-shell Pt-Ru particles. Results of related work on other Pt-based catalysts, including PtSn and PtFe will also be discussed.

SESSION M3: Catalysts for Oxygen Reduction and Reforming, and the Role of New Carbons  
Chairs: Hubert Gasteiger and Karen Swider-Lyons  
Tuesday Morning, November 30, 2004  
Fairfax A (Sheraton)

### 8:30 AM M3.1

#### **Increase in the Methanol Tolerance of DMFC Cathode by Controlled Nanostructure Design.** Seong Ihl Woo<sup>1</sup>, Won Choon Choi<sup>2</sup>, Min Ku Jeon<sup>1</sup> and Hee Jung Jeon<sup>1</sup>;

<sup>1</sup>Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; <sup>2</sup>Division of Advanced Chemical Technology, Korea Research Institute of Chemical Technology, Daejeon, South Korea.

Nanostructured graphite carbons and metals are important because of their technical applications as ultimate devices, hydrogen storage, catalyst support and quantum-electronic devices. Here we report that platinum-carbon nanocomposite (PtC nanocomposite) can be synthesized as interconnected arrays in an SBA-15 nanoreactor. Ultrafine platinum nanoparticles of the PtC nanocomposite arrays showing a size less than 0.9 nm at a Pt loading of 24 wt%, which can not be obtained with conventional sol-gel and the metal-impregnation method, are stabilized by a strong covalent Pt-C bond ( $R \approx 2.041 \text{ \AA}$ ). H/Pt ratio of 1.8 for the PtC nanocomposite indicates that nearly all Pt nanoparticles are accessible in the carbon wall containing micropores connected to mesopores. Outstanding features of these PtC nanocomposite arrays were realized in the electrocatalytic activity for oxygen reduction, 3.5 times higher than that at the cathode prepared by using the conventional metal-impregnation method. And also, its highly methanol-tolerant property makes the PtC nanocomposite used as a novel cathode material of direct-methanol fuel cells.

### 8:45 AM \*M3.2

#### **Oxide- and Phosphate-Based Catalysts for Oxygen Reduction at PEMFC Cathodes.** Karen Swider-Lyons<sup>1</sup>, Peter J. Bouwman<sup>1</sup>,

Wendy S. Baker<sup>1</sup>, Margaret E. Teliska<sup>1</sup> and Wojciech Dmowski<sup>2</sup>;

<sup>1</sup>Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

Oxide- and phosphate-based catalysts are being developed as low-cost alternatives to the state-of-the-art carbon-supported Pt clusters for oxygen reduction at PEMFC cathodes. The new catalysts are based on hydrous forms of tin oxide, tantalum phosphate, and iron phosphate, which are active for oxygen reduction when impregnated with 5 to 10% platinum. Their characterization with high energy X-ray diffraction, X-ray photoelectron spectroscopy and X-ray absorption spectroscopy indicates that the active catalysts have microporous channels on the order of 0.5 nm, and that the Pt is dispersed throughout as 2+ and 4+ ions. The catalysts are more active for oxygen reduction per weight platinum than carbon-supported Pt-cluster standards, as determined with a rotating disk electrode method. They are unique from the Pt/carbon standards as the oxides and phosphates must be activated before they are catalytically active. Because of their lack of Pt metal, the new catalysts do not adsorb carbon monoxide and are not deleteriously poisoned by sulfur dioxide. The platinum in the hydrous tin oxide materials can also be substituted by gold and palladium to make high-activity non-platinum catalysts. The activity of all of the catalysts is attributed to the ability of the oxides and phosphates to dissociate dioxygen to hydroperoxide groups at their surfaces.

### 9:15 AM M3.3

#### **One-Pot Synthesis Approaches to Reformer Catalysts and Fuel Cell Electrode Materials.** Scott Warren<sup>1,2</sup>, Francis DiSalvo<sup>2</sup> and Ulrich Wiesner<sup>1</sup>;

<sup>1</sup>Materials Science & Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

In this contribution we will describe efforts to combine highly structured mesoporous materials as the catalyst support with recently discovered catalyst materials. At Cornell, we have developed methods for making block copolymer-structured aluminosilicates, which have controllable pore sizes ranging from 10 to 40 nanometers.<sup>1</sup> Furthermore, we have incorporated superparamagnetic nanoparticles into the walls of the aluminosilicate, which demonstrates that these materials can be functionalized (Fig. 1b).<sup>2</sup> Using a similar approach, we now incorporate nanoparticles into the aluminosilicate walls that catalyze fuel cell reactions. The choice of catalytic materials is an important focus of the research. We currently investigate a broad class of intermetallic catalysts to determine suitable materials. PtBi and PtPb can compete with PtRu alloy, showing catalytic activity for methanol, ethanol, and longer-chain alcohols.<sup>3</sup> Additionally, these catalysts show resistance to poisoning and degradation. Incorporation of intermetallic nanoparticles into the aluminosilicate has the potential to produce a supported catalyst with high surface area that is extremely accessible to the fuel. We will show the development of a generic approach to introduce catalytic nanoparticles with adjustable particle size and particle position within the mesoporous material that allows simultaneous control of the materials pore size. This is an important first step towards developing a mesoporous electrode. These materials could be used immediately in the production of hydrogen

from natural gas, and other applications that depend on supported catalysts. 1. M. Templin, A. Franck, A. Du Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schaedler, U. Wiesner, Organically Modified Aluminosilicate Mesostructures from Block Copolymer Phases, *Science* 278 (1997), 1795. 2. C. B. W. Garcia, Y. Zhang, F. DiSalvo, U. Wiesner, Mesoporous Aluminosilicate Materials with Superparamagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Particles Embedded in the Walls, *Angew. Chem. Int. Ed.* 42, (2003), 1526. 3. E. Casado-Rivera et al., Electrocatalytic oxidation of formic acid at an ordered intermetallic PtBi surface. *ChemPhysChem*, 4 (2003), 193.

### 9:30 AM \*M3.4

#### **Pt-Co/C Electrocatalysts for the Oxygen Reduction Reaction in Low Temperature Fuel Cells.** Jose R. C. Salgado, Ermete Antolini and Ernesto Rafael Gonzalez; Fisico Quimica, Instituto de Quimica de Sao Carlos-USP, Sao Carlos, SP, Brazil.

Among the different fuel cell technologies, polymer electrolyte membrane fuel cells (PEMFC), working with hydrogen as a fuel, and direct methanol fuel cells (DMFC), both working at low temperatures, are promising candidates to be used as power sources for portable equipment and in transportation applications [1]. In these systems, platinum nanoparticles supported on carbon (Pt/C) are active catalysts used in the cathode for the oxygen reduction reaction (ORR) [2], which has a slow kinetics and is one of the factors that limit the fuel cell efficiency. Additionally, binary alloy catalysts Pt-M/C (M = Co, Ni, etc.), are being developed to improve catalytic activity and to reduce cost. Binary alloys may also be more tolerant to the presence of methanol, a situation found in the DMFC due to the crossover of methanol from the anode to the cathode through the membrane/electrolyte. The advantage of bimetallic materials with respect to Pt/C for the catalysis of the ORR is attributed to several factors, such as electronic effects, changes in the crystallographic structure, preferential crystalline orientation, more favourable Pt-Pt distance, and the effect on oxide formation. In this work, Pt/C and Pt-Co/C materials were prepared by different methods, like the alloying of Co on a previously formed Pt/C or the simultaneous reduction of appropriate precursors with hydrogen or borohydride [2]. The reduction with borohydride was tested in acid and alkaline media, leading to products with different characteristics. Reduction with formic acid was also tested, producing a non-alloyed bimetallic material. The effect of thermal treatments on the prepared materials was also considered in some cases. The catalysts were characterized by energy dispersive X-ray analysis (EDAX), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). The electrochemical characteristics were determined by cyclic voltammetry and the performance of the materials under operational conditions was evaluated in single fuel cells fed with H<sub>2</sub>/O<sub>2</sub> and methanol/O<sub>2</sub>. The results of this work show that the characteristics of Pt-Co/C materials, like the degree of alloying, particle size and electrochemical activity, depend strongly on the method of preparation. Pt-Co/C catalysts that combine an appropriate degree of alloying, morphology and particle size show an enhanced oxygen reduction kinetics and improved tolerance to the presence of methanol in comparison with Pt/C. [1] W. Vielstich, A. Lamm, H. A. Gasteiger, Handbook of Fuel Cells: Fundamentals, Technology and Applications, New York, 2003. [2] J. R. C. Salgado, E. Antolini, E. R. Gonzalez, Structure and Activity of Carbon Supported Pt-Co Electrocatalysts for Oxygen Reduction. *J. Phys. Chem. B*, 2004, in press.

### 10:30 AM M3.5

#### **Sulfur-Functionalized Carbon Aerogels as Nanoarchitectural Supports for Noble-Metal Fuel-Cell Catalysts.** Wendy S.

Baker<sup>1</sup>, Jeffrey W. Long<sup>1</sup>, Rhonda M. Stroud<sup>2</sup> and Debra R. Rolison<sup>1</sup>;

<sup>1</sup>Surface Chemistry, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Sensors and Materials Branch, Naval Research Laboratory, Washington, District of Columbia.

The design and fabrication of three-dimensional multifunctional architectures from the appropriate nanoscale building blocks presents a new tactic to optimize catalytic chemistries, including those of relevance in fuel cells. Carbon aerogels are ultraporous nanoarchitectures that combine a three-dimensional, high-surface-area network of highly conductive carbon with a through-continuous, three-dimensional porous network, making them attractive scaffolds to design fuel-cell electrodes. Carbon aerogels are not, however, good supports for the noble metal catalysts of relevance in fuel cells. We have overcome this disadvantage by synthesizing thiophene moieties into the precursor polymer aerogel. A traditional resorcinol-formaldehyde (RF) polymer gel is modified by acid-catalyzed reaction with 3-thiophenecarboxaldehyde. The thiophene-modified RF gel is supercritically dried from carbon dioxide to form the aerogel. Heterocyclic sulfur is retained upon pyrolyzing the insulating polymeric aerogel to its conductive carbon aerogel form, as shown by X-ray photoelectron spectroscopy. The sulfur-functionalized carbon (C S) mimics the thiophene-mediated binding of noble metals that occurs with Vulcan carbon, as

demonstrated by adsorbing pre-formed metal colloids (specifically 2.5-nm Pt) from aqueous colloidal solutions under conditions in which unmodified carbon aerogels cannot. The resulting Pt-C S aerogels can be characterized electrochemically for CO adsorption/stripping and catalytic activity for oxygen reduction, and contrasted with standard Vulcan carbon-supported Pt and Pt-colloid-modified Vulcan carbon. Greater than 75% of the Pt surface atoms on colloid-modified C S aerogels are active for CO adsorption and oxidative stripping for a carbon nanoarchitecture derived from RF gels with a large free volume ( $1 \text{ cm}^3/\text{g}$ ) and  $400 \text{ m}^2/\text{g}$  mesoporous/macroporous surface area.

#### 10:45 AM M3.6

##### **Catalytic Nanocarbon Electrodes for Fuel Cell Technologies.**

Keith J. Stevenson, Stephen Maldonado and Ryan Williams; Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas.

Classical carbons such as carbon blacks and activated carbons are frequently used as catalyst supports in fuel cells (FCs) due to specific features including corrosion resistance in highly acidic and basic media, and high electrical conductivity.[1] The primary role of carbon is to maintain the catalytically active phase (e.g., Pt) in a highly dispersed state. Recently, there has been increased interest in using newer carbon forms like carbon nanofibers (CNFs) and carbon nanotubes (CNTs) in FCs due to their purported exceptional structural, electronic, and mechanical properties.[2] Importantly, optimization of electrodes for FCs involves optimization of both the active catalyst, and the composition and structure of the catalyst support. In this presentation, we describe our continued work in the direct synthesis of heteroatom doped carbon nanofiber (CNF) electrodes produced by chemical vapor deposition (CVD).[3] Careful regulation of the CVD deposition parameters allows for controlled growth and doping of CNFs that can function not only as viable catalyst supports, but can also be rendered catalytically active in their own right. Specifically, we describe the preparation of nitrogen doped carbon nanofibers (N-doped CNFs) which exhibit enhanced catalytic activity over non-doped varieties for the chemical decomposition of hydrogen peroxide and for electroreduction of dioxygen. Electrochemical and gasometric methods are used to establish corresponding catalysis mechanisms and to quantify heterogeneous decomposition rate constants for hydrogen peroxide. Electrochemical data is presented which suggests that the oxygen reduction reaction can be treated as a catalytic regenerative process where  $\text{HO}_2^-$  is chemically decomposed to regenerate oxygen. The proposed electrocatalysis mechanism for dioxygen reduction is supported by the observed decomposition rate constants for hydrogen peroxide. These materials may offer promise in the construction of miniature air breathing fuel cells or air batteries. [1] Kinoshita, K. Carbon: Electrochemical and Physicochemical Properties, John Wiley: New York, 1988. [2] Serp, P.; Corrias, M.; Kalck, P.; Appl. Cat. A 253 (2003) 373. [3] Maldonado, S.; Stevenson, K. J.; J. Phys. Chem. B in press.

#### 11:00 AM M3.7

##### **Chemical Modification of Carbon by In-situ Generated Diazonium Salt.** Mathieu Toupin and Daniel Belanger; Chimie, Universite du Quebec a Montreal, Montreal, Quebec, Canada.

Fuel cells can be considered as a mature technology but several industrial, academic and government laboratories are actively involved in research aimed at improving the performance of the fuel cell and the stability of the components and materials as well as reducing the cost of the assembly. The long term objectives of this research project, specifically targeted for polymer electrolyte membrane fuel cell, are to improve the stability of the carbons, to maximize the catalyst utilisation, to improve the membrane-catalyst layer interface conductivity and to integrate the water management to the catalyst layer. An approach to solve these problems is based on the chemical modification of the carbon support. In-situ generated diazonium salts by amino containing molecules were used to modify a carbon black in a one-step synthesis. The Vulcan XC 72R carbon black was modified by reaction with N,N diethylphenylene diamine, 4-aminocarboxylic acid, 4-aminothiophenol, p-nitroaniline and sulfanilic acid. The surface of the modified carbons were characterized by X-ray photoelectron spectroscopy which showed the presence of the characteristic peaks for each of the previously named groups. Elemental analysis of the modified carbon was performed in order to estimate the surface coverage of the carbon by the groups. Thermogravimetric analysis in air showed that the moieties on the surface were fairly stable since mass losses, corresponding to the decomposition of the surface modifications, occurred between 200-400 C, the latter temperature being the burning of carbon.

#### 11:15 AM M3.8

##### **Evaluation of Carbon Nanotube Electrode Assemblies for Proton Exchange Membrane Fuel Cells.** Chad Huffman<sup>2</sup>, Pdraig Moloney<sup>1</sup>, Olga Gorelik<sup>2</sup>, Pasha Nikolaev<sup>2</sup>, Siviram

Arepalli<sup>2</sup>, Lara Oryshchyn<sup>1</sup> and Leonard Yowell<sup>1</sup>; <sup>1</sup>NASA Johnson Space Center, Houston, Texas; <sup>2</sup>GBTech Inc., Houston, Texas.

Fuel cells promise to be one of the most reliable and energy efficient ways to produce electricity in the coming years. One type of fuel cell that is especially promising for many applications is the proton exchange membrane (PEM) fuel cell. This type of fuel cell uses a solid polymer electrolyte (like Nafion™) to transfer protons between two porous electrodes. These fuel cells operate at relatively low temperatures (80°C) as compared to other fuel cells and do not use corrosive liquids as the electrolyte. These factors suggest PEM fuel cells to be suitable as a possible component to meet the demanding energy needs of human space flight applications. Within a membrane electrode assembly (MEA), the electrodes in PEM fuel cells act as a catalyst support (Platinum is the typical catalyst used) and for electrical connections to the application. The electrodes must be electrically conductive but still porous enough for hydrogen gas to diffuse to the catalyst. The surface area of the electrode also dictates the maximum amount of current that the fuel cell can produce. As the surface area of the electrode increases, the amount of hydrogen in direct contact with the electrode and therefore the output current increases as well. Carbon black has been used for electrodes because of the high surface area, chemical inertness under operating conditions, and electrical conductivity. Single wall carbon nanotubes (SWCNTs) meet or exceed carbon black in all these counts. SWCNTs are electrically conductive, they are inert under the operating conditions of PEM fuel cells, and have a high surface area. We will report the performance of fuel cells that incorporate SWCNTs instead of carbon black as the electrode. SWCNT electrodes were formed by filtration; platinum catalyst was deposited using a solution evaporation technique; and the MEA was formed by hot pressing. Chemical inertness, high surface area, electrical conductivity, and the ability to form a free standing structure are all advantageous attributes for PEM electrode material. These attributes will be characterized and comparison drawn between current carbon black technology and the aforementioned SWCNT structures using SEM, TEM and BET surface area analysis. Additional baseline characterization of the SWCNT electrode assemblies using non-destructive evaluation methods will also be presented.

#### 11:30 AM M3.9

##### **Fabrication of a Highly-Active Robust Catalytic Proton Exchange Matrix using Carbon Nanotubes and Pt Nanoparticles in Porous Substrates.** Kishore Uppireddi<sup>2</sup>, Fabrice Piazza<sup>2</sup> and Gerardo Morell<sup>1</sup>; <sup>1</sup>Dept of Physical Sciences, University of Puerto Rico, San Juan, PR, Puerto Rico; <sup>2</sup>Dept of Physics, University of Puerto Rico, San Juan, Puerto Rico.

A highly-active robust catalytic proton exchange matrix are fabricated by directly growing carbon nanotubes (CNTs) into porous membranes and soaking them with Pt nanoparticles. The CNTs are synthesized by hot filament chemical vapor deposition (HFCVD) at low methane concentrations (1-3%) with H<sub>2</sub> as the carrier gas. Long highly-interconnected ropes of CNTs with a negligible presence of amorphous carbon (a-C) are obtained. The synthesis of CNTs is studied by varying the CVD parameters, such as the total pressure, the substrate temperature, the methane concentration and by applying a substrate bias in situ. CNT's are grown on rough silicon, anodized silicon and anodized aluminum oxide substrates using iron oxide nano particles as the catalyst. The carbon nanotubes are characterized by SEM, TEM, XPS and Raman spectroscopy. The intercalation of Pt nanoparticles into the matrix is done electrochemically.

#### 11:45 AM M3.10

##### **Effect of SWNT Purity on PEM Fuel Cell Membranes.**

Herbert J. Ruf, Brian J. Landi, Christopher M. Schauerman and Ryne P. Raffaele; NanoPower Research Laboratories, Rochester Institute of Technology, Rochester, New York.

Considerable interest exists in the application of single wall carbon nanotubes (SWNTs) to proton exchange membrane (PEM) fuel cells. SWNTs have extremely high electrical conductivity, catalytic surface areas, and a large aspect ratio yielding low percolation thresholds, which make them potentially outstanding active materials for PEM electrodes. In previous studies, as-produced SWNTs were combined with commercially obtained E-TEK Vulcan XC-72 and a 5 wt. % Nafion® perfluorinated ionomer solution to produce composite electrode membranes. The addition of SWNTs resulted in fuel cell performance which was equal to or better than that of an equivalent weight percent doping of E-TEK alone, as measured by the maximum power point. This performance was achieved with as much as a 75% reduction in the quantity of platinum incorporated. In the present study we investigate fuel cell performance as a function of the purity and mass doping level of purified SWNTs in both the anode and cathode membranes. SWNTs were synthesized using the pulse laser vaporization technique, employing an Alexandrite laser (755 nm). The

laser pulse was rastered using GSI Lumonics mirrors over the surface of a graphite (1-2 micron) target doped with 2% w/w Ni (submicron) and 2% w/w Co (< 2 micron), at an average power density of 100 W/cm<sup>2</sup>. The reaction furnace temperature was held at 1150°C, with a chamber pressure of 700 torr under 100 sccm flowing Ar(g). The as-produced SWNT materials were purified through the use of solvent washes, acid reflux and oxidative treatment. The resulting purity, as defined as the percent mass fraction of SWNTs in the sample, was assessed by UV-Vis-NIR spectroscopy and thermogravimetric analysis. The SWNTs were also characterized by Raman spectroscopy, surface area analysis (BET) and near-field scanning electron microscopy. Test samples for use in electrode membranes were removed at various points in the purification process to yield materials varying in purity from the as-produced 20% w/w to the fully purified 95% w/w. Fuel cell performance under 1 ATM of hydrogen and oxygen was measured at room temperature using a galvanostatic technique. The resulting performance based the IV (current/voltage) curves as a function of electrode makeup will be presented.

SESSION M4: Fundamentals and the Design of  
Nanoscale Materials

Chairs: Juan Feliu and Carol Korzeniewski  
Tuesday Afternoon, November 30, 2004  
Fairfax A (Sheraton)

1:30 PM \*M4.1

**New Insight into the Mechanism of Bulk Co Oxidation at Pt(111).** Teresa Iwasita and E. A. Batista; Instituto de Quimica de Sao Carlos, Universidade de Sao Paulo, Sao Carlos, Brazil.

Carbon monoxide oxidation at platinum electrodes in acid solutions presents a characteristic behavior depending on the presence or not of dissolved CO in the bulk of the solution. Bulk carbon monoxide is responsible for the formation of a compressed adlayer structure at 0.05V on a Pt(111) electrode. Changes in the adlayer structure can be monitored by in situ FTIRS, through the bands for on-top, two-fold and three-fold bonded CO [1]. It is well known that stripping of CO adlayers at Pt(111) show the main oxidation peak at potentials above 0.7V. On the other hand, when CO is admitted in the cell at 0.05V, a cyclic voltammogram in CO saturated solution exhibits relatively high currents in the potential region below 0.7V [2]. For the latter condition, the current measured at a constant potential of 0.5-0.6V presents a "quasi-stationary" behavior. If CO is admitted in the cell at high potentials (above 0.6V), a marked decay in activity below 0.7V occurs. Under these conditions, infrared spectra show the co-adsorption of CO and H<sub>2</sub>O molecules. The vibrational frequency of the bending mode indicates that water forms an H-bonded structure. Activation of a single H<sub>2</sub>O molecule out of the water cluster can be very difficult; the oxidation of CO is thus inhibited. The influence of the CO partial pressure on the reaction rate was studied. According to these results, bulk CO oxidation follows a Langmuir-Hinshelwood mechanism. References [1] Villegas, I., Weaver, M. J., *J. Chem. Phys.* 1994, 101, 1648. [2] Wieckowski, A.; Rubel, M.; Gutiérrez, C. J. *Electroanal. Chem.* 1995, 382, 97.

2:00 PM \*M4.2

**CO-Tolerant Anode Materials: What We Know and What We Need to Do!** Andrzej Wieckowski, Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Two fuel cell anode materials for methanol oxidation, Pt/Ru and Pt/Os will be interrogated. Both display CO-tolerance that depends on the catalyst surface structure (from supported/unsupported nanoparticles to single crystal studies). Detailed surface CO dynamics data are known for Pt and Pt/Ru via NMR electrochemistry research, that is from EC-NMR with nanoparticle catalysts. The single crystal work, including recent study by sum frequency generation, provides high level of details on the CO oxidation or CO-tolerance mechanisms, furnishing information that has not been previously available. This opens new field of intellectual and technical exploration in search for more active fuel cell anode materials for use in molecular fuel cells. Additional coverage may be provided, and if it is so it will be dedicated to the Pd family of anode catalysts, including Pt/Pd for formic acid and methylformate anode fuel cell catalysis. Reference: A. Wieckowski, E. Savinova and C. Vayenas (Editors), "Catalysis and Electrocatalysis at Nanoparticle Surfaces", Marcel Dekker Inc., New York, Basel, 2003, pp 1-970.

2:30 PM M4.3

**Physical Properties and Electrochemical Response of Pt-Ru/C Supported Nanocatalysts for Direct Methanol Fuel Cells.** William Hernando Lizcano-Valbuena<sup>1</sup>, Carlos O. Paiva-Santos<sup>2</sup>, Erico Teixeira-Neto<sup>1</sup>, Rita Vinhas<sup>3</sup>, Robert Landers<sup>3</sup>, Carlos A. P. Leite<sup>3</sup>, Fernando Galembek<sup>4</sup>, Dayse C. Azevedo<sup>1</sup>, Martha Janete Giz<sup>1</sup>, Edson A. Ticianelli<sup>1</sup> and Ernesto Rafael

Gonzalez<sup>1</sup>; <sup>1</sup>Fisico Quimica, Instituto de Quimica de Sao Carlos-USP, Sao Carlos, SP, Brazil; <sup>2</sup>Instituto de Quimica, UNESP, Araraquara, SP, Brazil; <sup>3</sup>Instituto de Fisica, UNICAMP, Campinas, SP, Brazil; <sup>4</sup>Instituto de Quimica, UNICAMP, Campinas, SP, Brazil.

In this work, the physical characterization of Pt/C and Pt-Ru/C 82:18 electrocatalysts prepared by a modification of the chemical reduction with formic acid (FAM)[1] is discussed and correlated with the electrochemical response for methanol electrooxidation in half and single fuel cells. The characterization techniques used were: Energy Dispersive X-rays Analysis (EDX), Electron Back-scattering, X-Rays Diffraction (XRD), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM), X-Rays Absorption (XAS) and X-Rays Photoelectron Spectroscopy (XPS). The electrochemical response was evaluated by voltammetric techniques and cell potential vs current density curves obtained in a single DMFC. Pt and Pt-Ru catalysts supported on high surface area carbon were prepared as described recently [1] to obtain a homogeneous distribution of metal particles on the carbon support, observed in nanoscale by TEM and in microscale by backscattering. The particle size determined by XRD, using Scherrer equation and applying the Rietveld method to the XRD peaks was 3.9 - 4.0 nm (using the (111) and (220) reflection peaks) assuming a spherical form of the particles and considering the corrections due to the i) instrumental effects, ii) particle size and iii) strain lattice. The lattice parameter of Pt-Ru/C 82:18 (0.39052 nm) was lower than that for Pt/C (0.39161 nm) suggesting the insertion of Ru into the Pt fcc structure, but partial if compared with the Vegard law value. The broad particle size distribution was determined by HRTEM, founding in two cases an average value of 5.5 nm. The surface species determined by XPS show for Pt/C 68.5 % of metallic Pt (more than in Pt/C E-TEK) and 18 % of Pt(OH)<sub>2</sub>, higher than the 15.9 % of Pt/C E-TEK. For Pt-Ru/C 82:18, there is a considerable quantity (62.5 %) associated to metallic Ru and RuO<sub>2</sub> and 22.3 % of RuO<sub>3</sub> present as amorphous species. In the XANES spectra it was observed an increment of the white line with the Ru content due to electronic effects on the 5d band of Pt. EXAFS analysis indicates that Pt-Ru/C materials prepared by the FAM are not true alloys. Cyclic voltammograms obtained with thin film electrodes prepared with these catalysts show a very clean surface for both Pt/C and Pt-Ru/C. In a single DMFC the catalysts were tested with Nafion 112 membrane as electrolyte giving a maximum power density of 160 mWcm<sup>-2</sup>, when using 1 mgPtcm<sup>-2</sup> in the electrodes. From 30 to 90 C and between 1 and 3 atm pressure of O<sub>2</sub> the power density is similar or higher than that obtained with Pt-Ru/C 50:50 E-TEK catalysts. The better performance of FAM catalysts in comparison with commercial catalysts may be attributed to i) better morphology, ii) a cleaner surface and iii) a higher percentage of metallic Pt and Pt(OH)<sub>2</sub> species. [1] W. H. Lizcano-Valbuena, D. C. Azevedo, E. R. Gonzalez, *Electrochim. Acta* 49 (2004) 1289.

3:15 PM \*M4.4

**Parallel Reaction Pathways for Methanol and Ethanol Oxidation at Porous Fuel Cell Electrodes.** V. Paganin, G.R. P. Malpass and W. Vielstich; IQSC, University of Sao Paulo, Sao Carlos, Brazil.

The potential/time behavior at cathodes and anodes of small fuel cells (4.6cm<sup>2</sup>) is studied for methanol and ethanol oxidation. At 60-80°C a continuous flow of fuel and dry oxygen to the porous surfaces (PtRu/C and Pt/C) is used, the electrodes being separated by a Nafion 117 membrane. Alcohol crossover to the cathode occurs already at open circuit and causes a shift of the oxygen potential up to several hundred mV. The shift in potential is strongly dependent on alcohol concentration. Applying a constant load of 100mA/cm<sup>2</sup> (for ethanol) and 200mA/cm<sup>2</sup> (for methanol), a rather constant cell voltage is obtained after some minutes. Probes from the liquids in the outflow of anode and cathode, taken after 60-180min, are analysed by HPLC, for all reaction products. From the above data and the total consumption of alcohol a first estimation of alcohol crossover is possible. It is shown that the strong pathway distribution as observed with smooth electrodes does not determine the faradaic efficiency in fuel cell operation. Using methanol at concentrations below 0.5M, temperatures as low as 60°C and current densities above 100mA/cm<sup>2</sup>, the fuel crossover is of minor importance. Under such conditions, the number of electrons per methanol molecule obtained is near the maximum value of six. At porous electrodes, the unsuitable pathways with formic acid and formaldehyde as intermediates are obviously compensated by further reaction steps forming CO<sub>2</sub>.

3:45 PM M4.5

**Theoretical study on dissociation pathways for oxygen on platinum surfaces.** Satoshi Yotsuhashi<sup>1</sup>, Yuka Yamada<sup>1</sup>, Wilson Agerico Dino<sup>2,3,4</sup>, Hiroshi Nakanishi<sup>2</sup> and Hideaki Kasai<sup>2</sup>; <sup>1</sup>Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., Soraku-gun, Kyoto, Japan; <sup>2</sup>Department of Applied Physics, Osaka University, Suita, Osaka, Japan; <sup>3</sup>Japan Science and

The interaction of oxygen with platinum (Pt) surfaces has been intensively investigated due to their significance in various industrial processes, e.g., reactions in cathode electrodes used in fuel cells. One of the most important processes to be clarified is the dissociative adsorption of oxygen, which serves as a rate limiting step in various complex reactions. From experimental results using various surface science techniques, it has been clarified that oxygen chemisorption strongly depends on the Pt surface configuration. In order to gain a fundamental understanding of the mechanism from a theoretical point of view, the dissociative adsorption process for oxygen on the platinum surfaces of Pt(001) and Pt(111) are investigated based on first principles calculation. We calculate the total energy of the whole system, varying the distance between the surface and the center-of-mass of the O<sub>2</sub> molecule (*Z*), and the distance between the O atoms (*r*), and determine the reaction path. When *Z* is large enough, the equilibrium distance between O atoms corresponds to  $r \approx 1.2 \text{ \AA}$ , and the two O atoms form an O<sub>2</sub> molecule. As the oxygen molecule approaches the platinum surfaces, we find a potential minimum at  $Z \approx 1.2 \text{ \AA}$  and  $r \approx 2.8 \text{ \AA}$  on the Pt(001) surface, while we cannot find such a potential minimum on the Pt(111) surface. This result is in good agreement with the experimentally observed difference in reactivity between Pt(001) and Pt(111). This indicates the strong sensitivity of the oxygen dissociative adsorption on the local surface configuration, and the importance of surface local properties over bulk properties in understanding the oxygen dissociative adsorption mechanism.

#### 4:00 PM \*M4.6

##### Electrocatalyses on Pt Alloys at Fuel Cell Reactions Studied with Various Electrochemical In-Situ Spectroscopies.

Masahiro Watanabe, Clean Energy Research Center, University of Yamanashi, Kofu, Yamanashi, Japan.

By applying our convenient alloy preparations, we have found various electrocatalysts alloyed precious metals or precious and non-precious metals for the oxidations of CH<sub>3</sub>OH and the oxidation derivatives including CO and also for CO tolerant H<sub>2</sub> oxidation. Among them, Pt-Ru alloy is still one of the best catalysts for such fuel cell reactions. Recently, we have demonstrated that Pt alloys with transient non-precious metals exhibit a superior CO tolerance to H<sub>2</sub> oxidation, obtained at Pt skin-layer formed on the alloy surface after dissolving non-precious metals. The surface coverage of Pt skin with CO was lowered and the activity independent of CO coverage was in the same level to that of clean Pt surface. The catalysis has been explained by the increased 5d-vacancy of the skin Pt modified by underlying alloy property. In order to find a clue for designing more active or cheaper catalysts than the present levels, it is important to elucidate the mechanism of their oxidation on the above alloy and Pt skin electrodes. The author will show experimental results recently obtained by in-situ XPS, UPS, or ATR-FTIRS systems combined with electrochemical cell, and discuss about the catalyses. As-prepared Pt alloys with non-precious metals, e.g. Pt-Fe, show clear positive chemical-shifts in 4d or 4f core-electron orbital of Pt and a reduction of the electron population at Fermi-edge of the alloyed Pt, compared with that of bulky pure Pt, suggesting an electron transfer from Pt to Fe and the increased 5d vacancy. The same level modification was observed at Pt skin formed by the electrochemical pre-treatment. No noticeable back-donation of 5d electron but the donation of 5-sigma electron between Pt skin and CO molecule was observed, although the both electron transfers were clearly observed at bulky Pt. The former must cause the lowered CO coverage and bond strength at Pt skin surface sites (increased CO free sites for H<sub>2</sub> adsorption/oxidation or increased mobility of CO on the surface), resulting in the improved CO tolerance. The weakly bonded CO was desorbed in UHV or oxidized electrochemically more easily than that on bulky Pt. The similar modification of Pt electronic property by alloying with precious metals was observed. Due to always presence of the second atoms as neighbor sites for Pt, however, a different catalysis could be expected. At the in-situ ATR-FTIRS on Pt and Ru or Pt-Ru in 0.1 M HClO<sub>4</sub> with saturated CO or 1M CH<sub>3</sub>OH, adsorbed H<sub>2</sub>O molecule was observed distinctively at Ru and Pt-Ru, and adsorbed CO was done at all of the catalysts. The H<sub>2</sub>O decreased steeply together with the decrease of adsorbed CO, consisting with the increase of oxidation currents of CO or CH<sub>3</sub>OH at 0.2V less positive than those at Pt. On the alloy, Pt plays CO adsorption sites and Ru does those of H<sub>2</sub>O for CO oxidation. The results first support experimentally the bi-functional mechanism, previously proposed by us to the enhanced oxidation of CO and CH<sub>3</sub>OH on PtRu alloys.

#### 4:30 PM M4.7

##### Alloys Which Form Conductive and Passivating Oxides for PEM Fuel Cell Bipolar Plates. Margarita Petrova Thompson,

Simon S. Wang, Neil Aukland, Joseph V. Mantese, David S. Eddy and Abdellah Boudina; Delphi Research Labs, Delphi Corporation, Shelby Township, Michigan.

During the operation of proton exchange membrane (PEM) fuel cells, a high-resistance oxide is often formed on the cathode surface of base metal bipolar plates. Over time this corrosion mechanism leads to a drop in fuel cell efficiency and potentially to complete failure. To address this problem, we have developed alloys capable of forming oxides that are both conductive and chemically stable under PEM fuel cell operating conditions. Five alloys of titanium with tantalum or niobium were investigated. The oxides were formed on the alloys by cyclic voltammetry in solutions mimicking the cathode- and anode-side environment of a PEM fuel cell. The oxides of all tested alloys had lower surface resistance than the oxide of pure titanium. We also investigated the chemical durability of Ti-Nb and Ti-Ta alloys in more concentrated solutions beyond what is typically found in PEM fuel cells. The oxide films formed on the alloys remained conductive and chemically stable in these concentrated solutions. The stability of the oxide films was evaluated, and Ti alloys having 3% Ta and Nb were identified as potential candidates for bipolar plate materials.

#### 4:45 PM M4.8

##### Characterization and Performance Evaluation of

##### Carbon-Supported Platinum Nanoparticles for PEM Fuel Cells. Pyoungcho Choi<sup>1</sup>, Odysseas Paschos<sup>1</sup>, Manisha Rane<sup>1</sup>, Harry

Efstathiadis<sup>1</sup>, Nazarali Merchant<sup>2</sup>, Steve Buelte<sup>2</sup>, Rick Gaylord<sup>2</sup> and Pradeep Haldar<sup>1</sup>; <sup>1</sup>College of Nanoscale Sciences and Engineering, University at Albany - State University of New York, Albany, New York; <sup>2</sup>Plug Power, Latham, New York.

Proton-exchange membrane (PEM) fuel cells are rapidly gaining importance for being the power source for both mobile and stationary uses due to their improved performance at low temperatures. Recently, considerable attention has been given to the preparation of highly active nanoparticles of platinum-based electrocatalysts to increase electrode performance at low Pt loading. Although the relation between the particle size and electrocatalytic activity remains current subject of discussion, the synthesis of nanosized particles is considered to be one of the most challenging tasks in fuel cell research. Carbon supported Pt nanoparticles were prepared by impregnation, precipitation, and colloidal methods. The catalysts were analyzed by various characterization techniques that will help to understand and optimize the performance of the PEM electrodes. The particle sizes of Pt were in the order of 2-4 nm for low Pt loading of 10 % and 20 %, and 9-14 nm for 40 % Pt loading, as measured by Transmission Electron Microscopy and X-ray Diffraction techniques. The prepared Pt/C nanoparticles were compared to commercial electrodes from E-tek and Johnson Matthey in terms of their particle size and morphology. The performance of the prepared electrodes was studied in 50 cm<sup>2</sup> H<sub>2</sub>-O<sub>2</sub> fuel cells. Membrane Electrode Assemblies were prepared with PBI membrane and Pt/C (0.4 mg Pt/cm<sup>2</sup>) for the anode and cathode with various loadings of Pt on carbon from 10 to 40 %. The surface and sub-surface morphology of Pt/C electrodes on the gas diffusion layer were analyzed by Focused Ion Beam and Scanning Electron Microscopy. Also, the chemical composition and delineation of the fluorine and platinum distribution in the catalyst layer were determined by Energy Dispersive Spectroscopy and X-ray Photoelectron Spectroscopy. Fuel cell performance of the prepared Pt/C electrocatalysts will be presented. Correlation between processing, microstructure, and electrochemical performance of the electrocatalyst will also be presented.

#### SESSION M5: Poster Session

Chairs: Hector D. Abruna and Debra R. Rolison

Tuesday Evening, November 30, 2004

8:00 PM

Exhibition Hall D (Hynes)

#### M5.1

##### Methods for Preparing PtBi and PtPb Intermetallic Nanoparticles for Direct Fuel Cell Applications.

Laif Robert Alden,<sup>1</sup> Chemistry & Chemical Biology, Cornell University, Ithaca, New York; <sup>2</sup>Chemistry & Chemical Biology, Cornell University, Ithaca, New York.

Methods for the preparation of PtBi and PtPb intermetallics as nanoparticles. According to electrochemical performance data of bulk sample, these the materials show promise of being interesting catalysts in direct fuel cells. However, for real fuel cell applications, it will be necessary to synthesize these materials as nanoparticles. Nanoparticles of such materials are difficult to produce. The usual method of chemical reduction from metal salts often does not yield the desired small crystalline nanoparticles when the reduction potential of the two metal species differs by 1.13 V and 1.56 V, respectively. Nevertheless, PtBi nanoparticles can be reduced from corresponding metal chloride solutions by NaBH<sub>4</sub> with a mean particle size as small as 4nm, depending on solvent used, in the

presence of the surfactant N(Oct)4Br. PtPb nanoparticles with a mean particle size of 20nm can be reduced from corresponding metal chlorides with LiBH<sub>4</sub> in the presence of N(Oct)4Br.

#### **M5.2**

##### **Intermetallic Nanoparticles for Fuel Cell Applications: Syntheses and Characterization Studies.**

Chandrani Roychowdhury and Francis J. DiSalvo; Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

In the quest for improved anode electrocatalysts for direct fuel cells, several Platinum containing intermetallic systems have been investigated, focusing on attempts to synthesize pure phases of many such compounds in nanoparticle form. Various synthetic techniques have been attempted, and this has led to the formation of many intermetallic compounds with varying particle sizes. We present here, our results from different synthetic techniques that we have used to synthesize pure phases of Pt containing intermetallic nanoparticles. PtPb has been synthesized by reduction of the corresponding metal salts with hydrazine. The mean particle size has been of the order of 20nm and this can be controlled by use of different surfactants. Results from the characterization studies of these nanoparticles using XRD, SEM and UHV-STEM analyses, have been presented. The Polyol process has been used to synthesize other Platinum containing intermetallic nanoparticles like PtBi, and results from this synthetic technique are also presented.

#### **M5.3**

##### **Preparation and Characterization of Long-Lived Anode Catalyst for Direct Methanol Fuel Cells.**

Yuzuru Shimazaki<sup>2,3</sup>, Yoshio Kobayashi<sup>1</sup>, Masatoshi Sugimasa<sup>4</sup>, Shinji Yamada<sup>3</sup>, Takeyuki Itabashi<sup>4</sup>, Mikio Konno<sup>1</sup> and Takao Miwa<sup>4</sup>; <sup>1</sup>Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, Sendai, Miyagi Pref., Japan; <sup>2</sup>Tohoku Technoarch, Sendai, Miyagi Pref., Japan; <sup>3</sup>Advanced Research Laboratory, Hitachi Ltd., Hitachi, Ibaraki Pref., Japan; <sup>4</sup>Hitachi Research Laboratory, Hitachi Ltd., Hitachi, Ibaraki Pref., Japan.

Direct-methanol fuel cells (DMFCs) have been gaining interest because of their potentials for high power density and simplicity of recharging; only by replacing methanol cartridge. The power density of DMFCs is influenced by various factors such as (i) degree of turnover of the fuel into the cathode and (ii) surface area of catalyst in the anode. The surface area of catalyst is known to reduce with time in the anodic environment because high surface energy of the catalyst nanoparticles induces their aggregation. Therefore, the power density of DMFCs decreases with time, which is one of the crucial problems for the entry of DMFCs into the market. This paper presents a novel approach to maintain the activity of the anode catalyst. The catalyst contained PtRu alloy nanoparticles with porous skin layers on their surface, which were formed by reaction of surface-active PtRu nanoparticle colloids with silicate ions. The catalyst showed catalytic activity comparable to that obtained commercially, and maintained its catalytic activity for over 1000 hours in highly acidic condition (in 1.5 M H<sub>2</sub>SO<sub>4</sub> solution). The skin layers on the surface of PtRu nanoparticles would prevent aggregation, while the porous structure of skin layers would keep the paths of the reactants diffusing to / from the catalytic surface, resulting in such stable catalytic activity toward methanol oxidation. The catalyst thus prepared would be one of the candidates for long-lived anodes of DMFCs.

#### **M5.4**

**Highly Dispersed Pt Supported on Carbon Catalyst with High Loading for Direct Methanol Fuel Cell.** Chanho Pak, Dae Jong You, Seol-Ah Lee and Hyuk Chang; Materials and Devices Lab, Samsung Advanced Institute of Technology, Yongin-Si, Gyeonggi-Do, South Korea.

Direct methanol fuel cell (DMFC) is a promising power source for portable electronics because it can be operated at ambient condition with air and portable methanol. To reduce the thickness of electrode and increase the performance of DMFC, it is requested to prepare the highly dispersed carbon-supported Pt catalyst with high loading. In this presentation, highly dispersed carbon-supported Pt catalyst with 60wt% was prepared by new incipient-wetness impregnation method and applied to the DMFC single cell. The particle size of Pt, determined by X-ray diffraction, was decreased to 2.8nm from that of conventional impregnation method and the dispersion of Pt particle, estimated by transmission electron microscopy, on the carbon support was improved. The overall performance of single cell using this catalyst and Pt black catalyst at the cathode with 2 mg/cm<sup>2</sup> Pt loading was measured using methanol and air at 313K. Current density at 0.4V is 127 mA/cm<sup>2</sup> for the new catalyst prepared in this time and 72 mA/cm<sup>2</sup> for Pt black, respectively. It is suggested that the high dispersion and small particle size of Pt on the catalyst is contributed to increase the performance at 313 K.

#### **M5.5**

##### **Modification of Carbon: Application to Fuel Cell.**

Mathieu Toupin and Daniel Belanger; Chimie, Université du Québec à Montréal, Montréal, Québec, Canada.

Fuel cells can be considered as a mature technology but several industrial, academic and government laboratories are actively involved in research aimed at improving the performance of the fuel cell and the stability of the components and materials as well as reducing the cost of the assembly. The long term objectives of this research project, specifically targeted for polymer electrolyte membrane fuel cell, are to improve the stability of the carbons, to maximize the catalyst utilisation, to improve the membrane-catalyst layer interface conductivity and to integrate the water management to the catalyst layer. An approach to solve these problems is based on the chemical modification of the carbon support. In-situ generated diazonium salts by amino containing molecules were used to modify a carbon black in a one-step synthesis. The Vulcan XC 72R carbon black was modified by reaction with N,N diethylphenylene diamine, 4-aminocarboxylic acid, 4-aminothiophenol, p-nitroaniline and sulfanilic acid. The surface of the modified carbons were characterized by X-ray photoelectron spectroscopy which showed the presence of the characteristic peaks for each of the previously named groups. Elemental analysis of the modified carbon was performed in order to estimate the surface coverage of the carbon by the groups. Thermogravimetric analysis in air showed that the moieties on the surface were fairly stable since mass losses, corresponding to the decomposition of the surface modifications, occurred between 200-400 C, the latter temperature corresponding to the burning of carbon.

#### **M5.6**

##### **Platinum-Embedded PAN-Based Carbon Nanofibers.**

Lei Zhang<sup>1</sup>, Bin Cheng<sup>2</sup> and Edward T. Samulski<sup>1,2</sup>; <sup>1</sup>Curriculum in Applied Materials Sciences, University of North Carolina, Chapel Hill, North Carolina; <sup>2</sup>Chemistry, University of North Carolina, Chapel Hill, North Carolina.

Hexagonally-packed porous anodic aluminum oxide (AAO) templates are made by two-step anodization of highly pure aluminum foil. Close-packed PAN nanofibers containing a platinum compound were fabricated by polymerization of acrylonitrile in this AAO template. During pyrolysis, Pt(II) is reduced to elemental Pt with the Pt particles embedded in the PAN-based carbon nanofibers. The morphology and composition of the fibers were characterized by SEM, TEM and XPS. The catalytic activity of composite nanofibers is studied by rotating disc electrode (RDE) voltammetry.

#### **M5.7**

##### **Role of the Ti Buffer Layer on the Electrochemical Properties of Arrayed CNx Nanotubes on Silicon Substrates.**

Wei-Chuan Fang, Jin-Hua Huang, Oliver M. Chyan, Chia-Liang Sun, Li-Chyong Chen and Kuei-Hsein Chen; Center for Condensed Sciences, National Taiwan University, Taipei, Taiwan.

Effects of Ti buffer layers on arrayed nitrogen-containing carbon nanotubes (CNxNTs) on Si substrates have been investigated in this paper. After depositing Fe thin films as catalysts on Ti buffered Si, CNx NTs were directly grown on Si substrates by microwave plasma enhanced chemical vapor deposition (MWPECVD) process. The use of Ti layers does not affect the qualities of the CNxNTs in that the Raman spectra are similar for samples grown on Si with and without Ti layers. However, shorter CNxNTs, with lower number density, were observed on thick Ti-layer coated Si although they all kept good alignment. Furthermore, we used ferricyanide as the molecule probe to study the electrochemical properties of CNx NTs on Ti layers with different thicknesses. Our preliminary studies suggest that the morphology of CNx NTs and the resistivity of current collector on Si surface are important factors for the performance of the electrochemical microsystems with nanomaterial integration. Through cyclic voltammetry analyses, it is found that the highest current peak density from electrochemical reaction of Fe(CN)<sub>6</sub><sup>3-/4-</sup> can be achieved with the optimized Ti thickness of 20 nm.

#### **M5.8**

##### **An Electrochemical Method to Estimate the Diffusion Coefficients of Methanol in Anode Assembly of Direct Methanol Fuel Cell.**

Chien-Ming Lai<sup>1</sup>, Jing-Chie Lin<sup>1</sup>, Kan-Lin Hsueh<sup>2</sup> and Chiou-Ping Huang<sup>2</sup>; <sup>1</sup>Department of Mechanical Engineering, National Central University, Jhongli, Taiwan; <sup>2</sup>Materials Research Laboratories, Industrial Technology Research Institute, Hsin Chu, Taiwan.

Direct methanol fuel cells (DMFCs) are very attractive in the transportation and portable applications. However, methanol crossover from anode to cathode through the polymer membrane is a problem to cause poor performance of the DMFCs. In general, this crossover effect could be diminished by using either polymer

electrolytes that are methanol-impermeable or micro-porous layers that are coated on gas diffusion layer (GDL). The mass-transport of methanol in the anodic assembly should be concerned in this sense. It was of interest to develop a simple method to estimate the methanol transport in the component layers of the anodic assembly in DMFCs. Diffusion coefficients of the methanol in several commercial GDLs and Nafion membranes were estimated in terms of measurement of impedance using electrochemical impedance spectroscopy (EIS). The diffusion coefficients of methanol in each component layers were collected and combined. There is a good agreement in between the coefficients calculated from theoretical models and those measured by this method in some combination systems of the component layers. According to this model we are capable of expectation the crossover amount of methanol from anode to cathode in a DMFC.

#### **M5.9**

**Direct Preparation of Gd-CeO<sub>2</sub> Micro Tube Ceramics using Hydrolysis Reaction of Gel Precursor.** Yoshinobu Fujishiro, Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya, Japan.

Low temperature (<650°C) solid state oxide fuel cell (SOFC) have been much attention for compact generator such as APU system in Truck. GDC electrolyte is known as high ionic conductivity between 500-700°C, and it is possible to reduce working temperature in SOFC. For the purpose of preparation of the micro sized SOFC cell, we are carried out fabrication of GDC hollow fiber as SOFC electrolyte using sol-gel processing. When hybrid gel prepared by mixing both GaCl<sub>3</sub>-CeCl<sub>3</sub> solution and PVA polymer was put into NH<sub>4</sub>OH solutions, precursor of Gd-doped CeO<sub>2</sub> (GDC) fiber formed at room temperature. The prepared fibrous precursors showed hollow structure by washing inner gel. After sintering at 1400°C, the tube GDC formed with densification. Furthermore, multilayered SOFC cell coated electrodes on the surface of the prepared tube GDC ceramics. The structure and properties of the obtained products are presented.

#### **M5.10 TRANSFERRED TO M8.5**

#### **M5.11**

**In situ High Temperature Characterization of La-Cr-O Thin Films by Micro-Raman, XRD, and TEM.** Nina Orlovskaya<sup>1</sup>, David Steinmetz<sup>1</sup>, Sergey Yarmolenko<sup>2</sup>, Jag Sankar<sup>2</sup>, Chris Johnson<sup>3</sup> and Randall Gemmen<sup>3</sup>, <sup>1</sup>Drexel University, Philadelphia, Pennsylvania; <sup>2</sup>North Carolina A&T State University, Greensboro, North Carolina; <sup>3</sup>National Energy Technology Laboratory, Morgantown, West Virginia.

The deposition of an amorphous La-Cr-O thin film on a stainless steel was done by radio frequency magnetron sputtering to obtain a protective coating on the metallic interconnect for solid oxide fuel cells. The deposited film was amorphous, but underwent two phase transformations to the perovskite structure as a result of annealing at 700°C for 1 hour in air. The first transformation was from amorphous to the monoclinic LaCrO<sub>4</sub> monazite type compound. The second transformation was from LaCrO<sub>4</sub> to orthorhombic LaCrO<sub>3</sub> perovskite. As a result of the phase transformation nanostructured self-assembled dendritic structure was formed with the desired perovskite phase. The in situ high temperature structural characterization of the film was done by micro-Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM) with energy dispersive X-ray analysis (EDS). The mechanisms of the amorphous to the LaCrO<sub>3</sub> orthorhombic phase transitions have been studied.

#### **M5.12**

**Fabrication and Testing of a Planar Membraneless Microchannel Fuel Cell using Formic Acid and H<sub>2</sub>/O<sub>2</sub> Fuel Systems.** Jamie Lee Cohen<sup>1</sup>, Daron A. Westly<sup>2</sup>, Alexander Pechenik<sup>3</sup> and Hector D. Abruna<sup>1</sup>, <sup>1</sup>Chemistry and Chem. Bio., Cornell University, Ithaca, New York; <sup>2</sup>Cornell Nanofabrication Facility, Cornell University, Ithaca, New York; <sup>3</sup>-92-6, LLC, Ithaca, New York.

A novel design for a planar membraneless microchannel fuel cell (PM<sup>2</sup>FC) is presented. The design, which eliminates the need for a polyelectrolyte membrane (PEM), takes advantage of the laminar flow of fuel and oxidant streams generated at a tapered flow boundary. This gives rise to a "virtual membrane" with diffusion at that interface being the only mode of mass transport between the two solutions. In addition, proton conduction occurs readily, and fuel crossover is virtually eliminated. Our planar design also gives rise to large contact areas between the electrodes and fuel and oxidant streams. As electrodes, we have employed platinum evaporated onto a polyamide film (Kapton®), allowing for the reproducible preparation of large-area electrode surfaces, which are also convenient for testing. Silicon microchannels, of varying width and height, have been tested and parameter optimization has been carried out using formic acid as fuel and oxygen as oxidant. Power densities on the order of 180 mW cm<sup>-2</sup> have been obtained using this planar design. The open circuit

potentials, as well as the kinetic behavior, observed for the formic acid fuel using this micro-fuel cell are compared to those of macro-fuel cell systems. Using the above PM<sup>2</sup>FC design, we have also looked at the H<sub>2</sub>/O<sub>2</sub> fuel cell system. The versatile platform without the polyelectrolyte membrane allows the investigation of this fuel system in acidic electrolyte, as well as basic electrolyte, environments. Open circuit potentials of over 0.90 V and power densities of 0.75 mW/cm<sup>2</sup> have been observed when these H<sub>2</sub>/O<sub>2</sub> fuel cell systems were employed.

#### **M5.13**

**High Throughput Screening of CO-tolerant Anode Materials by IR thermography.** Yusuke Yamada, Atsushi Ueda, Hiroshi Shiyoyama, Tsutomu Ioroi, Kazuaki Yasuda and Tetsuhiko Kobayashi; RI for Ubiquitous Energy Devices, AIST, Ikeda, Osaka, Japan.

Development of highly CO tolerant anode material allows the utilization of reformed hydrogen including CO of relatively high concentration. Usually, the evaluation of CO tolerance of each anode candidate is performed by CO stripping measurement on cyclic voltammetry. For the measurements, we need to prepare electrode with each candidate. If we can evaluate the catalysis without preparation of electrode, we can accelerate the catalyst investigation due to the reduction of time consuming process. We have developed noble methodology for the evaluation of CO tolerance of anode materials by using IR thermography. The utilization of IR thermography realizes high throughput screening of catalyst library 2-dimensionally arrayed. The catalysis activities of hydrogen combustion in the presence of CO and water gas shift reaction on each candidate were evaluated in gas phase with IR thermograph. The catalysis on hydrogen combustion can be correlated to its electrocatalysis of hydrogen molecule decomposition. The activity on water gas shift reaction provides information about the removal of CO adsorbed on anode by the reaction with water. The combinatorial catalyst library consisting of Pt-A-B where A, B were chosen from Ti, Ge, Ce, Ta, Nb, Zr, Mo whose solubility of corresponding oxides to sulfuric acid is negligibly small. The ratios among Pt, A and B were systematically changed with 15 variations. A series of catalyst was evaluated at the same time. The catalyst array was put in a flask with gas inlet and outlet. The catalysts were exposed to 2000 ppm H<sub>2</sub> and 1000 ppm O<sub>2</sub> with/without 1000 ppm CO. Many catalysts suddenly lost their hydrogen combustion catalysis when CO was introduced to the reaction gas. On the other hand, some specific combinations of Pt-Ta-Ti, Pt-Ta-Ge, Pt-Mo-Zr and Pt-Mo-Ce system maintained H<sub>2</sub> combustion catalysis in the presence of CO. The electrochemical evaluation results of these catalysts will be also presented to be discuss the accuracy of the high throughput screening method. This work was financially supported by NEDO program of "Research and Development of Polymer Electrolyte Fuel Cell."

#### **M5.14**

**Analytical TEM Study of the Degradation Phenomena in Proton Exchange Membrane Fuel Cell.** Tomoki Akita, Junko Maekawa, Akira Taniguchi, Koji Tanaka, Masanori Kohyama and Kazuaki Yasuda; Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan.

Proton exchange membrane fuel cells (PEMFCs) are attractive power sources as a low-emission power source for electrically powered vehicles and distributed power generation. Small-sized PEMFCs (micro-fuel cells) have also been developed as power sources of portable equipment such as laptop computers, cellular phones, power tools, and so on. Reliability and lifetime are the most important issue in such power sources for practical use. However, the deterioration mechanisms of PEMFC are not well understood. Thus, it is quite important to investigate the degradation mechanisms under the various operation conditions. In this work, a single cell of PEMFC with Pt-Ru/C anode and Pt/C cathode catalysts after various accelerated tests were observed by analytical TEM in order to investigate the structural changes of electrode catalysts and PEM in micro- and nano-scale. Analytical TEM has great advantage that it can reveal the spatial distributions of the components and analyze the composition of local area. It is indispensable tool for the analyses of functional materials which has complex structure in nano-scale. The cross-sectional specimen of membrane electrode assembly (MEA) for TEM observation was prepared by an ultramicrotome. The fragment of MEA was supported on the Cu mesh with carbon micro-grid. The observations were performed by a JEOL JEM-3000F transmission electron microscope equipped with energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS) and annular dark field scanning transmission electron microscopy (ADF-STEM) systems. The thin area of electrode catalyst layer and the proton exchange membrane were successfully observed. The interface of catalyst layer and PEM was also observed. It was found that the mean diameter of Pt-Ru and Pt particle became larger after the cell reversal test in fuel starvation. The change was drastic in anode catalyst. Small particles under 2nm disappeared and mean

diameter increased from 2.6 nm to 5.0 nm. It was also revealed by EDS analyses that the Ru concentration decreased from 50% to 20% in the Pt-Ru/C anode catalyst. The compositions of each particle were also measured by STEM-EDS method. Some small particles consisted of Pt only. Moreover, it was found that the large particles about 10-50 nm were observed in the PEM after the potential cycling test. This result means the Pt dissolved and diffused, then the Pt aggregate in the membrane. It seems that potential changes of electrode promoted the dissolving and diffusion of Pt particles.

#### **M5.15**

##### **Mesoporous Carbon Molecular Sieves from Mesoporous Benzene Silica as Catalyst Support for Fuel Cells.**

Decio Coutinho, Zhiwei Yang, Fangxia Feng, John Ferraris, Duck Joo Yang and Kenneth J. Balkus, Jr.; Chemistry, University of Texas at Dallas, Richardson, Texas.

Mesoporous carbon molecular sieve was prepared from mesoporous benzene silica (MBS). MBS, which is synthesized using 1,4-bis(triethoxysilyl)benzene and octadecyltrimethylammonium surfactant, is a hybrid mesoporous composite with molecular scale periodicity in the pore walls. MBS also displays a homogeneous distribution of the phenyl rings within the pore walls. To prepare the mesoporous carbon, H<sub>2</sub>PtCl<sub>6</sub> was introduced into the pores of template free MBS by an incipient wetness process and the resulting MBS/H<sub>2</sub>PtCl<sub>6</sub> powder was heated under vacuum to 1150°C. This process produced a mesoporous graphitic framework with surface area of 950 m<sup>2</sup>/g and pore size in the 1.7-2 nm range. These materials were characterized by X-ray diffraction, scanning and transmission electron microscopy and nitrogen adsorption. The electrocatalytic activity of the catalysts under fuel cell operating conditions will also be discussed.

#### **M5.16**

##### **Electrocatalytic Activity of Ordered Intermetallic Phases for Fuel Cell Applications.**

Emerilis Casado Rivera, Hector D. Abruna, Francis J. DiSalvo, David J. Volpe, Craig Downie, Laif R. Alden and Chandrani Roy Chowdhury; Chemistry & Chemical Biology, Cornell University, Ithaca, New York.

The electrocatalytic activities of a wide range of ordered intermetallic phases toward a variety of potential fuels have been studied, and results have been compared to those of pure polycrystalline platinum (Pt). A significant number of the ordered intermetallic phases exhibited enhanced electrocatalytic activity for certain fuels when compared to that of Pt, in terms of both oxidation onset potential and current density. The PtBi, PtIn, and PtPb ordered intermetallic phases appeared to be the most promising electrocatalysts tested thus far for fuel cell applications. In the case of methanol oxidation PtPb showed an onset potential that was 100 mV less positive, and a peak current density 40 times higher, than those observed for Pt. The particularly promising candidates, PtBi, PtPb, and PtIn, were further characterized, using DEMS (differential electrochemical mass spectrometry) for the identification of gaseous products and intermediates. DEMS results obtained for the oxidation of formic acid on PtIn and PtPb indicated that the production of CO during the oxidation of formic acid was minimal and that carbon dioxide was the main product of the reaction. In the case of PtBi, CO and carbon dioxide were both main products of the oxidation reaction. In addition, the electrocatalytic activity of these materials is currently being tested using micro- and nano-particles to determine how competitive these materials would be as fuel cell catalysts when compared to commercially available PtRu nanoparticles. The ability to control the geometric and electronic structures of the electrocatalytic material by using ordered intermetallic phases has been shown to be a promising direction of inquiry in the search for superior electrocatalysts for fuel cell applications.

#### **M5.17**

**Manipulation of Disorder in Pyrochlore Structure.** Jie Lian, Lumin Wang and Rodney C. Ewing; Departments of Materials Science & Engineering and Nuclear Engineering & Radiological Sciences, Univ. of Michigan, Ann Arbor, Michigan.

Ionic conductors are the basis for technologies that utilize solid state electrochemical cells as a source of clean and efficient energy, such as in high-temperature batteries and fuel cells, and as sensors. A goal has been to increase ionic conductivity by increasing either the atomic-scale structural disorder or by fabricating nano-scale geometries that increase the boundary domain surface area. Gd<sub>2</sub>(Zr<sub>x</sub>Ti<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> pyrochlore is an extrinsic ionic conductor at low values of x, but it becomes an intrinsic fast-ion conductor at large x, and oxygen vacancies are the dominant migrating species. Variations in the ionic and electronic conductivity of pyrochlore compounds, A<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, are related to disordering of the A- and B-site cations and the oxygen anion vacancies. Here, we demonstrated the manipulation of disorder extent in Gd<sub>2</sub>(Zr<sub>x</sub>Ti<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> pyrochlore by ion beam

irradiation-induced order-disorder structural transformation and successfully created a nano-scale buried defect-fluorite structure within a single crystal Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlore matrix. A perfect lattice match between the buried fully disordered fluorite layer with pyrochlore matrix was observed by TEM techniques. This combines atomic-scale disorder on the cation and anion sites with a nanostructure that increases the interface area. Further flexibility in the composition and degree of disorder in the nanodomains can be obtained by combining radiation-induced disorder with ion beam implantation (Zr implanted into the Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>), and thermal treatments. This opens the possibility of developing new types of nano-scale mixed ionic-electronic conductors in pyrochlore ceramics, specifically for the development of monolithic solid oxide fuel cells.

#### **M5.18**

**Synthesis of macrostructurally patterned hierarchical porous carbons with mesoporous walls and their use as catalyst support in direct methanol fuel cell.** Jong-Sung Yu, Geun Seok Chai and Suk Bon Yoon; Chemistry, Hannam University, Daejeon, South Korea.

Fabrication of macrostructurally patterned highly ordered fully interconnected hierarchical porous carbons with uniform mesoporous walls has been demonstrated by template replication of aggregates of the small silica particles as molds, which were also templated by self-assembled ordered lattice of larger monodisperse polystyrene spheres. The size of the large macropores can be manipulated by controlling the diameter of the polystyrene spheres, while the size of the small mesopores and the overall specific surface area are determined by the silica particles. The mesopores can be easily regulated in the full mesopore range (5–50 nm) by proper size control of the silica particles. Due to unique structural properties of the porous carbon with fully interconnected ordered uniform bimodal porosity and high surface area, the carbon could work as an excellent catalyst support, resulting in great improvement for methanol oxidation activity in direct methanol fuel cell.

#### **M5.19**

##### **Thermal Cycling of YSZ-based Solid Oxide Fuel Cells**

##### **(SOFC's) in Unmanned Undersea Vehicle (UUV)**

**Applications.** Alan Burke<sup>1</sup>, Louis G. Carreiro<sup>1</sup>, Eric S. Greene<sup>2</sup> and Craig M. Deschenes<sup>3</sup>; <sup>1</sup>Propulsion Branch, Naval Undersea Warfare Center, Newport, Rhode Island; <sup>2</sup>Mechanical Engineering, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Systems Engineering, BAE Systems, Middletown, Rhode Island.

The US Navy is currently investigating the use of solid oxide fuel cells (SOFC's) for propulsion of unmanned undersea vehicles (UUV's). These vehicles require an energy source capable of sustaining long duration missions at relatively low discharge rates. Since batteries have limited energy storage capacity (energy density), SOFC's are being targeted to meet UUV power requirements. An SOFC power source offers several potential advantages over batteries: greater energy density on a systems basis; refillable fuel/oxidizer storage that allows UUV's to be re-launched at short notice; and the option of utilizing logistic fuels (liquid hydrocarbons) since internal reforming within the SOFC is possible. However, a limitation of the SOFC may be its ability to withstand thermal cycling with minimal loss in performance. Depending on the UUV operational mode, the temperature of the SOFC will vary over a wide range and this thermal fluctuation or cycling generally causes mechanical stress, which can eventually lead to fracture of the ceramic fuel cell elements. Furthermore, sealant materials used in cell stacks must also be able to endure thermal cycling, but this issue will not be addressed here. Instead, this work focuses on the stability and durability of the cell assembly materials (electrodes and electrolyte). Data is presented on the thermal cycling of both single cell and multiple cell stack anode-supported type SOFC's composed of a nickel cermet anode, (La,Sr)MnO<sub>3</sub> cathode, and YSZ electrolyte. Cycling experiments were performed in the temperature range of 500°C to 900°C in order to simulate the UUV in idle and run modes. After a given number of thermal cycles, both anode and cathode were characterized using scanning electron microscopy (SEM) and powder x-ray diffraction (XRD). Changes in microstructure and/or phase composition were then correlated to cell performance in terms of fuel/oxidizer efficiencies and cell power density.

#### **M5.20**

##### **Thermal analysis studies on (LaCrO<sub>3</sub>) powders prepared via combustion reaction.**

Adolfo Junior Franco and Cirilo Gomes Valente Neto; Matematica e Fisica, Universidade Catolica de Goias, Goiania, Goias, Brazil.

The lanthanum chromite (LaCrO<sub>3</sub>) powders were prepared by combustion reaction of liquid solution of metallic nitrite and urea. The exothermic reaction produces a sufficiently high temperature for crystallization of the structure to occur avoiding the necessity for

further calcination. The huge amount of gas evolved in the reaction inhibited particle agglomeration and yield soft powders suitable for dispersion and use. Powders were characterized by TGA/DTA and FTIR.

#### **M5.21**

**Lanthanum Chromite (LaCrO<sub>3</sub>): Sintering and Characterization.** Adolfo Junior Franco, Cirilo Gomes Valente Neto and Jesiel Freitas Carvalho; Matematica e Fisica, Universidade Catolica de Goias, Goiania-GO, Goias, Brazil.

The lanthanum chromite (LaCrO<sub>3</sub>) is largely used in solid oxide fuel cells (SOFC) interconnectors due to its properties such as good chemical compatibility with other components and good electric conductivity. This work presents a study of the synthesis of the lanthanum chromite from the combustion reaction in the presence of urea. XRD and SEM characterized the obtained powders. Pellets pressed in disc shape from nonometric powders were sintered at different temperatures up to 1600°C in air atmosphere for 12 hours. Electrical conductivity ( $\sigma$ ), dielectric constant ( $\epsilon$ ) and loss ( $\tan\delta$ ) were measured.

#### **M5.22**

**Development of a Membrane-Based Solid-Oxide Fuel Cell: Microfabrication and Performance Analysis.**

Benjamin A. Wilhite<sup>1</sup>, Joshua Hertz<sup>3</sup>, David Quinn<sup>2</sup>, Steven Weiss<sup>1</sup>, Harry Tuller<sup>3</sup>, Martin A. Schmidt<sup>4</sup> and Klavs F. Jensen<sup>1</sup>; <sup>1</sup>Chemical Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Aeronautics and Astronautics, MIT, Cambridge, Massachusetts; <sup>3</sup>Materials Science and Engineering, MIT, Cambridge, Massachusetts; <sup>4</sup>Microsystems Technology Laboratory, MIT, Cambridge, Massachusetts.

Solid-Oxide Fuel Cells (SOFCs), employing ceramic electrolytes, are a promising alternative to low-temperature PEM (proton-exchange membrane) fuel cells for portable power applications. The use of an oxygen-ion conducting electrolyte operating at high temperatures offers the potential for internal reforming of a variety of fuels, with improved tolerance to competitively-adsorbing species at the anode (e.g. CO), thus removing the need for pretreatment stages for conversion of hydrocarbon fuel to high-purity hydrogen. However, appropriate thermal management of this high-temperature fuel cell system is required to achieve an energy-efficient device. A chip-scale micromembrane architecture has been developed for thermally efficient thin-film applications<sup>1</sup>, and has been successfully demonstrated for hydrogen separation via ultra-thin palladium films. Resistive heaters placed directly upon a thermally isolated membrane allows for rapid heating and cooling of the supported thin film at a minimum of energy expenditure. In addition, the mechanical strength provided by the micromembrane support allows the use of sub-micron films for significant improvement in ion permeability. For these reasons, the micromembrane architecture has been investigated for solid-oxide fuel cell development. We describe the latest results of a collaborate effort to develop a prototype  $\mu$ SOFC device for portable-power applications. Efforts include determination of optimal free-standing fuel cell stack dimensions, integration of individual stacks into a reinforced membrane structure, design of current collectors, and electrical performance tests of fabricated devices. Stability tests of free-standing membranes of varying length scales and aspect ratios are performed for a variety of fuel cell stacks and individual stack layers, with results compared to mechanical models of layered free-standing films. The resulting information is then incorporated into the design of a silicon-nitride reinforced free-standing membrane architecture. Lastly, microdevice testing stations allow for performance studies of prototype microdevices. <sup>1</sup> Franz, A.J., K.F. Jensen, M.A. Schmidt and S. Firebaugh. Integrated Palladium-Based Micromembranes for Hydrogen Separation and Hydrogenation/De-hydrogenation Reactions. U.S. Patent 6,541,676, assigned to the Massachusetts Institute of Technology (2003).

#### **M5.23**

**Ab Initio Study of Hydrogen Permeation through Palladium Membrane.** Pil-Ryung Cha<sup>1</sup>, Eung-Kyu Lee<sup>2</sup>, Hyun-Kwang Seok<sup>3</sup> and Kibae Kim<sup>3</sup>; <sup>1</sup>School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea; <sup>2</sup>School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; <sup>3</sup>Advanced Metals Research Center, Korean Institute of Science and Technology, Seoul, South Korea.

Hydrogen permeation through dense palladium-based membranes has attracted many scientists due largely to their unmatched potential as hydrogen-selective membranes for membrane reactor applications. Although it is well known that the permeation mechanism of hydrogen through Pd involves various processes such as dissociative adsorption, transitions to and from the bulk Pd, diffusion within Pd, and recombinative desorption, it is still unclear which process mainly limits hydrogen permeation at a given temperature and hydrogen partial pressure. In this study, we report an all-electron

density-functional theory study of hydrogen permeation through Pd membrane. We use the local-density approximation for the exchange-correlation energy functional and Plane Augmented Wave (PAW) Pseudo-potential method to calculate adsorption energies and energy barriers for transitions to and from the bulk Pd, diffusion within Pd, and recombinative desorption in various surface coverages of hydrogen. It is found that transition energy barriers to the bulk Pd decreases with increasing hydrogen coverage, which means that hydrogen penetration into the bulk Pd limits the permeation at low hydrogen partial pressure. Based on calculated energy barriers, we find that nearly diffusion-limited permeation is expected at high temperature and hydrogen partial pressure and that low temperature permeation is limited by both desorption and transition to the bulk Pd. We also propose a plausible mechanism of hydrogen embrittlement.

SESSION M6: Nanomaterials-Alloys, Intermetallics, and Not

Chairs: Hector D. Abruna and Carlos Cabrera  
Wednesday Morning, December 1, 2004  
Fairfax A (Sheraton)

#### **8:30 AM \*M6.1**

**Ordered Intermetallic Compounds: A New Approach to (Electro)catalysts.** Francis J. DiSalvo<sup>1</sup>, R. B. van Dover<sup>2</sup> and H. D. Abruna<sup>1</sup>; <sup>1</sup>Chemistry & Chemical Biology, Cornell University, Ithaca, New York; <sup>2</sup>Materials Science & Engineering, Cornell University, Ithaca, New York.

Ordered intermetallic compounds have been little explored for catalytic applications. We have found that several simple binary compounds, such as PtBi and PtPb, show promise as anode electrocatalysts in PEM Fuel Cells (1,2). These electrocatalysts are insensitive to CO poisoning at 25 °C and are less sensitive to S (by over three orders of magnitude) than Pt or Pt/Ru. Thus, fuels such as impure H<sub>2</sub>, HCOOH and CH<sub>3</sub>OH can be oxidized at high rates in electrochemical cells. The limiting oxidation rate increases rapidly with temperature – by a factor of 10 at 85 °C over room temperature. Intermetallic phases with large enthalpies of ordering are likely to have stable, ordered surfaces. In ternary, quaternary and higher phases, such surfaces may present several different catalytic sites, perhaps allowing the complete oxidation of more complex fuels. The geometric and electronic features of these surfaces could be widely varied by choosing different compound stoichiometries, crystal structures and component elements as well as by varying the morphology of electrocatalyst particles. Such compounds represent a very large, unexplored class of electrocatalytic materials that may have applications to fuel cell technologies as well as general hetero-catalysis. Using high throughput methods, we are exploring a number of ternary and quaternary phase diagrams to identify the most promising of these materials for specific applications. Recent results and future plans will be discussed. (1) E. Casado-Rivera, Z. Gál, A.C.D. Angelo, C. Lind, F.J. DiSalvo, H.D. Abruña, *Chem.Phys.Chem.* **2003**, *4*, 193-199. (2) E. Casado-Rivera, D.J. Volpe, L. Alden, C. Lind, C. Downie, T. Vázquez-Alvarez, A.C.D. Angelo, F.J. DiSalvo, H.D. Abruña, *J.Am.Chem.Soc.* **2004**, *126*(12), 4043-4049.

#### **9:00 AM M6.2**

**In-situ Potential Cycling Experiments on PEMFCs.** Shyam Kocha, Rohit Makharia and Hubert Gasteiger; Research Center, General Motors Corporation, Fuel Cell Activities, Honeoy Falls, New York.

State-of-the-art membrane electrode assemblies (MEAs) for proton exchange membrane fuel cells (PEMFCs) utilize thin (10  $\mu$ m) catalyst layers derived from highly dispersed Pt/C and ionomer inks. The Pt particle size is of the order of 2-4 nm that result in in-situ electrochemical areas in MEAs of about 60-80 m<sup>2</sup>/g. The un-graphitized carbon supports often employed have BET surface areas of 240-800 m<sup>2</sup>/g. The voltage performance of these MEAs are as high 0.65 V at current densities of 1-1.5 A/cm<sup>2</sup> under H<sub>2</sub>-Air. Unlike residential or stationary fuel cell power plants where the fuel cell may be subject to a constant load, automotive power-plants stacks are subjected to variable load cycles that encompass no-load to idle to part-load to peak-power. Correspondingly, under normal operating conditions the PEMFC cathode undergoes potential cycling in the range 0.98 (OCV) to 0.65 (peak power) Volts. In addition, starting and stopping the fuel cell in an uncontrolled fashion results in a hydrogen-air front or air-hydrogen front passing through the anode and causing cathode potentials to cycle between load and 1.0-1.6 V on the cathode [1, 2]. It is well known that the carbon support employed in the electrodes corrode over the entire fuel cell operating regime above 0.207 V [3], but the corrosion currents reach significant levels at voltages above 1 V. In this voltage regime, the carbon support gets oxidized significantly (to CO<sub>2</sub>) leading to a thinning/collapse of the

catalyst layer and significant losses in cell performance. In addition, Pt also dissolves and diffuses to sinter and form larger particles due to potential cycling as well as the loss of carbon support that separates the dispersed Pt particles. From the Pourbaix diagram [3] it can be seen that Pt is especially susceptible to dissolution in a narrow pH range below pH 0 and in the potential range 1.0-1.2 V. Experimentally, MEAs in fuel cells were cycled over different potential regimes for thousands of cycles with intermittent measurement of the hydrogen adsorption area, which corresponds to the loss in surface area due to sintering of the Pt. This work discusses the degradation in surface area in the voltage range above 1 V on several Pt/C catalysts as a function of operating conditions such as temperature, scan rate and for different carbon support materials. Implications for fuel cell system operation will also be examined. References 1. Yang, Deliang, Steinbugler, M. M., Sawyer, R. D., Van Dine, L. L., and Reiser C. A., Patent Application Publication, Pub. No.: US 2002/0102443 A1, 2002. 2. Paul T. Yu, Shyam Kocha, Lesley Paine, Wenbin Gu, Frederick T. Wagner, 'The effects of air purge on the degradation of PEM fuel cells during startup and shutdown procedures', 2004 Annual Meeting AIChE, New Orleans, LA, April 25-29 3. Pourbaix, Marcel, 'Atlas of Electrochemical Equilibria in Aqueous Solutions' NACE 1974.

#### 9:15 AM M6.3

##### **Sequential Electrodeposition of Pt-Mo, Pt-Ru, and Pt-Ru-Mo on HOPG: A Morphology and Electrocatalytic Study.**

Carlos Raul Cabrera and Tatiana Morante; Chemistry, University of Puerto Rico, San Juan, Puerto Rico.

Platinum particles are used in heterogeneous catalysis due to their excellent catalytic properties with respect to a number of important reactions. In electrochemical systems, the platinum particles are usually supported on carbon. Efforts have made to improve the CO tolerance of these catalysts, combining Pt with other metals. Electrodeposition of Pt on HOPG substrate was made by electrochemical techniques, introducing metals such as Ru and Mo by sequential and simultaneous method. A fundamental study of the systems Pt, Pt-Ru, Pt-Mo and Pt-Ru-Mo, were made through electrochemical and morphological characterization (SEM, SPM and XPS and XRD) combined with an electrocatalytic test toward methanol oxidation by cyclic voltammetry and chronoamperometry. The step and sweep potential techniques showed better morphological and catalytic characteristics for Pt electrodeposition and these techniques were used to the addition of Ru and Mo. The PtRu, PtMo and PtRuMo electrocatalysts were prepared on HOPG by either sequential or simultaneous electrodeposition. The voltammetric behavior of electrodeposits in 0.5 M aqueous sulfuric acid were compared to that of Pt electrodeposits on HOPG in the hydrogen electroadsorption/desorption and early stages of electrooxidation potential regions of methanol. Morphological and microscopic surface characterization carried out with scanning electron microscopy (SEM) and atomic force microscopy (AFM), showed that the deposits consist of a number of aggregates. Scanning tunneling microscopy (STM) showed rounded clusters from 5 to 10 nm in diameter. For sequentially produced Pt-Ru, PtMo, PtRuMo electrodeposits, XPS and voltammetry data indicate an irregular distribution of the active materials and a non-homogeneous surface. The electrocatalytic activity of these electrodes for the oxidation of methanol in 0.5 M aqueous sulfuric acid showed better behavior for the system Pt-Ru-Mo. XPS analysis showed for the system Pt-Ru-Mo the formation of different species of Ru and Mo to the bimetallic catalysts studied PtRu and PtMo. The PtRuMo deposit was characterized by X-ray diffraction and was compared to the X-ray diffraction obtained for Pt, PtRu and PtMo catalysts electrodeposited on HOPG substrates. In general this showed a displacement of the angle compared to Pt polycrystalline particles, and it can be concluded that there is a presence of small amounts of Ru and Mo in the Pt lattice.

#### 9:45 AM M6.4

##### **PEM Fuel Cells with Pt-Coated Nanoporous Gold Electrodes.** Jonah Erlebacher, Joe Lee, Yi Ding and Greg Fritz; Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

We present a new material with application as electrodes in proton exchange membrane (PEM) fuel cells, platinum-plated nanoporous gold (Pt-NPG). In contrast to nanoparticle-based catalytic electrodes, the materials design strategy used here was to begin with a thin membrane of a mesoporous material ("nanoporous gold leaf", 100 nm thick) and uniformly coat it with an atomically thin conformal coating of precious metal catalyst. In this way, nearly every precious atom is a surface atom exposed to reactant flow, and catalytic surface areas are typically greater than 100 m<sup>2</sup>/g Pt. We will discuss methods to make catalytic electrodes with Pt loading less than 0.05 mg/cm<sup>2</sup>, simple methods to integrate this material into existing fuel cell architectures, and fuel cell performance using Pt-NPG.

#### 10:30 AM M6.5

##### **Gold and Alloy Nanoparticles as Fuel Cell Catalysts.**

Mathew M. Maye, Jin Luo, Nancy N. Kariuki, Peter Njoki, Lingyan Wang, Yan Lin, Derrick Mott and Chuan-Jian Zhong; Chemistry, SUNY-Binghamton, Binghamton, New York.

Gold-based nanoparticles (1-5 nm) have recently emerged as highly active catalysts. A major factor of their catalytic activity is related to the unique size- and composition-dependant structural properties. This presentation focuses on the investigation of the catalytic properties of gold and its alloy nanoparticles supported on carbon materials. The catalytic activity towards oxygen reduction reaction has been characterized. To delineate the size and composition correlation of the catalytic properties, we employed an array of surface analytical techniques to probe the structural and morphological evolution and reconstitution of the nanoparticles upon catalytic activation, including atomic force microscopy, transmission electron microscopy, surface infrared reflection spectroscopy, X-ray photoelectron spectroscopy, thermal analysis, and electrochemical quartz crystal nanobalance. The combined results of these characterizations have provided important insights into the tailoring of the nanostructured catalysts in terms of size and composition. The potential application for fuel cell catalysts will also be discussed.

#### 10:45 AM M6.6

##### **A First Principles Model for the Coupling between Chemical Adsorption and Surface Segregation in Pt-Alloy Catalysts.**

Byungchan Han, Anton Van der Ven and Gerbrand Ceder; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Characterizing the surface of Pt-alloy catalysts is crucial for developing a rational and quantitative understanding of the performance of these catalysts in low temperature fuel cells. First principles segregation studies on surfaces are often performed in vacuum. We have developed a model that makes it possible to study surface segregation in the presence of adsorbed species on the surface. Using the coupled cluster expansion technique the model can be parameterized on the basis of Density Functional Theory calculations up to full accuracy of the quantum mechanical Hamiltonian. Thermalized Monte Carlo simulations then allow one to study the chemistry of the surface (simultaneous adsorption coverage and alloy segregation) at any composition of the catalyst and chemical potential of the adsorbant. We have demonstrated to potential of this approach for Pt-Ru catalysts under varying degrees of oxygen chemical potential. These simulations show ordered surface structures with Ru surface segregation forming island structure with oxygen bound to it. Thus we concluded that oxygen environment can be very important factor affecting Ru surface segregations.

#### 11:00 AM M6.7

##### **Metastable Pt-Au Binary Alloy Nanoparticles for**

**Electrocatalysis in Fuel Cells.** Eric Irissou, Francois Laplante, Mohammed Chaker and Daniel Guay; Energie, Materiaux et Telecommunications, INRS, Varennes, Quebec, Canada.

Metastable Pt-Au nanoparticles have been prepared by means of cross-beam pulsed laser deposition (CBPLD) of two dissimilar targets (Pt and Au) in presence of a moderate He background gas pressure. By varying the deposition conditions, alloyed Pt-Au nanoparticles spanning the whole composition range (from [Pt] = 0 to [Pt] = 100 at.%) have been prepared. X-ray diffraction reveals that, independently of the [Pt] concentration, the alloyed nanoparticles are composed of a face centered cubic (fcc) phase. The crystallite size, as evaluated from an analysis of the width of the diffraction peaks, varies from 30 nm for [Pt] = 0 at.% to 7 nm for [Pt] = 100 at.%. Scanning tunneling microscopy shows that the nanoparticles have a spherical shape and that the mean nanoparticle diameter coincides with the crystallite size extracted from the X-ray diffractograms. X-ray photoelectron spectroscopy indicates that the surface composition coincides with the bulk concentration (determined by neutron activation analysis), indicating that there is no surface segregation. Upon annealing at moderate temperature (450 C) for 3 days, the X-ray diffraction pattern displays two sets of diffraction peaks, indicative of the presence of two distinct cubic phases, one with a lattice parameter of 0.4043 nm attributed to an Au-rich phase (with [Pt] = 21 at.%), and the second one with a lattice parameter of 0.3927 nm corresponding to a Pt rich phase Pt(Au) (with [Pt] = 91 at.%). This result confirms the metastable character of the Pt-Au nanoparticle prepared by CBPLD. Finally, the electrochemical properties of these nanoparticles will be reviewed.

#### 11:15 AM M6.8

##### **Electrocatalytic Activity of Ruthenium Sulfide in Hydrogen Oxidation Reaction in PEMFCs.** Hua Zhang<sup>1</sup>, Ysmael

Verde-Gomez<sup>3</sup>, Allan J. Jacobson<sup>1</sup>, Alejandra Ramirez<sup>2</sup> and Russell R. Chianelli<sup>2</sup>; <sup>1</sup>Chemistry, University of Houston, Houston, Texas; <sup>2</sup>Materials Research and Technology Institute, University of Texas at El Paso, El Paso, Texas; <sup>3</sup>Instituto Tecnologico de Cancun, Cancun, Quintana Roo, Mexico.

The development of non-platinum electrocatalysts for Polymer Electrolyte Membrane Fuel Cells is desirable for cost reduction and may play an important role for PEMFC large-scale commercialization. In previous work we have reported the synthesis and characterization of a transition metal sulfide anode electrocatalyst for PEMFCs. The present work focuses on the electrocatalytic activity of ruthenium sulfide for hydrogen oxidation. Electrodes were made by depositing ruthenium sulfide catalyst ink on a carbon substrate with a gas diffusion layer. Membrane electrode assemblies (MEAs) were fabricated by hot-pressing the ruthenium sulfide electrode and platinum electrode onto a Nafion 117 membrane. Cyclic voltammetry measurements of the ruthenium sulfide electrode as the working electrode were carried out in a conventional three-electrode cell with 0.5 M sulfuric acid solution and in a single PEM cell. The behavior indicates that electrocatalysis by ruthenium sulfide needs to be activated. The hydrogen oxidation behavior of activated ruthenium sulfide electrodes indicates that ruthenium sulfide is effective as an anodic catalyst in a PEM fuel cell. Single cell polarization curves with ruthenium sulfide as anode catalyst and platinum as cathode catalyst were measured in a Teflon single cell with 1 cm<sup>2</sup> active area at room temperature. The results show the evolution of the electrocatalytic activity of ruthenium sulfide with the electrochemical activation and that the current density and power density increase with the increase of ruthenium sulfide loading. Surface properties of ruthenium sulfide electrodes were studied by XPS analysis.

#### 11:30 AM M6.9

##### **Catalysts Based on Metallic and Ceramometallic Monoliths for Hydrogen Production via Partial Oxidation of Hydrocarbons.**

**Svetlana Pavlova<sup>1</sup>, Sergey Tikhov<sup>1</sup>, Vladislav Sadykov<sup>1</sup>, Olga Snegurenko<sup>1</sup>, Yulia Dyatlova<sup>1</sup>, Zahar Vostrikov<sup>1</sup>, Valerii Kuzmin<sup>1</sup>, Ilya Zolotarevskii<sup>1</sup>, Ludmila Bobrova<sup>1</sup> and Vladimir Ulianitsky<sup>2</sup>,** <sup>1</sup>Borek Institute of Catalysis, Novosibirsk, Russian Federation; <sup>2</sup>Laurentiev Institute of Hydrodynamics, SB RAS, Novosibirsk, Russian Federation.

The catalytic partial oxidation (CPO) and autothermal reforming (ATR) of hydrocarbons (HC) are presently considered as an attractive technology for the small-scale and distributed production of hydrogen in the stationary and mobile fuel processing, especially for fuel cell applications. In view of such applications, realization of these processes at short contact times (< 0.1 sec) to miniaturize the reactors is the most promising route, which requires application of monolithic catalysts having a low pressure drop. To prevent the temperature gradient, metallic high thermal conductivity monoliths can be used. In addition, metallic monoliths can be heated by passing an electric current through it. Due to internal electrical heating, heat is supplied to the catalyst more directly, thus making it possible to exert a better control over the reactions proceeding within the monolith during cold start-up periods. In the present work, some approaches to design of efficient catalysts for CPO and ATR of methane, isooctane and gasoline based on monolithic metallic supports of different types (honeycombs and foams) and microchannel ceramometal monoliths are presented. The honeycomb metal monolithic supports having a corrugated structure and up to 500 cells/in<sup>2</sup> density were made from a heat-resistant foil coated with a-Al<sub>2</sub>O<sub>3</sub> layer using proprietary procedures to ensure a strong and uniform covering. The Ni-Cr alloy foam supports with pores of the 1-4 mm diameter were used. Mechanically strong ceramometal monoliths (crushing strength 4-10 MPa/monolith) with the specific surface of 2-20 m<sup>2</sup>/g, having through channels with a density of 180-360/in<sup>2</sup> were formed as a result of powdered component encapsulation into the Al<sub>2</sub>O<sub>3</sub>/Al<sub>0</sub> matrix during hydrothermal treatment followed by calcination in air at 900-1200°C. Powders of mixed oxides (perovskites LaNiO<sub>x</sub>, CeO<sub>2</sub>, CexZr1-xO<sub>2</sub>) and Ni-Cr or Ni-Co alloys were used as additives. All monoliths were coated by nanocomposites comprised of binary metal particles (Ni-Pt) supported on a complex Ce-Zr oxide with a high bulk/surface oxygen mobility. The phase composition and textural properties of ceramometal monoliths depend on the additive nature affecting the aluminum reactivity toward oxidation and the interaction of remaining Al<sub>0</sub> as well. The thermal shock testing both honeycomb metallic and ceramometal monoliths shows their high resistance up to 1200°C. Effects of the inlet gas composition and temperature, contact time, monolithic support configuration on the catalysts performance (HC conversion and H<sub>2</sub> selectivity) in the autothermal mode were studied. The catalysts were shown to be very efficient and stable in the partial oxidation of gas and liquid fuels at short contact times.

#### 11:45 AM M6.10

##### **Prospective Mixed Ionic and Electronic Conductors for Hydrogen Separation.**

**Hengdong Cui, Annamalai Karthikeyan, Srikanth Gopalan and Uday Pal;** Manufacturing Engineering, Boston University, Brookline, Massachusetts.

Mixed ionic and electronic conducting (MIECs) membranes are receiving increasing attention in gas separation processes In

particular, oxygen and electron conducting MIECs have high potential for oxygen separation. However, the suitability of these MIECs for hydrogen production and separation has not yet been studied in detail. We are currently investigating several single phase and composite MIECs for hydrogen separation processes. Preparation of novel MIECs compositions, their stability, electrical and permeation properties are presently being investigated. Based on these studies a suitable MIEC membrane composition will be identified for hydrogen separation applications. In our approach, methane or reformato comprising CO and H<sub>2</sub> mixtures is fed to one side of the membrane, while water vapor is fed to the other side. Oxygen from the steam side of the membrane is transported through ambipolar diffusion across the membrane to the methane/reformato side to form products such as CO, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>; the exact composition being dependent on the operating conditions of the membrane. Thus, in principle hydrogen can be recovered from the steam feed side of the membrane and syn-gas (mixture of CO and H<sub>2</sub>) from the other side of the membrane. Very high methane to hydrogen conversion rates (up to 75%) can be obtained in principle through this process. There are a number of materials requirements for a membrane in any gas separation process. For the process currently under investigation, the MIEC material should have sufficient stability in water vapor atmospheres up to 1 atm as well as highly reducing conditions containing large amounts of CO<sub>2</sub>. Several single and dual-phase MIEC membrane compositions are being studied for application in this process. Single phase membranes including strontium or calcium doped lanthanum cobalt iron oxides (LSCF and LCF). Dual phase membrane compositions being studied include composites of n-type perovskites and oxygen ion conducting fluorite oxides. Results from materials stability tests, electrical conductivity, thermogravimetry (TGA) and conductivity relaxation tests will be reported. Conductivity relaxation experiments are very useful from the standpoint of measuring both the chemical diffusion coefficient and the surface exchange coefficients in one single experiment. Measurement of both of these parameters also provides a criterion for designing these membranes.

#### SESSION M7: Membranes I

Chairs: Andrew Bocarsly and Eugene Smotkin

Wednesday Afternoon, December 1, 2004

Fairfax A (Sheraton)

#### 1:30 PM M7.1

##### **New Tungsten Fuel Cell Catalysts.** Joel Christian, OSRAM SYLVANIA, Inc., Towanda, Pennsylvania.

A new tungsten fuel cell catalyst has been discovered for PEM fuel cells. This material is synthesized using high-purity chimie douce (soft chemistry) techniques. The material has shown activity as a fuel cell catalyst in a variety of test cell configurations and operating conditions, with power output levels demonstrated within an order of magnitude of conventional platinum electrocatalysts. Preliminary tests also show catalytic activity in reformato type fuel streams, up to and including pure CO (carbon monoxide).

#### 1:45 PM \*M7.2

##### **Recent Advances in Solid Acid Fuel Cells.** Sossina M. Haile, Dane A. Boysen, Calum R. I. Chisholm and Tetsuya Uda; Materials Science, Chemical Engineering, California Institute of Technology, Pasadena, California.

Fuel cells are attractive alternatives to combustion engines for electrical power generation because of their very high efficiencies and low pollution levels. Polymer electrolyte fuel cells, those most viable for mobile applications, suffer from the humidification requirements of the polymer, which limits the temperature of operation to 100°C, and from its permeability to methanol and hydrogen, which lowers fuel efficiency. Proton conducting "solid acids" address many of the issues facing polymer fuel cells. Solid acids are compounds which contain structural protons and whose chemistry and properties are intermediate between those of a normal acid and a normal salt. The proton conductivity of these materials can be as high as 10<sup>-2</sup> Ω<sup>-1</sup>cm<sup>-1</sup> when heated to slightly elevated temperatures. The transport process does not require humid atmospheres and the materials are stable to temperatures as high as 350°C. Unfortunately, all known solid acids of high conductivity suffer from solubility in water and extreme ductility in the high temperature phase. Furthermore, the vast majority of these materials are based on sulfates or selenates, which are reduced under hydrogen in the presence of typical fuel cell anode catalysts. We present recent results obtained using the solid acid CsH<sub>2</sub>PO<sub>4</sub> as a fuel cell electrolyte. Unlike sulfate and selenate solid acids, cesium dihydrogen phosphate is chemically stable under reducing conditions. However, the transition to the high conductivity phase occurs at a high temperature, 230°C, at which the compound requires stabilization against thermal dehydration via mild atmospheric humidification. A

layer of CsH<sub>2</sub>PO<sub>4</sub> was sandwiched between two electrocatalysis layers containing 18 mg Pt cm<sup>-2</sup>. For operation of direct methanol fuel cells, the anode electrocatalyst was replaced with 13 mg Pt<sub>0.5</sub>Ru<sub>0.5</sub> cm<sup>-2</sup>. These layers were then placed between two sheets of graphite paper and the entire assembly uniaxially pressed to yield a dense electrolyte membrane (260 μm thick) with good mechanical contact to the electrocatalyst layers. Fuel cell polarization curves were collected at 250-260°C. For the H<sub>2</sub>/O<sub>2</sub> cell, gases were passed through water held at 69-72°C in order to obtain the desired water partial pressure of 0.3 atm. For the direct methanol fuel cell, argon was passed through hot water (70°C), and gaseous methanol directly added it. The CH<sub>3</sub>OH:H<sub>2</sub>O molar ratio was held at 0.92. The water partial pressure at the cathode was maintained at 0.33 atm. Under these operating conditions, peak power densities of 50 and 35 mW cm<sup>-2</sup> were obtained, respectively, from the H<sub>2</sub>/O<sub>2</sub> and direct methanol fuel cells. In addition, over the course of a one hundred hour test, power output remained essentially unchanged. Thus, the long-term viability of solid acid fuel cells has been demonstrated and the key challenges now revolve around reduction of precious metal content and fabrication of cells with ultrathin membranes to increase power output.

### 2:15 PM M7.3

**Development of Novel Electrolytes for Proton Exchange Membrane in Fuel Cells Using Nanostructured Iron-Based Metal Oxanes.** Eliza M. Tsui, Maria M. Cortalezzi and Mark R. Wiesner; Civil and Environmental Engineering, Rice University, Houston, Texas.

We show that an iron-based ceramic material is a good candidate as electrolyte material for PEMFC. These membranes have comparable conductivity to the Nafion membrane with the advantages of lower material costs, and the ability to operate at higher temperatures. Iron oxide nanoparticles (ferroxane) and aluminum oxide nanoparticles (alumoxane) were prepared via an environmentally benign process, alternative to sol-gel process. The starting material for the metal oxane is metal oxyhydroxide: lepidocrocite (γ-FeOOH) for ferroxane and boehmite (γ-AlOOH) for alumoxane. Lepidocrocite is not commercially available and can be prepared via the oxidation of FeCl<sub>2</sub> in the presence of NaOH solution. In the preparation of ferroxane nanoparticles, lepidocrocite is reacted with acetic acid at a ratio of [Fe]/[AA] = 1.5. The hydrogen bonds in the structure of lepidocrocite are cleaved by acetic acid to yield the ferroxane nanoparticles. The final ferroxane retains the plate-like structure as lepidocrocite. The structure of ceramic material was characterized with FTIR, SEM and TEM; their protonic conductivity was studied by electrochemical impedance spectroscopy (EIS). Ceramic chips of ferroxanes and alumoxanes were prepared to study their suitability in fuel cell applications. Chips with thickness of 240 μm to 310 μm were made by suspending the metal oxanes nanoparticles into Millipore water and air drying at room temperature. Dried samples were sintered at 300 and 400°C to remove the acetic acid. The samples were sputter-coated with gold on both sides to create the electrodes. Protonic conductivity was measured using EIS in two-electrode mode at a frequency range of 0.01 Hz to 100 kHz. Samples of the green body and those prepared at different sintering temperatures were studied for their protonic conductivities at relative humidity of 58%, 81%, 97%, and 100% at room temperature by equilibrating with various salt solutions. The conductivity improved as relative humidity increased. However, sintered samples were less dependent on relative humidity. Conductivities of sintered samples were significantly higher than those of green bodies. The protonic conductivity of ferroxane derived ceramics fired at 300°C (ranging 1.5 to 2.5 × 10<sup>-2</sup> S/cm at various %RH) is comparable to that of Nafion.

### 2:30 PM M7.4

**Search for Higher Temperature Proton Conductors for the PEM Fuel Cell.** J. Halley, L. Jia and D. Nguyen; University of Minnesota, Minneapolis, Minnesota.

We report results of experimental and computational modeling studies of various alternatives to the standard Nafion membrane for a PEM fuel cell. The well known objective is to find a material which will have adequate proton conductivity at temperatures up to 150°C where the platinum catalyst in the electrodes will work more efficiently. Our preliminary results show very good conductivities in some ionic liquids up to 150°C. We report first principles electronic structure, molecular dynamics and Monte Carlo studies of the most promising materials which suggest possible proton transport mechanisms to account for the experimental results.

### 3:15 PM \*M7.5

**Water-Membrane Interactions In The Proton Exchange Membrane Fuel Cell: Construction Of A High Performance Elevated Temperature Hydrogen-Oxygen Cell.**

Andrew Bocarsly<sup>1</sup>, Lakshmi Krishnan<sup>1</sup>, Tao Zhang<sup>1</sup>, Jonathan Mann<sup>1</sup>, Brent Kirby<sup>1</sup>, Paul Majstrik<sup>1</sup> and Jay Benziger<sup>2</sup>;

<sup>1</sup>Chemistry, Princeton University, Princeton, New Jersey; <sup>2</sup>Chemical

Engineering, Princeton University, Princeton, New Jersey.

The hydrogen/oxygen (air) proton exchange membrane (PEM) fuel cell, a low temperature cell, presently operating in the 60-80°C range has been identified as the cell of choice for future automotive applications. However, these cells are subject to poisoning by the presence of trace amounts of carbon monoxide (10 ppm) in the hydrogen feed stream. In addition, managing the water content of the cell has proven difficult. One solution to these problems is the implementation of a PEM cell that operates at elevated temperatures (i.e. from 120-150°C) [1,2]. Even though, the currently employed perfluorinated sulfonated ionomer membranes such as Nafion are thermally stable through this region, above 80-90°C these materials have difficulty retaining water, this degrades their proton transport properties. We have found however, that modest pressurization of the cell in conjunction with the use of a composite membrane formed from the addition of a metal oxide to a Nafion matrix allows for reproducible, stable cell operation up to 145°C [1-3] even if reduced humidity is present in the cell. Metal oxide/Nafion composite membranes can be easily prepared via the direct addition of metal oxide nano- or mesoscale particles to a Nafion recasting suspension followed by evaporation of the recasting solvent [3]. The performance of the composite membrane in the 120-150°C temperature range is found to be a function of the type of metal oxide utilized, and the specific chemical details of the metal oxide-polymer interface. An incorrect choice of these parameters can lead to a membrane that provides an inferior response when compared to a pure Nafion membrane. On the other hand, optimal composite systems not only yield cells that are thermally stable, efficient energy converters in the desired temperature range, but show decreased sensitivity to carbon monoxide exposure and water content, allowing for at least 1000 ppm of CO in the hydrogen stream with performance that is comparable to low temperature Nafion cells in the absence of CO. The metal oxide component of the membrane is found to play two roles central to the elevated temperature performance of the cell. First, this component elevates the glass transition temperature of the Nafion membrane out of the cell operating temperature range. Secondly, the inorganic phase improves the dimensional stability of the membrane associated with swelling processes as the water content of the cell changes. This latter process affects both the conductivity of the membrane and the interfacial charge transfer resistance. Reference: 1. C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, and A. B. Bocarsly, J. Power Sources, 103, 1, 2001. 2. K. T. Adjemian, S. J. Lee, S. Srinivasan, J. Benziger, and A. B. Bocarsly, Journal of the Electrochemical Society, 149, A256 2002. 3. K. T. Adjemian, S. Srinivasan, J. Benziger and A. B. Bocarsly, J. Power Sources, 109, 356, 2002.

### 3:45 PM M7.6

**Chemical Modification of a Cation-Exchange Membrane by Formation of a Sulfonamide Bond.** Yannick Roussy-Huard, Gwenael Chamoulaud and Daniel Belanger; Chimie, Université du Québec à Montréal, Montréal, Québec, Canada.

The surface modification of a cation-exchange membrane, bearing sulfonate groups, by a cationic layer is described. Two different commercially available membranes (Neosepta-CMX and Nafion) were modified in this work. The modification procedure involved the chlorosulfonation of the sulfonate groups of the base membrane with thionyl chloride, followed by a reaction with an amine or a diamine to yield a sulfonamide bond. In the case of the diamine, the surface was terminated by amine groups. The latter could be quaternized by reaction with methyl iodide or protonated by soaking in acidic media. The membranes were characterized in detail by attenuated total reflectance Fourier transform infra-red and X-ray photoelectron spectroscopies as well as elemental analysis to confirm that the above reactions occurred. The effect of this layer on the transport of methanol was investigated. 1. Chamoulaud, G.; Belanger, D., Langmuir, 2004, 20, 4989.

### 4:00 PM M7.7

**Novel Inorganic/Organic Hybrid Proton Exchange Membranes.** Zhiwei Yang, Decio Coutinho, Fangxia Feng, John P. Ferraris and Kenneth J. Balkus, Jr.; Chemistry, University of TX at Dallas, Richardson, Texas.

In this study, a series of novel proton exchange membranes (PEM) based on Bronsted acid-base ionic groups, amine/trifluoromethanesulfonimide (HTFSI), have been explored. HTFSI doped PEI/SiO<sub>2</sub> nanocomposite membranes containing highly dense immobilized amine/HTFSI group exhibited proton conductivities (10<sup>-4</sup> S/cm) at 130°C and anhydrous conditions and 10<sup>-2</sup> S/cm at 90°C and fully hydrated conditions. The 3-dimensional cross-linked polysilsesquioxane membranes have the empirical formula of R-Si(O)<sub>1.5</sub>. The highly cross-linked Si-O backbone in the material provides chemical, thermal and mechanical stability. And the organic side chain, R, is terminated in HTFSI doped organic amines including diamine, dihydroimidazole or polyethylenimine, which provide

membranes the proton conducting properties. The prepared polysilsesquioxane membranes exhibited proton conductivity of  $10^{-3}$  S/cm at elevated temperature (130°C), water-free conditions and  $10^{-2}$  S/cm under fully hydrated conditions.

4:15 PM M7.8

**Fluid Permeability of Porous Silicon Nanostructures.**

Volodymyr Lysenko, Emeline Mery, Benjamin Hannes, Christophe Malhaire and Daniel Barbier; LPM, INSA de Lyon, CNRS, Villeurbanne, France.

Recently, porous silicon (PS) nanostructures were successfully applied for miniaturized fuel cells fabricated with using of silicon-based microtechnologies. However, in spite of great interest to apply PS in such micro-devices, mechanisms of fluids (gas and liquids) transport in this porous material are not yet studied in details. Being well described by Darcy's law, the gas (air and hydrogen) flow measurements allow to deduce PS permeability values which are measured for the first time to be  $10^{-16}$  -  $10^{-15}$  m<sup>2</sup> corresponding to the 50 - 70 % porosity range. Strong porosity dependence of the PS intrinsic permeability is found to be in a good agreement with slightly modified Kozeny's model. Influence of nanoscale morphology on the porous layer permeability is shown and discussed taking into account fractal-like nature of the PS nanostructures. A weak permeability dependence on nature of the used gas molecules is observed and explained by random physical interactions (Klinkenberg and trapping effects) between the travelling gas molecules and PS nanoscale morphology. In particular, liquid permeability of the PS nanostructure is estimated to be  $6.4 \cdot 10^{-18}$  m<sup>2</sup> from the observed Klinkenberg effect for gas flow. The estimation is confirmed by direct measurements of the PS permeability to liquid (ethanol) flows. Impact of the chemical coverage of the PS specific surface to the liquid transport is suggested.

4:30 PM M7.9

**Morphology Control of Proton-exchange Membrane Materials for Fuel Cells.**

Steven Swier, Montgomery T. Shaw and Robert A. Weiss; Dept. of Chemical Engineering and Polymer Program, University of Connecticut, Storrs, Connecticut.

Polymer blends are candidates for proton-exchange membranes (PEM) for fuel cells. They have the potential for achieving the stringent requirements of high proton conductivity combined with long-term mechanical and chemical membrane stability. Each component of the blend can be chosen to fulfill a different requirement. This talk will discuss various approaches for controlling the morphology of a polymer blend PEM. One particularly attractive morphology is a spinodal-like morphology in the membrane, where one interconnected phase optimizes proton conductivity, while the other provides the mechanical stability. Perfluorinated polymer electrolyte membranes such as Nafion<sup>®</sup> have been the principal PEM choice in the past. However, these materials are expensive, have relatively poor resistance to methanol transport (which is important in direct methanol fuel cells) and have poor mechanical properties when highly swollen by water. Contemporary PEM research involves the development of new polymer electrolytes based on hydrocarbon polymers. Poly(ether ketone ketone), PEKK, is a commercial high temperature thermoplastic that has high temperature stability, excellent chemical and solvent resistance and excellent mechanical properties. Because of a higher ketone content, PEKK has a higher glass transition temperature, melting point, stiffness and strength than poly(ether ether ketone), PEEK, which has also been used to prepare PEMs. Sulfonated poly(ether ketone ketone) (SPEKK) is a potential PEM material for fuel cell applications. Proton conductivities and MEA performance data are competitive with Nafion<sup>®</sup> under similar conditions. A large depression in glass transition and significant swelling, however, limits the long term durability of SPEKK membranes. Polymer blends based on SPEKK as the proton-conducting component and engineering thermoplastics like poly(ether imide) (PEI) and poly(ether sulfone) (PES) are being considered in this work as PEMs. A novel approach using blends of SPEKK with different sulfonation levels will also be presented. Membranes were cast from solution using N-methyl-2-pyrrolidone (NMP) or dimethylacetamide (DMAC). Of special interest in this respect is the ternary - polymer/polymer/solvent - phase diagram. Understanding the effect of variables such as the SPEKK sulfonation level, the blend composition and the casting procedure allows for tailor-made membrane properties. Three strategies for composite PEMs can be explored using the three systems: (i) a dispersed droplet morphology for SPEKK/PEI, (ii) an homogeneous morphology for SPEKK/PES and (iii) a co-continuous morphology for SPEKK/SPEKK. The last system results in the most promising PEM material, although increased interfacial adhesion is required for long-term integrity.

4:45 PM M7.10

Abstract Withdrawn

SESSION M8: Membranes II

Chairs: Hubert Gasteiger and Eugene Smotkin

Thursday Morning, December 2, 2004

Fairfax A (Sheraton)

8:30 AM M8.1

**Layer-By-Layer Solid State Electrochemical Systems:**

**Applications To Soft Fuel Cells, Electrochemical Cells And**

**Micropower Systems.** Tarek Rafic Farhat and Paula T. Hammond; Chemical Engineering, MIT, Cambridge, Massachusetts.

Layer-by-layer (LBL) technology that utilizes macromolecules such as polyelectrolytes and colloids is providing new ways to assemble complete electrochemical systems unlike any other conventional method. A major advantage gained from the LBL assembly technique include the utilization of a large family of cheap nontoxic polyelectrolyte material and colloids, fabrication processes that are economic and simple, and electrochemical components which can be miniaturized. A composite membrane made by LBL deposition of polyions on a porous framework is cheap, adaptable than any common commercial proton-exchange-membrane (PEM), and can deliver more than half the power. A stainless steel composite electrode made by LBL deposition of a polyion-colloid of platinum/carbon catalyst acted similar to a pure platinum electrode by furnishing the same open-circuit potential yet delivered higher currents and unlike solid platinum allowed the conduction of ions. The membrane-electrode-assembly (MEA) in a fuel cell can be made many times thinner and smaller while no hot pressing and gasketing is required. Performance plots of an LBL Carbon-Polymer solid state (a) electrochemical cell, (b) soft fuel cell, and (c) devise structure will be presented and discussed. Such electrochemical systems would have potential application in electrochemical, catalytic, electroanalytical, and micro- and macro-power devises that can benefit both the chemical and electronic industry.

8:45 AM M8.2

**Micofluidic Devices for Energy Conversion: Poly**

**(dimethylsiloxane) Membrane-covered Fuel Cells.**

Svetlana M. Mitrovski<sup>1</sup> and Ralph G. Nuzzo<sup>1</sup>; <sup>1</sup>Chemistry, University of Illinois at Urbana-Champaign & Frederick Seitz Materials Research Laboratory, Urbana, Illinois; <sup>2</sup>Chemistry, University of Illinois at Urbana-Champaign & Frederick Seitz Materials Research Laboratory, Urbana, Illinois.

We describe in this work the design and the performance of an entirely passive microfluidic fuel cell - one that incorporates thin-film electrodes deposited onto quartz and a soft-lithographically fabricated microfluidic network made from poly(dimethylsiloxane) (PDMS). The purpose of the PDMS elastomer is to serve as a self-supporting as well as a highly permeable membrane through which the reactants can be selectively supplied to electrodes fully immersed in a liquid electrolyte contained within the channels. We demonstrate that, due to the unique permeation properties of PDMS towards gases and other molecular species, these passive fuel cells can operate using both liquid (methanol, formic acid) and gaseous (hydrogen, oxygen) fuels, and are capable of supporting current densities of  $> 2$  mA cm<sup>-2</sup> and power densities of  $\sim 1$  mW cm<sup>-2</sup>, values that exceed those reported for similar dynamic microfluidic systems. More interestingly, we find that, when operated as oxygen reduction or hydrogen evolution half-cells, these membrane-covered devices produce significantly higher current densities than those measured in conventional electrochemical cells (by almost an order of magnitude). In this talk, I will discuss the effects of the characteristic design parameters of the devices on their performance (surface area, morphology and chemical composition of the electrodes, thickness of the PDMS membrane, nature of the fuel) as well as the major limitations of the present device design to obtaining higher power output.

9:00 AM M8.3

**Reinforcement of Proton-exchange Membranes via Cross-linking using Divalent Cations.**

Jeffrey Gasa<sup>1</sup>, R. A. Weiss<sup>1,2</sup> and Montgomery T. Shaw<sup>1,2</sup>; <sup>1</sup>Polymer Program, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Proton-exchange membranes composed of sulfonated Poly(ether ketone ketone) (PEKK) were found to have excellent proton conductivities (c.a. 0.1 S/cm) for moderate to high levels of sulfonation (c.a. IEC  $> 1.7$  meq/g). However, these membranes exhibited very poor dimensional, mechanical, and barrier properties in an aqueous environment at elevated temperatures (c.a. 60-90 oC), typical conditions for direct methanol fuel cells. This is due to their excessive water uptake (c.a.  $> 50$  wt% of water). To reinforce the membrane, the protons in sulfonated PEKK were partially exchanged

for divalent barium ions to form a physically cross-linked network structure. A solution cast SPEKK membrane was cross-linked in a post-treatment step using an aqueous barium acetate solution. The degree of cross-linking can be fine-tuned by varying the concentration of barium ions as well as the soaking time. The cross-linked membranes were characterized in terms of proton conductivity, water uptake, and methanol permeability at various levels of sulfonation and cross-link densities. Results show that the conductivity was reduced significantly upon cross-linking but the swelling and barrier properties were significantly improved. The cross-linked membranes exhibited excellent resistance to swelling in water at elevated temperatures. Sulfonated PEKK that were water-soluble (IEC > 2.5 meq/g) became water-insoluble after crosslinking with barium. The crosslinked membranes were also found to be stable in acidic environments.

**9:15 AM MS.4**  
**Anhydrous Polymer Electrolyte Fuel Cells Employing Bionics Proton Conductors.** Itaru Honma and Masanori Yamada; EEI, AIST, Tsukuba, Ibaraki, Japan.

The operation of polymer electrolyte membrane fuel cells (PEMFC) at intermediate temperature (100 - 200 C) has been considered to provide many advantages, such as improved CO tolerance of the Pt electrode, the higher energy efficiency, fuel managements, and co-generation. However, at higher temperature, ion-exchange membranes, such as Nafion<sup>®</sup>, suffer from a reduction of proton conductivity due to a loss of water from membrane and also an irreversible change of the polymer structures. Therefore, anhydrous electrolyte materials with high proton conductivity have been investigated extensively. In this study, we prepared an anhydrous proton conducting membrane using a composite of chitin phosphate (CP), one of discarded biopolymer, and uracil (U) molecules, which is in RNA. The CP-U composite material showed the high proton conductivity exceeding  $1 \times 10^{-3}$  S cm<sup>-1</sup> at 150 C and the resulting MEA generates electricity under anhydrous (water-free) conditions.

**9:30 AM MS.5**  
**PPSU based Hybrid Membranes for Polymer Electrolyte Membrane Fuel Cells.** Maria Luisa Di Vona<sup>1</sup>, Alessandra D'Epifanio<sup>1</sup>, Debora Marani<sup>1</sup>, Barbara Mecheri<sup>1</sup>, Enrico Traversa<sup>1</sup>, Marcella Trombetta<sup>2</sup> and Silvia Licoccia<sup>1</sup>; <sup>1</sup>Department of Chemical Science and Technology, University of Rome Tor Vergata, Rome, Italy; <sup>2</sup>Interdisciplinary Center for Biomedical Research (CIR, Campus Bio-Medico, Rome, Italy.

Proton Exchange Membrane Fuel Cells (PEMFCs) can provide both stationary and portable power for many applications, including vehicle power sources, distributed power and heat production, and even portable and mobile systems. Polymer electrolyte membranes (PEMs) are critical components of fuel cells; their main function being to conduct protons efficiently. The membrane must be characterized by low fuel crossover properties, and must also be robust enough to be assembled into a fuel cell stack and have long life. Although many polymers have been investigated over the years, most commercial systems today use Nafion, a perfluorinated sulfonic acid based polymers, as the membrane. Drawbacks of Nafion, the current industrial standard for PEMFCs, are operation below 1000°C, high cost, need of humidification, high methanol cross-over. Promising materials under investigation are hybrid organic-inorganic membranes containing organic polymers bonded to inorganic moieties on a molecular level. The organic part brings elastic and hydrophobic properties of the membranes and the inorganic component high proton conductivity along with hydrophilic behaviour. In the present work the focus has been on the preparation and characterization of organic-inorganic class II hybrid materials based on polyphenylsulfone (PPSU) as the organic backbone. PPSU is a fully aromatic polymer, commercially available, with good thermal stability and oxidation resistance. The conductivity of PSU is a function of the degree of sulfonation, in fact sulfonated cation-exchange membranes must have ion-exchange capacities with a minimum range of 1.4 to 1.7 meq/g to meet the requirements needed for DMFC. However the mechanical properties of PPSU tend to progressively deteriorate with sulfonation. Our approach to improve sulfonated PPSU mechanical properties consists in the introduction of an inorganic network linked to the organic backbone in order to modulate the ratio between hydrophilic and hydrophobic groups. The introduction of the inorganic component was performed by reacting PPSU with different metal chlorides, then hydrolysing the product. Materials were characterized by means of multinuclear NMR (Nuclear Magnetic Resonance) spectroscopy, thermogravimetric and differential thermal analysis (TG/DTA), Fourier transform infra-red spectroscopy (ATR-FTIR), electrochemical impedance spectroscopy (EIS), and testing in a prototype fuel cell

**10:15 AM MS.6**  
**Synthesis of sulfonated silica/heteropolyacid (HPA) composite membranes for high temperature PEM fuel cell applications.** Fangxia Feng, Zhiwei Yang, Decio H. Coutinho and

Kenneth J. Balkus, Jr.; Department of Chemistry, University of Texas at Dallas, Richardson, Texas.

Sulfonated silica/heteropolyacid (HPA) composite membranes were investigated for high temperature proton exchange membrane (PEM) fuel cells. HPAs included tungstosilicic acid (WSA) and tungstophosphoric acid (WPA). The influence of the HPA type, and HPA content on the proton conductivity and fuel cell performance was investigated. The incorporation of WSA increased the proton conductivity (from  $0.4 \times 10^{-2}$  to  $1.9 \times 10^{-2}$  S/cm) at 130C and 20% relative humidity (RH). With an increase in the WSA content, the conductivity increased significantly and reached a maximum value ( $1.9 \times 10^{-2}$  S/cm) with 67 wt.% WSA. The fuel cell H<sub>2</sub>/O<sub>2</sub> performance at 70C and 20% RH, sulfonated silica/50 wt.% WSA composite membrane showed a current density at 0.2 V of 1.56 A/cm<sup>2</sup> and a power output of 416 mW/cm<sup>2</sup>, which were much higher than those of sulfonated silica matrix only (0.60 A/cm<sup>2</sup> and 194 mW/cm<sup>2</sup>, respectively).

**10:30 AM MS.7**  
**Proton exchange membranes based on crosslinked Sulfonated Polystyrene micro particles dispersed in a Poly(dimethyl siloxane) matrix.** Smita B. Boob<sup>1</sup> and Montgomery T. Shaw<sup>1,2</sup>; <sup>1</sup>Polymer program, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Proton exchange membranes composed of highly sulfonated crosslinked polystyrene (SPS) particles dispersed in a poly (dimethyl siloxane) (PDMS) matrix were prepared. The effect of particle size on proton conductivity and water uptake was investigated. Proton conductivities as measured by impedance spectroscopy increased with the SPS particle concentration resulting in values higher than 0.1 S/cm at 40 % SPS in the membrane. The water uptake was measured by thermo gravimetric analysis and it was found that the membranes swelled increasingly with increasing SPS percentage. The PDMS used as the matrix in these membranes was a crosslinkable pre-polymer with a viscosity of about 500 cSt. A siloxane based matrix was selected so that the particles could be dispersed in the pre-polymer which could then be allowed to crosslink at room temperature. This averts the use of any solvent in the membrane preparation. The highly acidic particles did not inhibit the polymerization of matrix. Also no degradation of PDMS was found. An additional approach was used to enhance the proton conductivity of the membranes by creating proton transport channels. These channels were formed by aligning SPS particles under an AC electric field. PDMS with very low dielectric constant acted as a model matrix to obtain the particle chaining. The alignment of particles was confirmed by optical microscopy.

**10:45 AM MS.8**  
**Using neutrons to investigate the nano-structure of diblock copolymer films.** Laurent Rubatat<sup>1</sup>, Olivier Diat<sup>2</sup>, Zhiqing Shi<sup>3,4</sup>, Steven Holdcroft<sup>3,4</sup> and Barbara Frisken<sup>1</sup>; <sup>1</sup>Physics, Simon Fraser University, Burnaby, British Columbia, Canada; <sup>2</sup>UMR SPAM, 5819, CEA, Grenoble, France; <sup>3</sup>Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada; <sup>4</sup>Institute for Fuel Cell Innovation, NRC, Vancouver, British Columbia, Canada.

Block copolymer ionomer films have significant potential as an alternate membrane material in fuel cells. By combining properties of different polymers, we can achieve optimum fuel cell efficiency and membranes of original structure. In this structural study we have used diblock copolymer films made from fluorinated / sulfonated polystyrene polymers as a model system to investigate the correlation between the structure and the transport properties of these materials. The fluorinated diblock copolymers were synthesized by controlled radical polymerization [1], which allow control of the ionic exchange capacity (IEC) by adjusting either the length of the sulfonated polystyrene chains or their degrees of sulfonation. Films made from these materials have two advantages. Firstly, the two blocks are completely incompatible, assuring microphase separation. Secondly, the particular polymer synthesis used achieves a low polydispersity of polymer block length, and, as a consequence, very well-defined structures. The nano-structure of various polymer configurations has been studied by Small Angle Neutron Scattering (SANS) using contrast variation methods. These results will be reported and compared to images from transmission electron microscopy (TEM). This two-pronged approach in both Fourier space (with SANS) and real space (with TEM) is essential, because SANS gives volume average information from the micrometer to the Angstrom scale and TEM gives local information with nano-meter resolution. [1] Z. Shi and S. Holdcroft, *Macromolecules*, 37 (2004) 2084

**11:00 AM MS.9**  
**Assembling Latex Particles into Proton-Conductive Membranes.** Jun Gao<sup>1</sup>, David Lee<sup>1,2</sup>, Yunsong Yang<sup>2</sup>, Steven Holdcroft<sup>2,3</sup> and Barbara J. Frisken<sup>1</sup>; <sup>1</sup>Department of Physics, Simon

Fraser University, Burnaby, British Columbia, Canada; <sup>2</sup>Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada; <sup>3</sup>Institute for Fuel Cell Innovation, National Research Council Canada, Vancouver, British Columbia, Canada.

In this work, we present results from our investigation of the concept and practice of using surface-charged latex nanoparticles as building blocks for proton conductive membranes. Nanoparticle syntheses were conducted by free-radical emulsion co-polymerization in water of two hydrophobic monomers, butyl acrylate (BA) and methyl methacrylate (MMA), a crosslinker, N, N'-methylenebisacrylamide (BIS), and a charged monomer, sulfonate styrene sodium salt (NaSS). The resultant nanospheres were characterized by a combination of static and dynamic laser light scattering. Thin films were cast from concentrated dispersions of the particles followed by incubation at temperatures above the glass transition temperature of the polymers. Conductivity, water uptake and final charge content were monitored. The membranes have a higher conductivity at low charge content than polymer gels and polymer chain thin films with similar compositions. TEM images provide information about continuous hydrophilic channels in the membranes that form naturally in films consisting of close-packed surface-charged nanospheres

**11:15 AM M8.10 TRANSFERRED TO M8.7**