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

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

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

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

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). Previous work on the Ruddlesden-Popper (RP) phases have suggested this class of materials to be alternatives for the conventionally-used NiO-Y2O3 stabilized ZrO2 (YSZ), 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 an oxygen diffusivity through BSCF, which eliminates oxygen diffusion as the rate-limiting step in the overall electrode reaction 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 mW cm⁻² was achieved at 600 and 500 °C, respectively, using a 20 μm 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 electrode reaction process.

8:45 AM


Air Vehicle Research Section, Defence Research and Development Canada, Ottawa, Ontario, Canada; 2Institute for Chemical Process and Environmental Technology, National Research Council Canada, Ottawa, Ontario, Canada.

Previous work on the Ruddlesden-Popper (RP) phases has suggested these materials to be alternatives for the conventionally-used perovskites employed as solid-oxide fuel cell cathodes. In this study, an RP nickelate (LSGM) has been synthesized and evaluated as a solid oxide 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 (50 S/cm). Furthermore, ASR studies have shown that the performance of this material as a cathode on LSMG electrolyte is significantly improved in comparison to the previously-studied RP phase, La2NiO4+. 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

Performance Enhancement of SOFC Electrode Materials by Mechanical Particle Bonding Technique. C. C. Huang, Takehisa Nakamura, Jun-Min Kang, and Isabel Davidson.

Materials Science, Chemical Engineering, California Institute of Technology, Pasadena, California.

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. In this work, we have developed 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°C).

9:15 AM


Guosheng Ye and Donald Seccombe; 2Dept. of Manufacturing Engineering, Boston University, Brookline, Massachusetts; 3BTU International, N. Billerica, Massachusetts.

The aim of this research is to employ co-firing below 1250°C to fabricate anode-supported solid oxide fuel cells (SOFCs). The selection of the lower and higher temperatures of the mechanical Particle Bonding 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 anodizing temperatures. The challenge in this research is to densify the Ni-YSZ stabilized ceria electrolyte at reduced temperatures. In the present work, two kinds of YSZ powders, nano-scale (50 nm) and sub-micron-scale (0.15 μm), 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°C, 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 other micron-size oxides as dopants and liquid-phase sintering aids 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 anode-supported YSZ powders can contain some amount of contamination large YSZ grains (20 nm) 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-sample and the nano-scale YSZ powders that result in the densest sample with a uniform microstructure.
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 (LaMnO3) 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 and effective removal of organic molecules. The key feature of the preparation process, transmission electron microscopy was applied to analyse the microstructure of sintered YSZ electrolyte substrates before and after aging. The investigated samples were microtomed and conventional TEM images yield information about the polycrystalline nature 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. Redox reflections from the tetragonal phase show nanometer-scaled regions embedded in the cubic matrix. Two-beam bright-field images show contrast fluctuations on a scale of 10 nm which can be associated with strain fluctuations induced by compositional modulations. We attribute the presence of the tetragonal phase to partly reduced Y2O3 concentrations. Therefore, Y2O3 is not fully stabilized 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. In the as-sintered sample, the weak reflections pattern allows 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. The short-range order on the oxygen sublattice reduces the oxygen vacancy concentration available for diffusion, which has been observed 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.


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 500-700°C. The electrolyte, anode, and cathode materials in the SOFC system being investigated are based on lanthanum/strontium (La0.85Sr0.15) ceria (Zr0.85Y0.15), mullite (β-Ce0.85Zr0.15O2.015 or GDC) cermet, and LSGM-lanthanum cobaltite (La1-xSrxCoyFe1-y03, or LSCF) composite, respectively. These material choices are based on their property information available in the literature. Interfacial polarization for the LSCF electrodes for the LSGM electrolyte have been investigated by impedance spectroscopy technique. Among the cathode materials (LSM (La0.85Sr0.15O3) and LSCF), the pure LSM electrode had the worst 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 LSGM-LSCF 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 LSGM-LSCF composite electrodes. Addition of LSGM to LSCF did not significantly alter the oxygen reduction performance. The oxygen reduction activity of the LSCF electrode was found to be explained by short-range order of oxygen vacancies which is well known. 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.


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 500-700°C. The electrolyte, anode, and cathode materials in the SOFC system being investigated are based on lanthanum/strontium (La0.85Sr0.15) ceria (Zr0.85Y0.15), mullite (β-Ce0.85Zr0.15O2.015 or GDC) cermet, and LSGM-lanthanum cobaltite (La1-xSrxCoyFe1-y03, or LSCF) composite, respectively. These material choices are based on their property information available in the literature. Interfacial polarization for the LSCF electrodes for the LSGM electrolyte have been investigated by impedance spectroscopy technique. Among the cathode materials (LSM (La0.85Sr0.15O3) and LSCF), the pure LSM electrode had the worst 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 LSGM-LSCF 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 LSGM-LSCF composite electrodes. Addition of LSGM to LSCF did not significantly alter the oxygen reduction 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 LSGM-LSCF 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 LSGM-LSCF composite electrodes. Addition of LSGM to LSCF did not significantly alter the oxygen reduction performance. The oxygen reduction activity of the LSCF electrode was found to be explained by short-range order of oxygen vacancies which is well known. 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.
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) and rotating disk electrode (RDE) measurements. Integrated into a high throughput combinatorial workflow, stability, electrochemical activity and structure of a Pt-based ternary system is rapidly analyzed. Results from a carbon supported, high-surface-area catalyst alloy system will be discussed.

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 large number of compositions in a single experiment. In this work, we describe high throughput strategies to generate a large variety 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-variant 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 micrographs 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.

Recent studies on fuel cell electrocatalysts show that some intermetallic compounds have improved oxygen reduction 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 analyze 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 discover Pt-Bi-Pb spreads that cover the central 60% of the ternary phase diagram. Compositions that are rich in Pt show the best electrocatalytic activity, as expected. Other experimental results will be presented.

A combination of three-electrode cycling and rotating disk electrode (RDE) measurements. Combined with high throughput experimentation, stability, electrochemical activity and structure of a Pt-based ternary system is rapidly analyzed. RESULTS FROM A CARBON SUPPORTED, HIGH SURFACE AREA CATALYST ALLOY SYSTEM WILL BE DISCUSSED.
X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) experiments were performed on an operating liquid fuel cell DMFC. The Pt LIII-edge and Ru K-edge of unsupported Pt-Ru 1:1 anode electrolyst catalysts were studied in the transmission mode to initiate elucidation of oxides in methanol electrooxidation. Anode X-ray absorption spectra were obtained as a function of fuel cell potential and methanol concentration using a Pt 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 catalyst 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 hydride yielded Pt compositions of 20% or greater throughout 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, Ana- dirigentes Pinares, J. Vidal, Jose Solain, Enrique Herero and Antonio Algo. Instituto de 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 process between the reactivity monitored on well defined stepped surfaces enables to prepare analytical calibration curves. These results may be used 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, to more complex structure sensitive reactions, such as hydrogen and adion 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 place on Pt, PtRu, PtSn and PtFe, may be used to confirm the assignment based in this purely electrochemical method. Among them, ammonium oxidation in alkaline electrolytes has been shown to be specific to Pt(100) terrace sites on the surface of nanoparticles.


We used atomic pair distribution function (PDF) analysis and x-ray spectroscopy (XANES) to study the structure of 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 α-quartz (berlinite). The Fe2+, Fe3+ and phosphorus are tetrahedrally coordinated in a corner linked tetrahedral network structure and facilitate an iron 2+/4+ redox couple. In the catalysts with the highest RH, the catalytic activity 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 is responsible for the high density of Pt-Pt-Pt interactions 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 Electro catalysis of Cathodic Oxygen Reduction and Anodic CO and Methanol Oxidation: Combination of Electrochemistry and Synchrotron based In-situ XAS. Sanjeev Mukerjee1 and Vivek S. Murthi2.

1Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts. 2Chemistry 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, Pt-M + H2O → Pt-MOH + H+ + e−) plays a crucial role in determining the overpotential losses at both the cathode and anode (when using direct methanol or reformate feed). We have studied the cathode 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 hydride yielded Pt compositions of 20% or greater throughout 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.

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 [2]. 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 systems relative to Pt/C for the catalysis of the ORR is attributed to several factors, such as electronic effects, changes in the crystallographic structure, and 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 H2/O2 and methanol/O2. The results of this work show that the characteristics of Pt-Co/C catalysts 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. Viebiach, 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/C Electrocatalysts for Oxygen Reduction. J. Phys. Chem. B, 2004, in press.


The design and fabrication of three-dimensional multifunctional architectures from the appropriate nanoscale building blocks presents a new tactic to optimize catalytic performance. One advantage of these three-dimensional porous networks, 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 polymeric aerogel, resulting in a polymer 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 shape within mesoporous materials 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.
demonstrated by adsorbing pre-formed metal colloids (specifically 2.5-nm Pt) from aqueous colloidal solutions under conditions in which unsupported Pt colloids cannot. The Pt-NVNTs are 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 CNT-type Pt-NVNTs are active for CO adsorption and oxidative stripping for a carbon nanoarchitecture derived from RF gel with a large free volume (1 cm$^3$/g) and 400 m$^2$/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 heterogeneous doped carbon nanofibers (HFCNF) 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 also be modified 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 electrocatalytic reduction 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 in which adsorbed oxygen reduction reaction can be treated as a catalytic regenerative process where HO$_2$ is chemically decomposed to regenerate oxygen. The proposed electrocatalytic 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 fuel cell. The long-term objectives of this research project specifically targeted for polymer electrolyte membrane fuel cells are to improve the stability of the carbon, to maximize the catalyst utilization, to improve the membrane-catalyst 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 reacting azo compounds with hydrogen halides 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-diethylphenylamine, 4-aminocarboxylic acid, 4-aminophenol, p-nitroaniline and sulfamic acid. The diazonium salts 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

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 NaftionTM) to transport protons between two porous electrodes. These fuel cells operate at relatively low temperatures (80-85 °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 minimum amount of catalyst required. The maximum 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 an 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 suggest SWCNTs to be characterized and compared 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, Fabrica Piazza and Gerardo Morelli; 1 Dept of Physical Sciences, University of Puerto Rico, San Juan, PR, Puerto Rico; 2 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 H2 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. CNTs are grown on rough silicon, anodized aluminum oxide substrates, and silicon nitride oxide nanoparticle catalytic carbon nanotubes. The carbon nanotubes are characterized by SEM, TEM, XPS and Ramann spectroscopy. The intercalation of Pt nanoparticles into the matrix is done electrochemically.

11:45 AM M3.10

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 porosization 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 wt. % Naftion® 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 work was achieved with as much as a 75% reduction in the quantity of precious metal used. 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 W (1-2 microns), at an average power density of 100 W/cm2. The reaction furnace temperature was held at 1100°C, with a chamber pressure of 700 torr under 100 sccm flowing Ar(g). The as-produced SWNTs were purified through the use of solvent washes, acetylene gas, and oxidative treatments. 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, and high-resolution transmission 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 2% w/w to the fully purified 95% w/w. Fuel cell performance was measured 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

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 FTIR, 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} shows 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 H2O molecules. The vibrational frequency of the bending mode indicates that water forms an H-bonded structure. Activation of a single H2O 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.; Gutierrez, 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 Next. Jerzy 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 also relevant to 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 dedicated to the Pd family of anode catalysts, including Pt/Pd for carbon monoxide oxidation at Pt(111). Teresa Iwasita and E. A. Batista; Instituto de Quimica de Sao Carlos, Universidade de Sao Paulo, Sao Carlos, Brazil.

The potential/time behavior at cathodes and anodes of small fuel cells (4.6cm²) is studied for methanol and ethanol oxidation. At 60-80°C a continuous flow of fuel and dry oxygen to the porous surfaces (Pt/Ru/C and Pt/C) is used, the electrodes being separated by a Nafion 117 membrane. Alcohol crossover 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/cm² (for ethanol) and 200mA/cm² (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 electrode does not determine the faradic efficiency in fuel cell operation. Using methanol at concentrations below 0.5M, temperatures as low as 60°C and current densities above 100mA/cm², 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 formate are essentially compensated by further reaction steps forming CO2.

2:30 PM M4.3
Physical Properties and Electrochemical Response of Pt-Ru/C Supported Nanocatalysts for Direct Methanol Fuel Cells. William Hilal, Ricardo-Luis-Valbuena, Carlos O. Pava-Santos,*, Ernico Teixeira-Neto,*, Rita Vinhas,*, Robert Landers,*, Carlos A. P. Leite,*, Fernando Galembek,*, Dayse C. Azevedo,*, Martha Janete Gis,*, Edison A. Ticianelli* and Ernesto Rafael Gonzalez; 1 Fisico Quimica, Instituto de Quimica de Sao Carlos-USP, Sao Carlos, SP, Brazil; 2 Instituto de Quimica, Unesp, Araraquara, SP, Brazil; 3 Instituto de Fisica, Unicamp, Campinas, SP, Brazil; 4 Instituto de Quimica, Unicamp, Campinas, SP, Brazil.

In this work, the physical characterization of Pt/C and Pt-Ru/C supported nanocatalysts 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 Backscatter, 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 cyclic voltammetry and current 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 nanoparticles 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 Ru/C 68.5 % of metallic Ru (more than in Pt/C E-TEK) and 18 % of Pt(OH2), higher than the 15.9 % of metallic Pt (more than in Pt/C E-TEK). For Pt-Ru/C 82:18, there is a considerable quantity (52.3 %) associated to metallic Ru and RuO2 and 23.3 % of RuO3 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 voltamograms obtained with thin film electrodes show that 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⁻², when using Pt-Ru/C 82:18. Compared to Pt/C 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(OH2) species. [1] W. H. Lizardo-Valbuena, D. C. Azevedo, E. R. Gonzales, Electrochim. Acta 49 (2004) 1289.

3:15 PM *M4.4
Parallel Reaction Pathways for Methanol and Ethanol Oxidation at Porous Fuel Cell Electrodes. V. Pagagnin, G.R. P. Malpass and W. Veličković, I€.UC, University of Sao Paulo, Sao Carlos, Brazil.

The potential/time behavior at cathodes and anodes of small fuel cells (4.6cm²) is studied for methanol and ethanol oxidation. At 60-80°C a continuous flow of fuel and dry oxygen to the porous surfaces (Pt/Ru/C and Pt/C) is used, the electrodes being separated by a Nafion 117 membrane. Alcohol crossover 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/cm² (for ethanol) and 200mA/cm² (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 electrode does not determine the faradic efficiency in fuel cell operation. Using methanol at concentrations below 0.5M, temperatures as low as 60°C and current densities above 100mA/cm², 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 formate are essentially compensated by further reaction steps forming CO2.

3:45 PM M4.5
Theoretical study on dissociation pathways for oxygen on platinum surfaces. Satoshi Yotsuhashi, 1 Yuka Yumad, 1 Wilson Agencio Dino, 2, 3, 5, 4 Hiroshi Nakatani, 2 and Hideaki Kasai, 2; 1 Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., Osaka-gun, Kyoto, Japan; 2Department of Applied Physics, Osaka University, Suita, Osaka, Japan; 3Japan Science and Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., Osaka-gun, Kyoto, Japan; 4Department of Applied Physics, Osaka University, Suita, Osaka, Japan; 5Japan 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 major concerns is the decrease in electronic conductivity due to the 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. 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) is 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 $\mathrm{O_2}$ molecule ($Z$), and the distance between the $O$ atoms ($\rho$), and determine the reaction path. When $Z$ is large enough, the equilibrium distance corresponds to $\rho = 1.2 \AA$, and the two $O$ atoms form an $O_2$ molecule. As the oxygen molecule approaches the platinum surfaces, we find a potential minimum at $Z = 1.2 \AA$ and $\rho = 1.8 \AA$ 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 differences 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.

By applying our convenient alloy preparations, we have found various electrocatalysts alloyed precious metals or precious and non-precious metals for the oxidations of $\mathrm{CH}_3\mathrm{OH}$ and the oxidation derivatives including CO and also for CO tolerant H2 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 transition non-precious metals exhibit improved CO tolerance to H2 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 neighboring O atoms as neighbor sites for Pt, however, a different catalysis could be observed at Pt skin formed by the electrochemical pre-treatment. No noticeable back-donation of 5d electron but the donation of 5-sigma electron to O atom 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 to O atom was observed at Pt skin formed by the electrochemical pre-treatment.}

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 catalysts for bipolar plate materials.
presence of the surfactant N(Oct)4Br. PtPb nanoparticles with a mean particle size of 20nm can be reduced from corresponding metal chlorides with LiBH4 in the presence of N(Oct)4Br.


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 estimated by transmission electron microscopy, on the carbon support catalyst and Pt black catalyst at the cathode with 2 mg/cm² Pt loading. Results from the characterization studies of these nanoparticles using XRD, SEM and UHV-STEM analyses, have been presented. The Polyol process has used to synthesize other Platinum containing intermetallic nanoparticles like PrBi, and results from this synthetic technique are also presented.

M5.3 Preparation and Characterization of Long-Lived Anode Catalyst for Direct Methanol Fuel Cells. Yumuru Shimazaki, 2,3 Yoshio Kobayashi 2,3, Masatoshi Sugimasa 2,3, Shinji Yamada 2,3, Takeyuki Hsueh 2 and Chiou-Ping Huang 2; 1. Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, Sendai, Miyagi Pref., Japan; 2Tohoku Technoarch, Sendai, Miyagi Pref., Japan; 3Research Laboratory, Hitachi Ltd., Hitachi, Ibaraki Pref., Japan; 4Hitachi 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 PrRu alloy nanoparticles with porous skin layers on their surface, which were formed by reaction of surface-active PrRu nanoparticles 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 M H2SO4 solution). The skin layers of PrRu 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. Chunchuk Pak, Daeyeon Yu, Seol-Ah Lee and Hyuk Chang; Materials and Devices Lab, Samsung Advanced Institute of Technology, Yongin-Si, Gyeonggido, 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 enhance the thickness of electrode and increase the performance of DMFC, it is requested to prepare highly dispersed carbon-supported Pt catalyst with high loading. In this presentation, highly dispersed carbon-supported Pt catalyst with 60wt% Pt 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/cm² Pt loading was measured and compared at 313K. Current density at 0.4V is 127 mA/cm² for the new catalyst prepared in this time and 72 mA/cm² 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.

M5.6 Platinum-Embedded PAN-Based Carbon Nanofibers. Lei Zhang 1, Bin Cheng 2 and Edward T. Samulski 1,2; 1Curriculum in Applied Materials Sciences, University of North Carolina, Chapel Hill, North Carolina; 2Chemistry, 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(I) is reduced to elemental Pt with the Pt particles embedded in the carbon matrix. The Pt 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-Hsien 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, CNxNTs 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 with-out 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 ferrocyanide as the molecule probe to study the electrochemical properties of CNxNTs on Ti layers with different thicknesses. Our preliminary studies suggest that the morphology of CNxNTs 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/Co3F2 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, Jing-Chie Lin, Kao-Lin Hauch 1 and Chiou-Ping Hung 2; 1Department of Mechanical Engineering, National Central University, Jhongli, Taiwan; 2Materials 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 each component layer should be considered in detail. It was of interest to develop a simple method to estimate the methanol transport in the component layers of the anode assembly in DMFCs. Diffusion coefficients of the methanol in several commercial GDLs and Naion membranes were determined 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 the expectation that methanol from anode to cathode in a DMFC.


Low temperature (~350°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 GaC3-GeC3 solution and PVA polymer was put into NH2OH solutions, precursor of Gd-doped CoO2 (GDC) fiber formed at room temperature. The prepared fibrous in glass forms shows homogenous 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 M5.5

M5.11 In situ High Temperature Characterization of La-Cr-O Thin Films by Micro-Raman, XRD, and TEM. Nina Orlovskaya1, 2, Dean Steinmetz3, Sergey Yarmolenko4, Jeg Sankar5, Chris Johnson6, and Randall E. Oreziok5. Pennsylvania State University, University Park, PA, USA.

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 LaCrO4 monazite type compound. The second transformation was from LaCrO4 to orthorhombic LaCrO3 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 in situ high temperature micro-Raman, X-ray diffraction (XRD), transmission electron microscope (TEM) with energy dispersive X-ray analysis (EDS). The mechanisms of the amorphous to the LaCrO3 orthorhombic phase transitions have been studied.

M5.12 Fabrication and Testing of a Planar Membraneless Microchannel Fuel Cell using Formic Acid and H2/O2 Fuel Systems. Jamie Lee Cohen1,2,3,4, Daron A. Westley1,5, Alexandre Pedchenko6,7 and Hector D. Abruna1,2,3,4,5,6,7,8.

A novel design for a planar membraneless microchannel fuel cell (PMFC) is presented. The design, which eliminates the need for a polyethylene membrane (PEM), takes advantage of the laminar flow of fuel and oxidant streams generated at a tapered flow channel. This gives rise to a "virtual membrane" with diffusion that is 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, varying in width and height, have been fabricated 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⁻² 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 cells with PEM design. Using the high temperature characterizing the H2/O2 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/cm² have been observed when these H2/O2 fuel cell systems are employed.

M5.13 High Throughput Screening of CO-tolerant Anode Materials by IR thermography. Yusuke Yamada, Atsushi Ueda, Hiroshi Shioyama, Tsutomu Ioroi, Kazuaki Yasuda and Tetsuhiko Kobayashi; RI for Ubiquitous Energy Devices, AIST, Ibeda, 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 catalyst is performed by CO poisoning method using CO as a single gas. To evaluate the catalytic activity in such a complex situation, we developed a high throughput screening system using IR thermography. The IR thermography realizes high throughput screening of catalyst library 2-dimensionally arranged. The catalysis activities of hydrogen combustion in the presence of CO and water gas shift reaction on each catalyst 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 where A were chosen from Bi, Fe, Ce, Ta, Ni, Sr, 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 catalysts was evaluated at the same time. The catalytic array was put in a flask with gas inlet and outlet. The catalysts were exposed to 2000 ppm H2 and 1000 ppm O2 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-Ta, Pt-Ta-Ga, Pt-Mo-Zr and Pt-Mo-Ce system maintained H2 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."


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 laptops, computers, cellular phones, power tools, and so on. Reliability and lifetime are the most important issue in such power sources for practical use. Therefore, 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 catalyst 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 have nanoscale structure. 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 put on micro-grid. The observations were performed by a JEM, JEM-300F with transmission electron microscope equipped with energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS) and angular dark field scanning transmission electron microscopy (ADF-STEM) systems. The thin area of electron 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 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 nanoparticles. The composition of Pt-only was also measured by STEM-EDS method. Some small particles consisted of Pt-only. Moreover it is found that the large particles about 10-50 nm were observed in the PEM after the potential cycling test. This result means that the Pt-Ru and Pt-only aggregated in the Pt 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 D. Susko, Jr.; Chemistry, University of Texas at Dallas, Richardson, Texas.

Mesoporous molecular sieve was prepared from mesoporous benzene silica (MBS). MBS, which is synthesized using 1,4-bis(triethoxysilyl)benzene and octadecytrimethylammonium surfactant, is a hybrid mesoporous composite with molecular scaling periodicity in the pore walls. MBS also displays a homogeneous distribution of the phenyl rings within the pore walls. To prepare the mesoporous carbon, H2PtCl6 was introduced into the pores of template free MBS by an incipient wetness process and the resulting MBS/H2PtCl6 powder was heated under vacuum to 1150°C. This process produced a mesoporous graphitic framework with surface area of 950 m²/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.


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 PtRu/PtRh and PtIr/Cu ordered intermetallic phases appeared to be the most promising electrocatalysts tested thus far for fuel cell applications. In the case of methanol oxidation PtRu/C 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, PtRu/PtRh and PtIr/Cu, were further characterized, using DEMS (differential electrochemical mass spectrometry). The results obtained for PtIr/Cu and PtIr/Cu 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 PtIr/Cu, CO and carbon dioxide were both main products of the oxidation reaction.

In addition, the electrocatalytic activity of these materials is 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. Gd2(2Zr0.1Ti0.9)2O7 is a nanocrystalline xerogel formed by synthesis of the A- and B-site cations and the oxygen anion vacancies. Here, we demonstrated the manipulation of disorder extent in Gd2(ZrTi1-x)2O7 pyrochlore by ion beam irradiation-induced order-disorder structural transformation and successful created a nano-scale buried defect-fluorite structure within a perfect fluorite matrix. A perfect fluoride/matrix was formed between the buried fully disordered fluoride 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 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 Gd2Ti2O7), 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, Geon Seok Choi and Suk Bon Yoon; Chemistry, Hannam University, Daegu, 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 recreated in the full mesoporous (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 Barlow, Louis G. Carreiro, Eric S. Greene and Craig M. Deschenes; Propulsion Branch, Naval Undersea Warfare Center, Newport, Rhode Island; Mechanical Engineering, University of Connecticut, Stornrs, Connecticut; 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 liquid 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 requirements, 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, of nickel cermet anode, (La0.8Sr0.2)MnO3 cathode, and YSZ electrolyte. Cycling experiments were performed in the temperature range of 500°C to 900°C in order to accumulate 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 (LaCrO3) 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 (LaCrO3) powders were prepared by combustion reaction of liquid solution of metallic nitrate and ure. The exothermic reaction produces a sufficiently high temperature for crystallization of the structure to occur in avoiding the necessity for
further calcination. The huge amount of gas evolved in the reaction 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 system architecture has been developed for thermally efficient thin-film applications, 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 collaborative effort to develop a prototype µSOFC 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 collector, and electrical performance tests of fabricated devices. Stability tests of free-standing membranes of varying length scales and supported thin films of fuel cell architecture 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, microdive testing stations allow for performance studies of prototype microdevices.}

**SESSION M6: Nanomaterials-Alloys, Intermetallics, and Heterocatalysis**

### Wednesday Morning, December 1, 2004

**Chairs:** Hector D. Abruna and Carlos Cabrera

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

**Ordered Intermetallic Compounds: A New Approach to (Electro)catalysts.**

**Francis J. DiSalvo,** R. B. van Dower and H. D. Abruna


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 28 °C and are less sensitive to S (by over three orders of magnitude) than Pt or Pt/Rh. Thus, fuels such as impure H2, HCOOH and CH3OH 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 catalyticities 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 should 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. Gdíl, A.C.D. Angelo, C. Lind, F.J. DiSalvo, H.D. Abruna, Chem. Phys. Chem. 2003, 4, 193-199. (2) E. Casado-Rivera, D.J. Volz, L. Ailden, C. Lind, C. DiSalvo and A.C.D. Angelo, F.J. DiSalvo, H.D. Abruna, J. Am. Chem. Soc. 2004, 126(12), 4034-4049.

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

**Ab Initio Study of Hydrogen Permeation through Palladium Membrane.**

**Pil-Ryung Cha**, Eung-Kyu Lee, Hyun-Kwang Seok and Kibae Kim; 1School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea; 2School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; 3Advanced 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 Palladium 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 and Plane Augmented Wave (PAW) Pseudo-potential method to calculate adsorption energies and energy barriers for transitions to and from the bulk Pd, diffusion r within Pd, and recombinative desorption in various surface coverages of hydrogen. It is found that the major energy barriers in the bulk Pd decreases with increased 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-limit 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.
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. Electrodeposited Pt, Pt-Ru, Pt-Mo, and Pt-Ru-Mo electrocatalysts were made through electrochemical techniques, introducing metals such as Ru and Mo by sequential or simultaneous method. A fundamental study of the surface area in the voltage range above 1 V on several Pt/C catalysts was carried out for Pt, PtRu, and PtMo catalysts electrodeposited on HOPG substrates. In general this showed a displacement of the angle of operation will also be examined.

References


We present a new material with application as electrodes in proton exchange membrane 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 nanoporous 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 atom in the surface atom exposed to reactant flow, and catalytic surface areas are typically greater than 100 m^2/cm^2. We will discuss methods to make catalytic electrodes with Pt loading less than 0.05 mg/cm^2, simple methods to integrate this material into existing fuel cell architectures, and fuel cell performance using Pt-NPG.


Gold-based nanoparticles (1-5 nm) have recently been highly active catalysts. A major factor of their catalytic activity is related to the unique size- and composition-dependent electron delocalization in 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 describes the degradation in surface area in the potential 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


Gold-based nanoparticles (1-5 nm) have recently been highly active catalysts. A major factor of their catalytic activity is related to the unique size- and composition-dependent electron delocalization in 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 describes the degradation in surface area in the potential 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

The development of non-platinum electrocatalysts for Polymer Electrolyte Membrane Cells has not yet been realized 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 depositing the ruthenium sulfide electrode and platinum electrode onto a Nafton 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 100 mg cm⁻² loading. 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 cm² 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.


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 minimize the reactor 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 with the monoliths during cold start-up periods. In the present work, some approaches to design of efficient catalysts for CPO and ATR of methane, iso-octane and gasoline based on monolithic metallic supports of different types (honeycomb monoliths and ceramic, ceramometal monoliths) are presented. The honeycomb metal monolith supports having a corrugated structure and up to 500 cells/in² density were made from a heat-resistant foil coated with a-Á1203 layer using proprietary methodologies. Metallic monolithic supports having a pore diameter of 1-4 mm were coated by nanocomposites comprised of binary metal particles (Ni-Pt) in order to minimize the reaction zone and thereby the cost of the catalyst layer. The honeycomb monoliths were then coated with a catalytic layer containing ruthenium and noble metals. The coated monoliths were characterized using XRD, BET, TGA, ICP, XPS, and SEM. The coated monoliths were then tested in a CPO reactor in order to evaluate their performance and stability under realistic conditions. The results show that the coated monoliths have high activity and stability under realistic conditions and can be used for the production of hydrogen from hydrocarbons.


A new tungsten fuel cell catalyst has been discovered for PEM fuel cells, and this material is synthesized using high-purity chinine dioxide (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. The results of these tests also show catalytic activity in reformate 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 and 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 10⁻¹⁴ S cm⁻¹ 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 CsH₃PO₄ 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 atmosporhonic humidification. A
layer of CsH2PO4 was sandwiched between two electrolysis layers containing 18 mg Pt cm−2. For operation of direct methanol fuel cells, the anode catalyst was replaced with 13 mg Pt cm−2. 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 electrolyte. Fuel cell electricity was collected at 250-260°C. For the H2/O2 gas, cells 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 (70°C) water (3:15 PM *M7.5)

We show that an iron-based ceramic material is a good candidate as an 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 suspended in Millipore water and electrolyte material for PEMFC. These membranes have comparable conductivity to that of Nafion. The hydrogen bonds in the structure of lepidocrocite (1.5) even if reduced...
membranes the proton conducting properties. The prepared polysilsesquioxane membranes exhibited proton conductivity of 10^-3 S/cm at elevated (130°C, water-free conditions and 10^-2 S/cm under fully hydrated conditions.

4:15 PM MT.8
Fluid Permeability of Porous Silicon Nanostructures.
Volodymyr Lysenko, Emeline Mery, Benjamin Hannes, Christophe Malhaire and Daniel Barbir-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^-15 - 10^-14 m^2 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 the nature of the used gas molecules is observed and explained by random physical interactions (Klinkenborg 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 10^-14-10^-12 m^2 from the observed Klinkenborg effect for gas flow. The estimation is confirmed by direct measurements of the PS permeability to liquid (ethanol) flows (impact on the chemical coverage of the PS specific surface to the liquid transport is suggested.

4:30 PM MT.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 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. But PEKK has a higher glass transition temperature, melting point, stiffness and strength than poly(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 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 thermoplastic polymers 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's with different sulfonation levels will also be presented. Membranes with a methyl-2-glycerol (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/PEEK. The last system results in the most promising PEM material, although increased interfacial adhesion is required for long-term integrity.

8:45 AM MS.8.
Svetlana M. Mitrovski and Ralph G. Nuzzo, Chemistry, University of Illinois at Urbana-Champaign & Frederick Seitz Materials Research Laboratory, Urbana, Illinois. 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 permittivity 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 exhibit higher catalytic current densities of 10^2 mA cm^-2 and power densities of ~ 1 mW cm^-2, 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, we will discuss the effects of the characteristic design parameters of the microfluidic systems 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 MS.8.

Proton-exchange membranes composed of sulfonated Poly(ether ketone) (PEEK) 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. > 50 wt% of water). To reinforce the membrane, the protons in sulfonated PEKK were partially exchanged
Anhydrous Polymer Electrolyte Fuel Cells Employing Bionics as electro-conductive materials.

Sulfonation, in fact sulfonated cation-exchange membranes must have significantly upon cross-linking but the swelling and barrier properties were significantly improved. The cross-linked membranes exhibited excellent resistance in wetting with inorganic ion solutions. 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.

Anhydrous Polymer Electrolyte Fuel Cells Employing Bionics as electro-conductive 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/heteropolycation (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 x 10^-2 to 1.9 x 10^-2 S/cm) at 130°C and 20% relative humidity (RH). With an HPA content increased significantly and reached a maximum value (1.9 x 10^-2 S/cm) with 67 wt. % WSA. The fuel cell H2/O2 performance at 70°C and 20% RH sulfonated silica/WSA composite membrane showed a current density of 1.2 V of 1.56 A/m2 and a power output of 416 mW/cm2, which were much higher than those of sulfonated silica matrix only (0.60 A/cm2 and 194 mW/cm2, respectively).

Proton exchange membranes composed of highly sulfonated crosslinked sulfonated polysiloxane (SSPS) particles dispersed in a polysiloxane (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 SSPS particle concentration resulting in values higher than 0.1 S/cm at 40 % RH in the membrane. The water uptake was measured by thermogravimetric analysis and it was found that the membrane swelled increasingly with increasing SSPS percentage. The PDMS used as the matrix in these membranes was a crosslinkable pre-polymer with a viscosity of about 500 cS. 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.

Using neutrons to investigate the nano-structure of diblock copolymer films. Laurent Rubatat1, Olivier Diaz2, Zhiqiu Shi3,4, Steven Holdcroft5,6, Barbara Friskin7; 1Physics, Simon Fraser University, Burnaby, British Columbia, Canada; 2UMR SPAM, 5819, CEA, Grenoble, France; 3Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada; 4Institute 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 degree of sulfonation. Films made from these materials have two advantages. Firstly, the two blocks are completely incompatible, allowing 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 nanostructures of diblock copolymer membranes have 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-probed approach with 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.

Assembling Latex Particles into Proton-Conductive Membranes. Jun Guo1, David Lee2, Yunsong Yang3, Steven Holdcroft2,3 and Barbara J. Friskin1; 1Department of Physics, Simon Fraser University; 2Department of Chemical Engineering, University of British Columbia; 3Chemical Engineering and Materials Science, University of Alberta.

Membranes. Jun Guo1, David Lee2, Yunsong Yang3, Steven Holdcroft2,3 and Barbara J. Friskin1; 1Department of Physics, Simon Fraser University; 2Department of Chemical Engineering, University of British Columbia; 3Chemical Engineering and Materials Science, University of Alberta.

Membranes. Jun Guo1, David Lee2, Yunsong Yang3, Steven Holdcroft2,3 and Barbara J. Friskin1; 1Department of Physics, Simon Fraser University; 2Department of Chemical Engineering, University of British Columbia; 3Chemical Engineering and Materials Science, University of Alberta.
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'-methylenbisacrylamide (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.