PREPARATION AND CHARACTERIZATION OF SOLID ELECTROLYTES:
FUEL CELL APPLICATIONS

Final Report
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SYNOPSIS

The intent of this project with Federal Energy Technology Center (FETC)/Morgantown Energy Technology Center (METC) is to develop research infrastructure conducive to Fuel Cell research at Southern University and A&M College, Baton Rouge. A state of the art research laboratory (James Hall #123 and #114) for energy conversion and storage devices was developed during this project duration. The Solid State Ionics laboratory is now fully equipped with materials research instruments: Arbin Battery Cycling and testing (8 channel) unit, Electrochemical Analyzer (EG&G PAR Model 273 and Solartron AC impedance analyzer), Fuel Cell test station (Globe Tech), Differential Scanning Calorimeter (DSC-10), Thermogravimetric Analyzer (TGA), Scanning Tunneling Microscope (STM), UV-VIS-NIR Absorption Spectrometer, Fluorescence Spectrometer, FT-IR Spectrometer, Extended X-ray Absorption Fine Structure (EXAFS) measurement capability at Center for Advanced Microstructure and Devices (CAMD - a multimillion dollar DOE facility), Glove Box, gas hood chamber, high temperature furnaces, hydraulic press and several high performance computers. In particular, a high temperature furnace (Thermodyne 6000 furnace and a high temperature oven were acquired through this project funds. The PI Dr. R. Bobba has acquired additional funds from federal agencies include NSF-Academic Research Infrastructure program and other DOE sites. We have extensively used the multimillion dollar DOE facility “Center for Advanced Microstructures and Devices (CAMD)” for electrochemical research. Our students were heavily involved in the experimental EXAFS measurements and made use of their DCM beamline for EXAFS research.

The primary objective was to provide hands on experience to the selected African American undergraduate and graduate students in experimental energy research. The goal was to develop research skills and involve them in the Preparation and Characterization of Solid Electrolytes. Ionically conducting solid electrolytes are successfully used for battery, fuel cell and sensor applications. The above mission was accomplished during the project duration and the project was 100% successful since all the proposed technical objectives described in the proposal were attempted and executed with care. A total of six students (three undergraduates (Ms. Dinesha L. Hawkins, Mr. Jerry LeBlanc, and Mr. Jaymes Baker) and three graduate (Mr. Donald G. Prier, Mr. Tommy Rockwood, Mr. Saleem Hasan, and V. Rayanki) and two faculty members (Dr. Rambabu Bobba and Dr. T. Wang) were involved and supported through this project to accomplish the technical objectives of the project. Out of these six students, four of them graduated and Mr. Prier is a candidate for MS degree soon and now undergoing co-op training in the fuel cell research group at Los Alamos National laboratory (LANL). Mr. Tommy Rockwood was also involved in this project. He has developed a model for experimental validation of polymer electrolyte fuel cell and is developing graduate thesis under the supervision of staff scientists at LANL.
We have investigated the electrode-electrolyte interfacial reactions, defect structure and defect stability in some perovskite type, transition metal electrocatalysts, perfluorinated ionomer Nafion type solid electrolyte materials for fuel cell applications using synchrotron radiation based Extended X-ray Absorption Spectroscopy (EXAFS), surface analytical (HVC STM, SEM, and TEM) and Impedance Spectroscopic techniques. In the general effort to establish the doped ceria electrolyte for use in solid oxide fuel cells because of its well known advantages, the equally well known problems involved with the ceria material, we have measured the AC impedance and K edge EXAFS of the entire family of rare earth dopants in Cerium Oxide. Our objective was to understand the effect of dopants on the conductivity and its impact on the structural properties of Cerium Oxide. Doped ceria was considered an electrolyte or an electrode for solid oxide fuel cells (SOFCs) because of its relatively high ionic and electronic conductivity. The host lattice ceria was more compatible with a wider range of trivalent dopants compared to zirconia, hafnia and thoria. We have measured the AC impedance and K edge EXAFS of the entire family of rare earth dopants in Cerium Oxide to understand the effect of dopants on the conductivity and its impact on the structural properties of Cerium Oxide. All of the systems showed an increase in the conductivity over undoped ceria with ceria doped Gd, Sm and Y showing the highest values. The conductivity increased with increasing ionic radius of the dopant cation. Among the trivalent cations, anomalous behavior has been reported for Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, and La$^{3+}$, yielded highest conductivities, where as for Sc$^{3+}$ doped ceria much smaller ionic conductivity compared to their counter parts. The dopant ionic radie and its effect on the host crystal lattice structure are a major factor in providing mixed ionic and electronic conductivities which are desirable in some applications such as electrode/electrolyte interfaces. To verify the local structure and short range order around a defect or dopant in order to explain the variations in conductivities, we have measured the K edge of the EXAFS of these dopants. Our objective was to understand the nature of the defect clustering between oxygen vacancies and trivalent ions. Very interesting results were obtained in the doped ceria, this project helped us to measure the EXAFS first time on this system. The L$_{111}$ and K edge NEXAFS measurements in the Ce$^{4+}$, La$^{3+}$, Gd$^{3+}$, Y$^{3+}$, In$^{3+}$, were measured using the Double Crystal Monochromator beamline at CAMD under normal operating conditions. A preliminary results were presented in 10th SSI conference and the detailed work will be published in the refereed journal. We are providing the detailed EXAFS spectra in this report. The initial intent was to collaborate with scientists at Morgontown Energy Technology Center (METC) to fabricate the solid oxide fuel cells using doped ceria samples in their laboratory and then evaluate their performance characteristics in our laboratory. In this task, we were not successful. However, we strongly believe, that Ce$_{0.9}$Gd$_{0.1}$O$_{1.9}$ electrolyte will be ideal candidate for the fabrication of intermediate or high temperature SOFCs. In any case, during this project duration, we have built our own research capability to measure the performance characteristics of the fuel cells in general.
In this project, we have also attempted to develop new organic and inorganic cathodic catalysts as alternatives to the conventional perfluorinated membranes for long term optimal performance of polymer electrolyte fuel cells (PEFCs). Our students were involved in the catalyst preparation, membrane integration, modeling or parameter studies, qualifications of the structural and electrochemical characteristics and identification of useful PEMs by investigating the charge transfer reactions at the electrode-electrolyte interface. The overall goal of this project was to minimize the cathode flooding problems, decrease proton exchange membrane resistance in order to minimize the membrane ohmic polarization, and increase membrane's proton transfer abilities (i.e. maximize the proton transference number) and also to overcome the methanol cross over in the cathode. The direct methanol fuel cell (DMFC) is a particularly attractive alternative to the H₂/O₂ Cell. Although not as high as hydrogen, the energy density of methanol is the highest among the organic fuels. Another advantage of the DMFC is rapid start up and operation with little or no emission/noise signature. This has led to an intense research effort over the past 20 years. In recent years, the DMFCs have received increasing attention due to interesting electrochemical performance achieved with the use of solid polymer electrolyte membranes. Traditionally, the PEM has been Nafton® 117, 115 or 112. Despite the progress, DMFCs have been plagued by its low power density which has been attributed to the methanol crossover from anode to cathode and vice versa. Methanol cross over from the anode to cathode results in consumption of fuel and also impacts the performance of the cathode causing the cell to operate at lower overall efficiency. Figure 1 show the schematics of a fuel cell describing the probable methanol crossover events.

\[
\begin{align*}
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{H}_2\text{O} \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{O}_2
\end{align*}
\]
The crossover rate is largely determined by the electrochemical, thermal and structural activity of electrode catalysts, and permeability of the membrane. Perfluorinated ion conducting polymers with lower equivalent weight such as Nafion 117 presents high ionic conductivity but also permeable to methanol. In the present study, we focused on electrochemical (cyclic voltammetry, in-situ current and potential step) measurements of different cathodic catalysts and ionomeric membranes to understand the problem of "Methanol Crossover in DMFCs". We have successfully completed the fuel cell performance measurements utilizing the low cost carbon supported transition metal catalysts. We have demonstrated that transition metal alloy catalyst show superior or similar performance as that of conventional noble metal catalysts used in the existing fuel cell technologies. We have attempted to utilize the power that was generated from our fuel cell system to operate a toy car. Our goal is to extrapolate the design ideas towards commercial vehicles in the future. The XANES sulfur-K edge in perfluorinated polymer electrolyte (Nafion® 112, 115, 117, 417 and 450) membranes were analyzed under different heat treatments and in acidic treatment with H₃PO₄. The structure of H₃PO₄ treated Nafion® changes and was reflected in the higher energy peak of the XANES. The observed structural changes in the Nafion® are best explained by considering the role played by the phosphoric acid for the enhancement of proton transport. In the non-treated Nafion®, the proton transport is totally dependent on the incorporation of water in the structure and its role in the treated Nafion® is minimized. The phosphoric acid and its hydrogen bonding abilities enhanced the ionic conductivity of the membrane. To elucidate cathodic and anodic oxidation of methanol crossover events i.e. CO poisoning in the Direct Oxidation of Methanol Fuel Cells (DMFCs), Cyclic Voltammetry measurements were carried out on carbon supported electrodes (Pt, C, Pt/C, Pt-Fe/C, Pt-Co/C, Pt-Ni/C, Pt-Cu/C, Pt-Ru/C, and Pt-Ru/ Nafion®). The transition metal alloy electro-catalysts were evaluated as low cost alternatives to DMFCs and compared with generally accepted noble metal and alloy catalysts. The effect of methanol concentration in sulfuric acid, temperature, and catalyst surface area were evaluated and matched with the proper electro-oxidation mechanisms. The alloy catalyst Pt-Co/C was found to be a better catalyst for methanol oxidation in acid solution compared to other VIIIb transition metals. The observed current oscillations in Pt-Cu/C in low and medium temperature regions were due to the dual role played by the surface reaction between MOH and PtCO. Pt/C/Nafion® showed the highest resistance (10⁶ Ω/cm²) compared to Pt-Ru/C (280mΩ/cm²).

Fuel cells of varying combinations of anodes and cathodes were evaluated using H₂ and compared with liquid feed methanol fuel cell. Our students have also attempted to use ethanol, formic acid, butanol and propanol as an alternate liquid feed in the fuel cell systems. The results were satisfactory and further work is needed to consolidate the hypothesis. Globe Tech MEAs and E-TEK MEAs were used in the initial experiments. Finally, with the help of LANL scientists, we have made our MEAs using the procedures developed by Wilson, Gottesfeld and their co-workers in our laboratory. The validation of the experimental system and the initial performance measurements are very promising. The detailed report regarding the data generated in our system is presented in this report.
One of the objectives of this project is to collaborate with industrial partners. The scientists in Motorola endorsed our proposal initially to explore the new and innovative procedures for making solid electrolytes and to explore their applications in the device issues. Dr. P.S.S. Prasad of Motorola has suggested, that we should use sol gel process for the preparation of glasses and thin film samples. In this project site, during this project duration, we have learned the art of preparing glasses and films using sol gel process. Compared to thermal evaporation, co-evaporation, co-precipitation and electrochemical deposition techniques, the relatively new sol gel process technology is an excellent method for fabricating variety of semiconductors in the form of bulk as well as thin films with high purity and homogeneous products at low temperatures. Specialty products like thin films, coatings, fibres, and monoliths are difficult to obtain by ceramic route but can be easily obtained by sol gel process. So essentially the sol gel process is quite simple. A solution containing the desired oxide or non oxide precursor is prepared. It is applied to a substrate by spinning, dipping, or draining. The process is able to apply a coating to the inside and the outside of complex shapes simultaneously. The films are typically one micron thick, uniform over large areas, and adherent. The sol gel prepared thin films and glasses have the advantage of having more channels, than the conventionally prepared materials. This technique, unlike its high vacuum counterparts is simple, inexpensive, involves negligible waste of materials, and is ideal for large scale production.

We have initiated a collaborative effort with faculty members at University of Pondicherry, Pondicherry, India. To develop sol gel process and technology, we have brought exchange visitor to prepare sol gel glasses. Various compositions of silver based quaternary superionic conducting (SIC) [AgI-Ag2O-(SeO2 + P2O5 (SSP))] glasses were prepared by melt quenching technique. The nature of the compounds were confirmed by X-ray diffraction. Electrical and electronic conductivity studies were carried out to select the high ionic conducting composition of the SSP system for the fabrication of batteries. Different dopant salt (AgI) compositions in the AgI- Ag2O- SeO2 -V2O5 (SSV) system were prepared by melt quenching technique. All the prepared compositions of the SSV system were characterized by X-ray diffraction, IR and DSC.

The PI and his students have presented some of their results in DOE workshops and conferences including DOE/PETC/HBCU/Private Sector conference held in North Carolina A&T State University, Southern University A&M College and at University of Maryland, Easternshore. Our students have earned first prize in DOE/EpSCOR and other DOE student competitions. This project has provided travel support to seven students to attend these conferences. The PI has submitted a new proposal for continuation of the work presented above.


3. Fuel Cell Project at Southern University, D.Prier, M.Prier, Tommy Rockwood and B.Rambabu

4. Southern University-Dow Chemical Company Fuel Cell Development Project for Transportation Applications, B. Rambabu (SUBR) and Stephan Noding (Dow, Plaquemine) Exhibit [5th DOE-FETC, LA]

5. Surface Characterization of NOx on some selected single crystal surfaces. Hieke Geisler and B. Rambabu [5th DOE-FETC, LA]


7. Photovoltaic Modules: Prospectus, Tameka L Page and B. Rambabu {DOE-FETC, LA, 5th conference}


7. Mr Tommy Rockwood and Ms. Leah Warrington (presented their Fuel Cell work in the LANL annual meeting)

8. Methanol Crossover in DFMCs: A Study of Electrochemical and Structural Characterization of Cathodic Electrodes and Membranes; accepted for oral presentation in the 11th International Conference on Solid State Ionics to be held in Hawaii. (Nov 16-23, 1997). ** the manuscript will be published in the journal Solid State Ionics, Spring 1998. *** Obtained full travel support from the conference committee and also from the Asian Society of Solid State Ionics. B. Rambabu, Tamika Page, Leday Shamona, Josef Homes and Steve Noding

9. Characterization of Silverselenophosphate Glasses, N. Satyanarayana et al and B. Rambabu, p accepted for oral presentation in the 11th International Conference on Solid State Ionics to be held in Hawaii. (Nov 16-23, 1997). ** the manuscript will be published in the journal Solid State Ionics, Spring 1998. *** Obtained full travel support from the conference committee and also from the Asian Society of Solid State Ionics.
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LABORATORY RESOURCES
Experimental Facilities for Fuel Cell and Battery Materials Research at SUBR

A 2000 square foot room (100 ft X 20 ft, room #123) and 1600 square foot room (40 ft X 40 ft, Room #114) on the first floor of the James Hall are available for this project. These laboratory rooms are conveniently designed for setting up surface physics experiments. The department has recently acquired funds for facilities renovation and is planning to develop a clean room for developing device structures and surface physics laboratory (Room #114, James Hall).

* Impedance Spectroscopy (EG&G E'Chem Research Station PAR model 273A Galvonostat/Cyclic Voltameter)
* Fuel Cell research station (Globe Tech)
* FT-IR Spectroscopy (Nicolet 7000 series) dual beam spectrometer
* DSC and TGA techniques
* Materials Testing System for Mechanical properties
* Scanning Tunneling Microscopy
* Scanning Electron Microscopy
* Transmission Electron Microscopy
* Optical Spectroscopy Techniques
* X-Ray Diffraction
* Center for Advanced Microstructures and Devices (CAMD)
* Extended Absorption Fine Structure Spectroscopy

The J. Bennet Johnston Sr. Center for Advanced Microstructures and Devices (CAMD): The X-ray Spectroscopy analysis will be performed at CAMD. DOE has established CAMD, a multimillion dollar facility in Baton Rouge to promote energy and defense related research in Louisiana. The advanced light source is stationed 10 miles away from Southern University. The PI has been actively involved in developing a new synchrotron radiation beamline (SEA Sync) for materials researchers in minority institutions to facilitate EXAFS research at CAMD. At present he is using the Brazilian beamline i.e Double Crystal Monochromator beamline (port 5A) at CAMD for EXAFS measurements.
In order to evaluate the newly synthesized or prepared solid electrolytes, all the above experimental techniques were acquired, installed and operated during this project duration. This section show the figures of several electrochemical instruments and their experimental set ups used in this project. The ceramic samples prepared using ball milling and sintering procedures, whereas Fast Ion Conducting (FIC) glasses were prepared using sol-gel techniques. For preparation of glasses, we have used melt quenching techniques. We have attempted to prepare membrane electrode assemblies (MEAs) in our laboratory. We have acquired all the necessary infrastructure for the preparation of MEAs and learned the procedures. Two of our students who were involved in this project have developed procedures for making MEAs at Los Alamos National Laboratory (LANL).

FIGURE 2.1

Temperature controlled current-voltage measurements (EG&G PAR Model 273 Potentiostat/Galvanostat, AC impedance (Solartron AC impedance analyzer) for conductivity. This instrument is designed for integrated amperometry, dc amperometry, conductivity, and cyclic voltammetry modes of detection. When the time constant of the EMF cell is sufficiently low, it will be possible to follow the intensity of a product or intermediate formed in an electrochemical reaction as a function of applied potential. AC impedance spectra will be measured using the Princeton Applied Research Model 273A potentiostat and Solartron model 1255 frequency response analyzer using PAR M383 software. This is a very effective combination for catalysis studies and particularly useful for the investigation of electrode-electrolyte materials to be used in solid state fuel cells.
FIGURE 2.2

FUEL CELL WORK STATION (Globe Tech HP6060 B electronic load)

The workstation will be used to monitor the operation of fuel cells. It includes independent microprocessor based temperature controls for both fuel and oxidizer. Initially we will acquire ready-made fuel cells for testing and evaluation. The system will allow us to determine conventional rate constants over a wide range of temperatures and pressures, for a variety of catalytic systems.
Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyzer (TGA) (TA Instruments DSC10, TGA). DSC and TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and predict their thermal stability at temperatures up to 1200 °C. TGA experiments provide important information that can be used to select materials, predict product performance and improve quality. The technique is particularly useful for determining 1. composition of multicomponent systems, 2. thermal stability of materials, 3. oxidative stability of materials, 4. decomposition kinetics of materials, and 5. the effect of reactive or corrosive atmospheres on materials.

UV-VIS-IR optical absorption measurements by using Varian E5 (from high temp to 0 K) for analysis of optical properties.
Scanning Tunneling Microscopy (STM) for structural, interfacial and surface morphology studies. The McAllister Technical Services will be installing an Ultra High Vacuum Scanning Tunneling Microscope unit with a provision to upgrade the STM chamber with other surface characterization. With an 4-mesh Rear View LEED and suitable electronics, we would be able to use LEED and AES together using UHV chamber equipped with STM. Metal -oxide interfaces are of fundamental importance for the lot of phenomena such as, heterogeneous catalysis or photochemistry. The oxide support seems to play a prominent part in particular when the oxide involved in the system is reducible oxide. Using LEED and AES, we would be studying the growth of the metal on the oxide support and the influence of the stoichiometry of the support on the structure of the deposit.
Extended Absorption Fine Structure Spectroscopy (EXAFS) for geometric and electronic structure measurements. Double Crystal Monochromator beamline (port 5A) at CAMD for EXAFS measurements. This beam is equipped with a double crystal vacuum monochromator of the Lemmonier type for which several sets of crystals are available allowing measurements between about 700 eV and 18 keV. Thus it is possible to investigate all elements from Z = 9 (F) up to Z = 92 (U) at least at one suitable X-ray edge. Experiments can be carried out using the standard transmission technique and also using the total electron yield mode. A semiconductor detector (with a rather low resolution) for fluorescence detection is available but has to be taken into operation.

**FIGURE 2.6**

**CENTER FOR ADVANCED MICROSTRUCTURES AND DEVICES**

**CAMD Facility Layout**

X-Ray Lithography Sector  Basic Sciences Sector

**Beam Lines**

- 5A: Micro-Machining X-Ray Lithography 1 (XRM1)
- 5B: Micro-Machining X-Ray Lithography 2 (XRM2)
- 5C: Phase Grating Monochromator (PGM)
- 481: 5m Toroidal Grating Monochromator (TGM/5m)
- 485: Spherical Grating Monochromator (SGM)
- 483: X-Ray Microscope Probe (XMP)
- 486: Double-Crystal Monochromator (DCM)

**Note:** Diagrams and labels indicate various experimental setups and facilities within the CAMD facility.
FIGURE 2.7

GLOVE BOX, SOL-GEL WORK BENCH, FURNACES, SINTERING EQUIPMENT FOR PREPARATION OF SOLID ELECTROLYTES
INTRODUCTION

Fossil fuels are one of the most important sources of energy. The combustion of fossil fuels gives off carbon oxides, sulfur oxides and nitrogen oxides which pollute the atmosphere. Carbon dioxide is expected to be the reason for global warming. Sulfur oxides give acid rain and nitrogen oxides which are emitted from the exhaust of automobiles cause air pollution in large cities. The continuous and accurate monitoring of these oxides is the first step in pollution control. In 1973, the oil price quadrupled and the world had a sudden awareness of its petroleum dependence. Resources of fossil fuels are decreasing and complexity of power distribution is increasing. Mobile power system dependencies are increasing. Environmental pollution is increasing. In order to solve these global problems and to provide alternative and viable energy resources, the US Department of Energy has been consistently strives to explore new technologies such as Solid State Ionics (SSI) technologies. Their applications range from small batteries (1), to high power batteries for energy storage systems, electrochromic windows for energy conservation (3), sensors for chemical pollution detection, etc. Superionic conductors (SICs) or Fast Ionic Conductors (FICs) or Solid Electrolytes (SEs) are the class of materials which exhibit high ionic conductivity comparable to liquid electrolytes. These materials are characterized by a) the electrical conductivity as high as $10^{-6}$ S/cm to 1 S/cm, b) the principle charge carriers are ions with negligible electronic conductivity, c) the low activation energy for the ion migration and d) the conducting pathways across intergranular and interparticle boundaries for ion migration. The study of FIC materials have been receiving more and more importance owing to their potential applications to advanced solid state ionic devices. The applications include solid state batteries, fuel cells, high energy density batteries for vehicular traction, gas sensors, electrochemical capacitors, electrochromic displays, analog memory devices, miniature cells etc [1-3]. The intent of this project was to exclusively investigate solid electrolytes for fuel cell applications.
The solid electrolyte is one of the essential components of a solid state ionic device. Ideally, an electrolyte is a ionic conductor and an electronic insulator. It is used both as an internal ionic conductor and as a separator between two chemical compounds: the reactants of the device. In addition to possessing high ionic conductivity, some application require a material which also possess high selectivity and prevents the displacement of other charge carriers. The preparation and characterization of solid electrolyte materials is very important issue in the development of new ionically conducting devices.

An acceptable solid electrolyte must usually exhibit negligible electronic conductivity and an ionic transport number of the reactant ion which tends to 1. The region in which the electronic conductivity is less than one percent of the total conductivity is called the electrolyte domain. Besides having these conductivity properties the solid electrolyte must be stable in the environment of its application. In these conditions solid electrolyte transduce the ratio of the chemical potential of the electroactive component of interfaces directly into an electrical voltage. The next step is the choice of electrodes. From a simple SSI device viewpoint, an electrode can be defined as a location in a chain of electrical conductors where the conductivity changes in nature from electronic to ionic. The electrodes relate external electrical circuit to the SSI materials and in aprticular to the electrolyte. Electrochemical reaction occuring at the electrode requires charge transfer of electrons and ions. Such a charge transfer reaction is then restricted physically to regions which are simultaneously linked to the current collector by an electronically conducting bridge. In the monophasis electrodes with high ionic and electronic mobilities, the charge transfer reaction would occur over the entire volume of the electrode. While in the different cases two of the two phase electrodes the charge transfer reaction would only occur over the entire electronic-ionic conductor interfacial area. This limitation of the reaction electrode zone may lead to kinetic problems and polaraization effects during the charge carrier flowing. The SSI technologies refers to all electrochemical devices which contain at least one solid electrolyte i.e. a solid with unusually high diffusion coefficients and conductances for specific ions. As compared to traditional power generation systems, the ability of fuel cells for direct conversion of chemical energy into electricity offer significant advantages. Fuel Cell systems offer a new and interesting option to convert fossil fuels to electric energy with high efficiency and high power density, for example as a heat and power system or for transportation applications. A fuel cell, in short, is an apparatus which converts chemical energy directly into electrical energy. In general, Fuel Cells are being considered as notable energy sources due to, not only their potential for obtaining high energy conversion efficiencies, but also environmental sensitive features. The development of environmental friendly and high performance fuel cells are important due to the problems relating to global environmental pollution which is regarded as a very serious social issue [4-6].
In this project, we have attempted to develop mixed ionic and electronic conducting oxides that exhibit fast ionic transport properties as an electrode materials for Solid Oxide Fuel Cell (SOFC) applications. SOFCs offer the potential for high efficiency, low cost electric power plants for many applications. Introduction of SOFC into a combined cycle has the potential to improve the total electrical conductivity by more than 10%. To realize the importance of operating SOFC at high temperature, we have attempted to explore the high conductivity solid electrolytes and electrode materials for the development of fuel cell research at Southern University. Our goal was to focus on both low temperature and intermediate temperature fuel cells for stationary and transportation applications. There are many reasons to believe that the study of catalysis and the development new and innovative catalysts have becoming increasingly popular in next generation vehicle (NGV) technologies and in many chemical industries. Since this is an educational project, we have involved our students in Catalysis research i.e. development new organic and inorganic catalysts for fuel cell applications. In this two year project, we have investigated solid electrolytes rare earth dopants in cerium oxide for Solid Oxide Fuel Cells (SOFCs) and transition metal electrocatalysts for Direct Oxidation of Methanol Fuel Cells (DMFCs).

Mixed conductors are expected to able to replace the state of the art SOFC cermet anodes. Mixed conductors, in which both electrons and ions are mobile, promote the charge transfer reactions over the whole area of the solid gas interface. Zirconia based mixed conductors can be partially or fully stabilized zirconia with mixed valence dopants, like CoO, Fe₂O₃, MnO and CeO₂. As mentioned earlier, in this project we have investigated the rare earth dopants in CeO₂ for SOFC applications. Doped CeO₂ possesses ionic conductivity at 800 °C comparable to that of stabilized ZrO₂ at 100 °C. However, under typical fuel cell conditions with oxygen activities lower than 10⁻¹⁶ to 10⁻²⁰ and temperatures 800 -1000 °C ceria exhibits deviation in oxygen stoichiometry with 10⁻⁵ to 10⁻²² in CeO₂, accompanied by a reduction to Ce³⁺ to Ce⁴⁺. This result in the creation of oxygen vacancies and n type defects localized at Ce site. Some perovskite type solid solutions based on SrCeO₃ and BaCeO₃ exhibit protonic conduction under hydrogen containing atmosphere at elevated temperatures. They also show the hole conduction under relatively high partial pressure of oxygen. Earlier investigations on these systems are aimed to understand ionic conductivity and other material properties [7-10]. However very little is known about the valence state of the impurity and their occupied position in the lattice. Dopant cation size and crystal lattice structure is believed to be major factor in the ionic conductivity of the solid electrolyte. This results in the onset of mixed conduction, and in the case of a solid oxide fuel cell, internal shorting across the electrolyte leading to a reduction in faradic efficiency. It is important to investigate this thoroughly. The host lattice of ceria is most compatible with a wider range of trivalent dopants compared to zirconia, hafnia, and thoria and proved to be an excellent oxygen ion conductor because of its stable defect structure at elevated and intermediate temperatures and pressures. The dopant ionic radii and its effect on the host crystal lattice structure are major factor in providing mixed ionic and electronic conductivities which are desirable in some application such as electrode/electrolyte interfaces. We are studying the structure
and the ionic conductivity of ceria doped with all naturally occurring rare earth elements to explore the suitability of these materials for fuel cell applications. The dopant cation size and its effect on the host crystal lattice structure are a major factor determining the ionic conductivity of solid electrolytes. In order to understand the precise role the dopant plays in modifying the properties of the oxide the primary information that is required is the exact location of the dopant in the host lattice. However, in many systems this problem can not be resolved by conventional diffraction techniques. For example, the concentration of the dopant may be very low (less than 1 mol%), the dopant may be indistinguishable from the host (as in atoms with similar atomic numbers), the dopant may introduce complex disorders into the lattice or the material may be amorphous. In this project, we have attempted to use AC impedance and other advanced X-ray Spectroscopy techniques like EXAFS to obtain complete structural information.

Despite the progress, DMFCs have been plagued by its low power density which has been attributed to low-activity catalysts for the methanol anode.[11-14] The degradation of commonly used electrode catalysts (Pt, Ag and others) and corrosion of carbon substrates are making commercialization of fuel cells incorporating present day technologies economically problematic. Usually a few milligrams of a precious metal such as platinum are employed, but the cost escalates with high loadings of these catalysts. By using the binary alloys of base transition metals (i.e., V, Cr, Ti, Co, Ni, and Cu etc.) with Pt, the level of electro-catalytic activity increase. The cathodic reactions enhance the performance of proton exchange membrane fuel cells (PEMFCs). However, most of this research was emphasized on the improvements in phosphoric acid fuel cells (PAFCs). Therefore, it is important to investigate these binary alloy systems to explore their utility in the PEMFCs. In this project, we have investigated the methanol crossover problem in DMFCs.

During this project duration, we were involved in the preparation and characterization of SIC glasses. Various compositions of silver based quaternary superionic conducting (SIC) [AgI-Ag₂O-(SeO₂+ P₂Os) (SSP)] glasses were prepared by melt quenching technique. Different dopant salt (AgI) compositions in the AgI- Ag₂O-SeO₂-V₂Os (SSV) system were prepared by melt quenching technique.

The prepared samples are characterized by the following experimental probes: 1) X-Ray Diffraction (XRD), 2) Differential Scanning Calorimetry 3) AC Impedance 4) X-ray Absorption Fine Structure Spectroscopy. The crystalline and the galssy nature of the compounds are confirmed by the XRD. The diffraction pattern of the powdered samples are obtained by using Phillips X-ray generator. Change in temperature of the samples is due to either endothermic or exothermic reactions. The change in temperature during chemical or physical change was detected by different methods such as Differential Scanning Calorimetry. Glass is prepared bypassing the crystallization and the liquid to glass transition temperature Tg. We have measured the glass transition temperature using the DSC 10 TA instruments. Powdered glass samples of 15-20 mg are used and the sample is heated at the rate of 10°C/min.
AC impedance data on rare earth dopants in CeO2 was obtained using PAR model 273 potentiostat galvanostat and EG&G impedance analyzer. X-ray absorption measurements were carried out using synchrotron radiation mainly at the DCM beamline of the storage ring of the Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge (USA). During the experiments the ring was operated at 1.3 GeV with an average current of about 120 mA. Radiation was monochromotized using double crystal X-ray monochromator of the Lemmoiner type equipped with InSb(111) crystals providing a resolution of about 0.7 eV in the energy region of interest. In general, spectra were taken between 2440 eV and 2520 eV with a step width of about 0.6 eV in the region of interest and a step width of about 0.3 eV in the pre-edge region and behind the XANES features. Integration time was about 0.5 sec. Spectra were obtained in the standard X-ray absorption technique using ionization chambers as monitor and detector. While the accuracy of the relative scale is better than 0.1 eV, the absolute scale was estimated to be better than 0.2 eV. The relative energy scale was calibrated.

Experiments were conducted in a three-compartment electrochemical cell, containing freshly prepared, oxygen free (purged and blanked with nitrogen) 0.5 M H2SO4 or 0.5 M H2SO4 + CH3OH. The electrochemical cell was located in a water bath for controlling temperature. The following carbon supported membranes were employed as the working electrodes: Pt/C, 20%Pt, 0.4 mg/cm² Pt loading; Pt-Ru/C, 20% Pt/Ru/C (1:1/a/o), 0.4 mg/cm² Pt/Ru loading; 20% Pt/Ni/C (1:1/a/o), 0.5 mg/cm² Pt/Ni loading; 20% Pt/Cu/C (1:1/a/o), 0.5 mg/cm² Pt/Cu loading; 20% Pt/Fe/C (1:1/a/o), 0.5 mg/cm² Pt/Fe loading; 20% Pt/Co/C (1:1/a/o), 0.5 mg/cm² Pt/Co loading; All carbon supported membranes were purchased from GlobeTech, Inc. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials in the following will be referenced to the SCE scale. A carbon rod was used as the counter electrode. The cyclic voltammetric response was measured using EG&G PAR Model 270 potentiostat/galvanostat and wave form sweep programmer. A cycle was started at the open circuit potential of the cell and was swept negative at 0.35 V to map the initial state of hydrogen absorption sites on the Pt. The positive potential of the measurements was limited to 1.60V to minimize oxygen generation. Cyclic voltammetry experiments were utilized for determination of solid membrane resistance. The resistance of different CMEs was measured by chronopotentiometry with 10mA current steps. The relative energy scale was calibrated against the white line (i.e., first strong resonance of ZnSO4 at 2481.44 eV. In order to analyze the near edge region, a linear background was subtracted from the raw data. Spectra were normalized at 2510 eV where the variation in the photo absorption cross section was very small. This enabled direct comparison of the relative oscillator strengths of the various electron transitions. Samples were taken from commercially available membrane sheets (Aldrich Company). Thin films with a thickness of about 30 micrometers were prepared using a microtone. Samples were dried for 7 h at 60 C and for 18 h at 110 C followed by treatment with phosphoric acid. After the first measurement, the dried samples were put into distilled water for about 1 hr. Then, another spectrum of the same samples was taken. The X-ray absorption near edge spectra (XANES) of K edge sulfur in Nafion 112, 115, 117, 417 and 450 were analyzed [14-19].
The MEAs were loaded into a single test fixture and the performance using a Globe Tech Fuel Cell workstation (HP6060 B electronic load) was measured. The single cell test fixture was composed of two copper current collector end plates and graphite plates containing rib channel patterns that allowed the methanol vapor access to the anode and humidified oxygen to the cathode. The Globe Tech Fuel Cell Test Station was acquired during this project duration and installed in our laboratory for the purpose of electrochemical investigations of proton exchange membranes (or solid polymer electrolyte), alkaline, and phosphoric acid fuel cells single cells and electrochemical cell stacks. This test station was used during the course of the investigations to evaluate the single cells and multicell stacks with electrode areas covering 5-12 cm². The performance evaluations are made over the temperature range of 23 - 200°C and pressure range of 1 to 7 atm. Our initial measurements on fuel cell performance characteristics and EXAFS are made on commercial membranes Pt/Ru/Nafion 115, 117 and 110. The performance of the DMFCs is believed to be considerably improved by increased catalyst loadings. The upper limit at 4 mg/cm² and 12 mg/cm² in order to estimate the improvement that can be achieved in the cell performance. We have initiated this study with a goal to 1. reduce the cost of the Pt catalyst and ionomeric membrane 2. increase the efficiency and power density of the PEFC 3. optimize the system for operation on the organic fuels and air and 4. solve key technical issues that impede the development of the DMFC. We have measured I-V and polarization characteristics of H₂-H₂O, fuel electrode/electrolyte/oxygen electrode, O₂, system.
REFERENCES

STRUCTURAL INVESTIGATIONS OF TRIVALENT RARE EARTH DOPANTS IN CERIUM OXIDE FOR SOLID OXIDE FUEL CELLS

3.1 Introduction

As compared to traditional power systems, the ability of the fuel cells for direct conversion of chemical energy into electricity offers significant advantages [1]. In comparison with other type of fuel cells, solid oxide fuel cells (SOFCs) operated at 900-1000 °C have the advantage of rapid reaction kinetics with out the need of expensive noble metals. The ability to produce high quality heat also makes power and heat cogeneration an attractive option. The use of solid ceramic materials in SOFCs also eliminates the corrosion and liquid electrolyte management problems associated with other type of fuel cells [2,3]. However, the high operating temperature has placed considerable constrain on the material requirements, which also increases the price of the cell manufacture. To overcome these problems Steele suggested that the combination of ceria based electrolytes operating over the temperature range 500-700 °C offers the most cost effective way forward for systems operating on either natural gas or methanol fuels. In this project, we have studied the structural and transport properties of rare earth dopants in cerium oxide.

Earlier research on doped ceria systems has reported the conductivities of electrolytes with dopants such as $\text{Y}_2\text{O}_3$, $\text{CaO}$ and rare earth oxides. Many of these doped ceria materials have conductivities at lower temperatures surpassing those at higher temperatures and low oxygen partial pressures, limits the lower limit of $\text{O}_2$ under which, the condition is predominantly ionic. The vacancies introduced in the crystal lattice by the dopant allows ionic conduction to occur when the activation energy for oxide ion movement in the lattice is raised. The transport depends greatly on kinetics of vacancy motion at the atomic level. It also depends on the thermodynamic process that trap vacancies locally, making them unavailable for bulk transport. Ionic mobility can be anticipated in materials possessing both a rigid lattice and interstitial sites partially occupied by mobile ions. Ideally these sites crystallographically equivalent and share common interface. Furthermore, such interface should possesses highly polarizable boundary ions so that passage of mobile ions not be significantly impeded. It has also been pointed out that to achieve high ionic conductivity in solid electrolytes , the most influential factor may not necessary be the presence of inherently high concentration of mobile ions, but rather be related to the geometry of the lattice structure and the potential energy profiles through which the mobile ions must migrate. To understand these issues, conventional XRD showed limitations in obtaining information on defect and electronic structure of the phases formed during high temperature sintering . Thus we have attempted to obtain emperical crystallographic parameters with XAS, which could be correlated with experimentally measured activation energies for ionic conduction and ionic conductivity of doped cerium oxide. The dopant cation size and its effect on the host crystal lattice structure are major factor in determining the ionic conductivity of the solid electrolytes. In order to understand the precise role of the dopant plays in modifying the major properties of the oxide, the primary information required is the exact location of the
dopant in the host lattice. However, in many systems that has proved to be difficult problem that can not be resolved by conventional XRD techniques. For example, the concentration of the dopant may be very low (less than 1 mol%), the dopant may be indistinguishable from host, the dopant may introduce complex disorder in to the lattice or material may be amorphous. It is very important to employ Synchrotron Radiation based experimental technique EXAFS to obtain the structural information correctly. The local structural environments of trivalent ceria has not been reported so far. We have attempted to prepared doped ceria and BaCeO$_3$ samples to investigate the vacancy trapping using several experimental techniques in this project.

3.2 Preparation of the Samples

The experimental procedures of sample preparation was reported in LLNL UCRL-JC-116378. The stoichiometry of the rare earth impurity was varied to make the solid solutions. Ceria mixed with appropriate quantities of rare earth oxides was ball milled in a spex mixing with a tungston crucible mixing ball for several minutes, and then mixed further in Tubula mixing mill for about an one half hour. One gram of powder was pressed at 140 Mpa into pellets and then sintered at 1600 °C in air. The particle size of the ceria powders had a strong influence on the behavior of the pressed pellets during sintering. Intense ball milling was crucial step in the powder processing. Dry milled powder, pressed to compacts, was sintered 97% dense, at 1200 °C (4h). In the past ceria has been difficult to densify (better than 97% of theoretical density), even at high temperature. Using the above mentioned procedures, we prepared the entire of the family of rare earth doped cerium oxide (except promethium).

3.3 AC Impedance Measurements

We have made an attempt to obtain AC impedance spectra using Princeton Applied Research Model 273 potentiostat and Solartron model 1255 frequency response analyzer. The experimental data was generated on these with the assistance of Brayan Balazas at LLNL. The initial measurements were made at LLNL using their samples.

The experimental set up was shown in the previous section. An automated apparatus based on phase synchronous detection has been assembled for measurements of complex impedance of fast ion conduction. Figure 3.1 show the ionic conductivity (log T, S Cm$^{-1}$ K) vs 1000/T (K$^{-1}$) plot of the entire family of rare earth dopants in cerium Oxide. Trivalent rare earth ion doping increases the concentration of oxygen vacancies result an increase in the ionic conductivities. Among the trivalent cations, anomalous behavior has been reported for Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$ and La$^{3+}$, yielded highest ionic conductivities. The dopant ionic radie and its effect on the host crystal lattice structure will be major factor in providing mixed ionic conductivities which are desirable for some applications such as electrode/electrolyte interface. The cations of different ionic radii than that of Ce$^{4+}$ were
Oxide conducting solid electrolytes for SOFCs

\[ \text{MO}_2\text{-M'O or MO}_2\text{-M''}_2\text{O}_3 \quad (M=\text{Zr, Ce}; M'=\text{Ca, Mg}; M''=\text{rare-earth}) \]

\[ \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.9} \; ; \; (\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2} \]

![Graph showing \( \log(\sigma T, \text{S cm}^{-1} \text{K}) \) vs. \( 1000/T (\text{K}^{-1}) \) for different compositions of Ce-based oxides.](image)
chosen for our XAS investigations and compared with the ac impedance measurements. We have correlated our results with the conductivity data. The maximum conductivity observed (at 600 °C) was $1.2 \times 10^{-2}$ S cm$^{-1}$ for Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$. The conductivity of yitteria doped ceria varied substantially with the dopant concentration.

### 3.4 EXAFS

The cations of different ionic radii (over sized and undersized) than that of Ce$^{4+}$ were chosen for EXAFS measurements and compared with the ac impedance measurements. In X-ray Absorption Spectroscopy, the absorption coefficient is measured as a function of incident photon energy across the absorption edge of the core level (K or L) electron. The XAS spectra of Ce$^{4+}$, La$^{3+}$, Gd$^{3+}$, Y$^{3+}$, In$^{3+}$, Li$_{111}$ edge and Sc$^{3+}$ K edge were performed using DCM beamline at CAMD under operating conditions (1.5 GeV, 160 mA). Some of the measurements are made by Dr. Josef Hornes who is providing professional services to the PI and helping PI to analyze EXAFS.

Figure 3.2 show an overview of the EXAFS spectrum of Nd$^{3+}$ : CeO$_2$. To begin with, we have probed the Ce L$_{111}$, Ce L$_{11}$ and Nd L$_{111}$ edges and plotted the absorbance vs energy. EXAFS and NEXAFS was considered to probe the Ce. XANES measurements were made to probe the impurity. In a separate measurement and in an expanded scale, we have recorded the individual edges for analysis. Figure 3.3 and 3.4 show the Ce- L$_{111}$ edge. Figure 3.5 and 3.6 show the NEXAFS measurements of La$^{3+}$ : CeO$_2$ and Pr$^{3+}$ : CeO$_2$.

Looking at the data from Ce, there are hardly any differences in their first and second coordinations shells. To really look these things, one has look from the dopant. Florescent measurements are needed. There is such facility at CAMD. A preliminary data was obtained from Universitat Germany.

XAS data for the dopant cation in 5 mol% -Sc$_2$O$_3$ or 5 mol% Gd$_2$O$_3$ doped ceria were measured fluorescent excitation spectra using large solid ion chamber as the fluorescent detector. All other measurements were made in ion transmission mode, using chambers filled with N$_2$. All the spectra were measured at room temperature. EXAFS data were converted to k space and all the FT and curve fitting calculations were performed using k$^{-3}$ weighted data. The structural parameters of the solid solutions obtained from the best fit were then compared with various defect models and the structures of the second nearest neighbours (cation-cation) pairs are analyzed using the Fourier Transform of the EXAFS. Figure 3.7, 3.8 and 3.9 show the FT of EXAFS data measured on these samples.

A unit cell of CeO$_2$ consists of eight small cubes containing anions at their corners, with every alternative cube having a cation at their corners, with every alternate cube having cation at its center. When trivalent cations substitutes for Ce$^{4+}$ one oxygen ion vacancy is introduced for every two cations in order to compensate for the lower cation charge. For a dilute solid solution, an elementary picture of defect structure postulates an equal number of MCe-O pairs and isolated MC-e, both randomly distributed spatially. We have attempted to develop the model to interpret qualitatively the observed electrical properties with dopant concentrations.
Ce/Nd - Overview

Absorbance [a.u.]

Energy [eV]

5600 5700 5800 5900 6000 6100 6200 6300 6400

Ce - L-III

Nd - L-III

Ce - L-II

-0.2

0.0

0.2

0.4

0.6

0.8

1.0

1.2

1.4

AAbb. 1
CeO$_2$.10La$_2$O$_3$  Ce L$_3$  La Ce L$_2$ Kanten
CeO$_2$.10La$_2$O$_3$
CeO$_2$.10La$_2$O$_3 \quad$ Ce L$_3$
Fourier transform

\[ \mathcal{F} \circ \mathcal{F} = \mathcal{F}^2 \]

exft: Fourierfilterung

\[ k^2 \]

square

- \text{pe1: 1.48-4.5 Å}
- \text{pe2: 1.29-4.5 Å}

\[ R [\text{Å}] \]

\[ k [\text{Å}^{-1}] \]
Vergleich der Cer Proben

\[ \text{Mod}_{sq} \]

\[ r \ (\text{Å}) \]
Cer Probe A  Pr

Energie (eV)

Intensität

5750  5800  5850  5900  5950  6000  6050  6100  6150
In this work, we have come to an understanding that CeO$_2$ based electrolytes are possible candidates for use in intermediate temperature SOFCs. Extensive research has been undertaken on a number of different CeO$_2$ based electrolytes. At low partial pressures, however, CeO$_2$ is prone to developing electronic conductivity, where Ce$^{4+}$ ion is reduced to Ce$^{3+}$, and hence can limit its use as an electrolyte in SOFCs. However, we have attempted to utilize Ce$_{0.9}$Gd$_{0.1}$O$_{1.9}$ electrolyte as a possible candidate for SOFCs. Measurements of the current voltage characteristics were not complete at this time. However, we have measured I-V polarization characteristics of H$_2$-O$_2$ electrode/electrolyte/oxygen electrode, O$_2$ system. In order to gain further experience in fuel cells, we have continued to work on Direct Oxidation of Methanol Fuel Cells. Several conference and two MS thesis have resulted from support of this project with Federal Energy Technology Center (FETC).

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METHANOL CROSSOVER IN DMFCs: A STUDY OF ELECTROCHEMICAL AND STRUCTURAL PROPERTIES OF CARBON SUPPORTED ELECTRODES AND MEMBRANES

INTRODUCTION

Fuel cells are widely observed as excellent possibilities for power devices where light weight, power efficiency and negligible emissions are required. They are being considered as alternative power sources for transportation and stationary applications [1-3]. Ideally such power systems would operate at relatively low temperatures (60°C-130°C) which strongly suggests using fuel cell technology based upon the proton exchange membrane (PEM). Without question, hydrogen is a very desirable fuel choice. However, the difficulties associated with the production and the routine handling of hydrogen severely limit its commercial use. The direct methanol fuel cell (DMFC) is a particularly attractive alternative to the \( \text{H}_2/\text{O}_2 \) Cell. Although not as high as hydrogen, the energy density of methanol is the highest among the organic fuels. Another advantage of the DMFC is rapid start up and operation with little or no emission/noise signature. This has led to an intense research effort over the past 20 years [4-5]. In recent years, the DMFCs have received increasing attention due to interesting electrochemical performance achieved with the use of solid polymer electrolyte membranes. Traditionally, the PEM has been Nafion\textsuperscript{®} 117, 115 or 112 [6]. Other perfluorosulfonated ionomers (PFSI) such as perfluorosulfonic acid (PFSA) with branched polymer backbone have been investigated. [7] The PFSAs can incorporate many more sulfonate groups in the polymer which help to increase the hydrogen ion transfer. In general, the greater the density of anions on the polymer backbone, the better the transport which results in higher current density and cell efficiency.

Despite the progress, DMFCs have been plagued by its low power density which has been attributed to low-activity catalysts for the methanol anode. [8-11] The degradation of commonly used electrode catalysts (Pt, Ag and others) and corrosion of carbon substrates are making commercialization of fuel cells incorporating present day technologies economically problematic. Usually a few milligrams of a precious metal such as platinum are employed, but the cost escalates with high loadings of these catalysts. By using the binary alloys of base transition metals (i.e., V, Cr, Ti, Co, Ni, and Cu etc.) with Pt, the level of electro-catalytic activity increase. The cathodic reactions enhance the performance of proton exchange membrane fuel cells (PEMFCs). However, most of this research was emphasized on the improvements in phosphoric acid fuel cells (PAFCs) [12]. Therefore, it is important to investigate these binary alloy systems to explore their utility in the PEMFCs.

The anions of perfluorinated sulfonic acid polymer are only weakly absorbed on Pt. In contrast, the phosphate anions are strongly adsorbed. A number of catalysts have been studied including the following: Pt-C, cobalt phthalocyanines (CoPc) with and without carbon supports, Pt alloys such as Pt/Ru, etc., as well as others. [13-14] Activity improvement can be achieved by increasing the surface area, both geometric and internal,
or the catalysts. In addition, improvement can be made in setting up conditions which facilitate the removal of water from the conductive parts of the electrode/membrane/electrode arrangement. The interface between the electrodes and electrolyte are essential to improving the output longevity of the fuel cell. By improving the conductivity and the transport of the system, this can be achieved.

In addition to the catalysts, another problem which predominates is that of methanol crossover[15]. Crossover can occur because methanol is a neutral molecule, and it can easily wet a membrane such as Nafion®. Nafion® allows cations but not anions to move from the anode side of the fuel cell to the cathode side. There a neutral molecule like methanol can crossover to the cathode. In addition, CO and other neutral molecules indicated below can also crossover; although it is not as favorable due to solubility and other factors. Therefore, any restriction or barrier to neutral reactants or products would increase the fuel cell efficiency and longevity.

However, methanol as a fuel is relatively electrochemically inert, so that kinetics of the methanol oxidation is slow. The products of methanol oxidation in acidic media include formaldehyde, formic acid, methylformate, dimethoxymethane, carbon monoxide, and carbon dioxide. Generally, the mechanism of methanol oxidation was proposed as consisting of the following reactions:[16-19]

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{HCHO} + 2 \text{H}^+ + 2 \text{e}^- \\
\text{HCHO} + \text{H}_2\text{O} & \rightarrow \text{HCOOH} + 2 \text{H}^+ + 2 \text{e}^- \\
\text{HCOOH} & \rightarrow \text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \\
\text{CH}_3\text{OH} & \rightarrow \text{CO} + 4 \text{H}^+ + 4 \text{e}^- \\
\text{CH}_3\text{OH} & \rightarrow \text{COH} + 3 \text{H}^+ + 3 \text{e}^- \\
\text{HCHO} + 2 \text{CH}_3\text{OH} & \rightarrow \text{CH}_3(\text{OCH}_3)_2 + \text{H}_2\text{O} \\
\text{HCOOH} + \text{CH}_3\text{OH} & \rightarrow \text{HCOOCH}_3 + \text{H}_2\text{O}
\end{align*}
\]

Carbon monoxide poisons noble metal anode catalysts. Platinum and Pt based binary alloy electrodes have been extensively studied for methanol electro-oxidation in acid electrolyte at ambient and elevated temperatures. As the anode catalyst, Pt is highly active for the adsorption and dehydrogenation of methanol. To oxidize CO to CO\(_2\), a second oxygen atom is required from an adjacent water molecule. Bi-functional alloys composed of Pt and a second metal (M), are able to activate H\(_2\)O at low potentials. Therefore, they are excellent candidates as materials for methanol oxidation.

\[
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} & \rightarrow \text{Pt-CH}_3\text{OH}_{\text{ads}} \\
\text{Pt-CH}_3\text{OH}_{\text{ads}} - & \rightarrow \text{Pt-CO}_{\text{ads}} + 4 \text{H}^+ + 4 \text{e}^- \\
\text{M} + \text{H}_2\text{O} & \rightarrow \text{M-H}_2\text{O}_{\text{ads}}
\end{align*}
\]

Methanol crossover from the anode to the cathode results in consumption of fuel and also impacts the performance of the cathode causing the cell to operate at a lower overall efficiency. The crossover rate is largely determined by the permeability/diffusiveness of methanol towards the membrane and the electrode structure. In a fuel cell using a proton
exchange membrane (PEM), the membrane acts as a separator and as the electrolyte. The conductivity of the PEM is very dependent on its degree of hydration. During operation, water molecules can move from the anode to the cathode which can result in membrane dehydration on the anode side of the membrane. In addition, flooding occurs on the cathode side. Water is produced at the cathode by the electrochemical reduction of oxygen. Water replenishment by back diffusion alone is insufficient to keep the anode side of the membrane hydrated. This is especially true at high current densities. As the membrane becomes dehydrated, the pores within the membrane shrink which results in even lower back-diffusion rates of water. Any fluctuation in temperature control can result in even more dehydration. The transport of water and ions in a PEM fuel cell is controlled by the presence of the sulfonate groups of the polymer backbone of the Nafion® membrane. This transport is more efficient when the membrane is ultra-thin and uniformly hydrated. A number of models have been developed to show that back diffusion of water from the cathode to the anode is insufficient to keep the membrane hydrated at high power densities. Therefore, the anode gas stream, hydrogen, should be humidified. In addition, it would be beneficial to humidify the cathode, oxygen or air.

When methanol is used as fuel, a voltage drop as well as significant thermal management problems can be encountered. The later being the chemical oxidation of methanol at the platinized carbon on the cathode. These systems have been developed to enhance the reduction of oxygen and oxidation of hydrogen. The conventional method of preparation uses Pt-C and PTFE loaded carbon which are mixed and hot-pressed on highly conductive carbon paper. This carbon electrode was impregnated with PFSI solution. The solvent was removed by vacuum and temperature. Two of the resulting electrodes were hot-pressed on both sides of the membrane which usually was Nafion®. These carbon electrodes provide added surface area and added catalytic reaction efficiency for the reduction of oxygen. The use of catalyst impregnated carbon paper allows increased catalyst utilization and uniform continuity of the catalyst.

Methanol crossover especially under relatively high temperatures is a very significant issue for membranes such as Nafion®. Nafion®117 possesses high ionic conductivity but is highly permeable towards methanol. Generally, Nafion® membranes with higher equivalent weight have lower methanol permeability and higher ionic conductivity. Figure 1 shows the schematic of the methanol crossover issue. A basic way of looking at methanol crossover is its ability to wet membranes like Nafion®. This wetting is accelerated at high temperatures. Phosphoric acid can diminish this affect, but not eliminate it. Phosphoric acid changes the structure of the Nafion®, which makes it more difficult for the methanol to wet the membrane. The membrane is highly hydrated after treatment with the phosphoric acid, and, therefore the membrane structure prefers water over methanol. Therefore, it is important to discover membranes which methanol membrane wettability or permeability. Because of this preferential difference, it would be very useful to know the structure of the phosphoric acid treated Nafion®. Once the structure is known, other types of membranes may be discovered which are similar or even better at limiting methanol from influencing the fuel cell mechanism. Though extensive work [1-5] was conducted on platinized electrodes for both the oxidation and the
Experiments were conducted in a three-compartment electrochemical cell, containing freshly prepared, oxygen-free (purged and blanked with nitrogen) 0.5 M H$_2$SO$_4$ or 0.5 M H$_2$SO$_4$ + CH$_3$OH. The electrochemical cell was located in a water bath for controlling temperature. The following carbon supported membranes were employed as the working electrodes: Pt/C, 20%Pt, 0.4 mg/cm$^2$ Pt loading; Pt-Ru/C, 20%Pt/Ru/C (1:1a/o), 0.4 mg/cm$^2$ Pt/Ru loading; 20% Pt/Ni/C (1:1a/o), 0.5 mg/cm$^2$ Pt/Ni loading; 20% Pt/Cu/C (1:1a/o), 0.5 mg/cm$^2$ Pt/Cu loading; 20% Pt/Fe/C (1:1a/o), 0.5 mg/cm$^2$ Pt/Fe loading; 20% Pt/Co/C (1:1a/o), 0.5 mg/cm$^2$ Pt/Co loading; All carbon supported membranes were purchased from GlobeTech, Inc. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials in the following will be referenced to the SCE scale. A carbon rod was used as the counter electrode. The cyclic voltammetric response was measured using EG&G PAR Model 270 potentiostat/galvanostat and wave form sweep programmer. A cycle was started at the open circuit potential of the cell and was swept negative at 0.35 V to map the initial state of hydrogen absorption sites on the Pt. The positive potential of the measurements was limited to 1.60V to minimize oxygen generation. Cyclic voltammetry experiments were utilized for determination of solid membrane resistance. The resistance of different CMEs was measured by chronopotentiometry with 10mA current steps.

X-ray absorption measurements were carried out using synchrotron radiation mainly at the DCM beamline of the storage ring of the Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge (USA). During the experiments the ring was operated at 1.3 GeV with an average current of about 120 mA. Radiation was monochromatized using double crystal X-ray monochromator of the Lemmoineur type equipped with InSb(111) crystals providing a resolution of about 0.7 eV in the energy region of interest. In general, spectra were taken between 2440 eV and 2520 eV with a step width of about 0.6 eV in the region of interest and a step width of about 0.3 eV in the pre-edge region and behind the XANES features. Integration time was about 0.5 sec. Spectra were obtained in the standard X-ray absorption technique using ionization chambers as monitor and detector. While the accuracy of the relative scale is better than 0.1 eV, the absolute scale was estimated to be better than 0.2 eV. The relative energy scale was calibrated against the white line (i.e., first strong resonance of ZnSO$_4$ at 2481.44 eV. In order to
analyze the near edge region, a linear background was subtracted from the raw data. Spectra were normalized at 2510 eV where the variation in the photo absorption cross section was very small. This enabled direct comparison of the relative oscillator strengths of the various electron transitions. Samples were taken from commercially available membrane sheets (Aldrich Company). Thin films with a thickness of about 30 micrometers were prepared using a microtone. Samples were dried for 7 h at 60°C and for 18 h at 110°C followed by treatment with phosphoric acid. After the first measurement, the dried samples were put into distilled water for about 1 hr. Then, another spectrum of the same samples was taken. The X-ray absorption near edge spectra (XANES) of K edge sulfur in Nafion 112, 115, 117, 417 and 450 were analyzed.

The MEAs were loaded into a single test fixture and the performance using a Globe Tech Fuel Cell workstation (HP6060 B electronic load) was measured. The single cell test fixture was composed of two copper current collector end plates and graphite plates containing rib channel patterns that allowed the methanol vapor access to the anode and humidified oxygen to the cathode.

RESULTS AND DISCUSSION

ELECTROCHEMICAL STUDY OF CARBON SUPPORTED MEMBRANE ELECTRODES (CMEs)

To relate the methanol oxidation processes at Pt-based catalyst electrodes, a mechanism that is direct analog of the methanol electro-oxidation mechanism at bi-functional alloys composed of Pt and second metal (M) and capable of activating H2O at low potentials is shown below:

1) \[ \text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt-CH}_3\text{OH} \rightarrow \text{Pt-CH}_3\text{OH}_{\text{ads}} \]
2) \[ \text{Pt} - \text{CH}_3\text{OH}_{\text{ads}} \rightarrow \text{Pt-CO}_{\text{ads}} + 4 \text{H}^+ + 4 \text{e}^- \]
3) \[ \text{M} + \text{H}_2\text{O} \rightarrow \text{M-H}_2\text{O}_{\text{ads}} \]
4) \[ \text{M} - \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{M-OH}_{\text{ads}} + \text{H}^+ + \text{e}^- \]
5) \[ \text{Pt-CO}_{\text{ads}} + \text{M-OH}_{\text{ads}} \rightarrow \text{Pt} + \text{M} + \text{CO}_2 + \text{H}^+ + \text{e}^- \]

At carbon supported pure Pt catalyst:

3a) \[ \text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt-H}_2\text{O}_{\text{ads}} \]
4a) \[ \text{Pt} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{PtOH}_{\text{ads}} + \text{H}^+ + \text{e}^- \]
5a) \[ \text{Pt} - \text{CO}_{\text{ads}} + \text{PtOH} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + \text{e}^- \]

Besides the surface reaction between Pt-bonded CO-like species and OH species on M sites, the hydroxyl species can participate in the process by which an "oxide film" is formed at high potential (4):
6) \( \text{PtOH} \rightarrow \text{PtO} + \text{H}^+ + e^- \)

or

7) \( \text{MOH} \rightarrow \text{MO} + \text{H}^+ + e^- \)

Figure 1 shows the CVs on different CMEs for a high methanol concentration (2.0M) in sulfuric acid at room temperature. The oxidation current peaks in both forward and reverse scan decreased with increasing \( \text{CH}_2\text{OH} \) concentration for Pt-Ru/C, Pt-Co/C, Pt-Ni/C and Pt-Cu/C CMEs. The surface reactions between Pt-bonded CO species and OH species on M sites, eqs. 5 and 5(a), become the rate-determining step at room temperature. Pt-CO adsorbed on the surface and decreased the number of active sites on the electrode due to higher methanol concentration. The oxidation current increased with increasing methanol concentration for Pt/C and Pt-Fe/C due to high surface real area (the roughness factors are 702 and 465 for Pt-Fe/C and Pt/C respectively).

Figure 2 shows the typical CVs of Pt/C and Pt-Ru/C membrane electrodes in 1M H\(_2\)SO\(_4\) + 1M CH\(_3\)OH. The oxidation of methanol started ca. 385mV and 300mV at Pt/C and Pt-Ru/C, respectively. The oxidation of methanol on Pt-Ru/C was shifted negatively more than 85mV compared with that on pure Pt/C. The oxide film formed minimized the number of active sites on surface and inhibit the methanol oxidation. In addition, the oxidation current is much larger at the Pt-Ru/C electrode than at the Pt/C electrode. These results showed that the bimetallic Pt-Ru/C electrode was a better catalyst for methanol oxidation in acidic solution. The bi-functional mechanism proposed [eqs. (1) - (5)] could be used for the explanation of experimental results observed. In Figure 2, the forward sweep increase in current was due to the oxidation of methanol. After the current peak, the oxidation current decrease was the result of a substantial amount of OH species absorbed on surface being transformed to the oxides, eq.(6), which break the active sites on electrode surface. In the reverse sweep processes, the oxides can be reduced:

8) \( \text{PtO} + \text{H}_2\text{O} + e^- \rightarrow \text{PtOH} + \text{H}^+ \)

or

9) \( \text{PtOH} + \text{H}^+ + e^- \rightarrow \text{Pt} + \text{H}_2\text{O} \)

The electrode surface was cleaned and oxidation current peak was observed again according to eqs. 5 and 5(a).

Figure 3(a) and (b) show the methanol oxidation of Pt/C and Pt-Ru/C CMEs at different temperatures. The oxidation currents at these CMEs increased with increasing temperature. It means that a larger amount of PtOH or MOH reacted with an intermediate formed during the oxidation of methanol, eqs. 5 and 5(a) at high temperature. The activity for methanol oxidation in Pt-Ru/C CME showed a 3-5 fold increase compared with that on Pt/C even on a real surface area basis. In addition, no oxide formed on the surface of Pt-Ru/C at high temperature.
To demonstrate that transition metal CMEs can be an alternative and low-cost electrode materials for DMFCs, Pt-Fe/C, Pt-Co/C, Pt-Ni/C and Pt-Cu/C were investigated as catalysts. Figures 3(c)-(e) show the CVs of Pt-based group VIIIb of the first transition row metals (Fe, Co, Ni) CMEs. The highest oxidation current was obtained with Pt-Co/C CME. Specifically, a lower amount of oxide could be formed on Pt-Co/C surface. It indicated that the Pt-Co/C CME was a better catalyst for methanol oxidation in the acid solution compared to other VIIIb transition metals. However, for the first transition row metal CMEs, the higher operation temperature seemed necessary to avoid the passivation effect in sulfuric acid (e.g. Fe$_2$O$_3$ or Ni$^{++}$-A--OH are formed).

Figure 3(f) shows the CVs at Pt-Cu/C CME. The current oscillations observed at low and medium temperature regions are due to the dual role played by the surface reaction between MOH and PtCo eq. 5 and copper dissolution. The formation and elimination of both Cu$^+$ and Cu$^{2+}$ on electrode surface may cause the current or potential oscillation. In acid solution, the reaction of copper dissolution may be described as follows:

\[
\begin{align*}
10) & \quad \text{Cu} \rightarrow \text{Cu}^+ + e^- \\
11) & \quad \text{Cu}^+ \rightarrow \text{Cu}^{2+} + e^- 
\end{align*}
\]

In general, the apparent activation energy for all of the catalysts studied decreased with increasing temperature. The potential of onset for methanol oxidation ($E_{on}$) shifted negatively at high temperature, compared to its value at low temperature. The apparent activation energy for MOH$_{ads}$ formation was overcome at lower potentials as the temperature is increased. The different potentials for the onset of CH$_3$OH oxidation on carbon supported CMEs are given below in Table 1.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Pt/C</th>
<th>Pt-Ru/C</th>
<th>Pt-Fe/C</th>
<th>Pt-Co/C</th>
<th>Pt-Ni/C</th>
<th>Pt-Cu/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>385</td>
<td>300</td>
<td>375</td>
<td>395</td>
<td>370</td>
<td>345</td>
</tr>
<tr>
<td>50</td>
<td>345</td>
<td>280</td>
<td>345</td>
<td>345</td>
<td>335</td>
<td>280</td>
</tr>
<tr>
<td>75</td>
<td>320</td>
<td>250</td>
<td>330</td>
<td>270</td>
<td>280</td>
<td>260</td>
</tr>
</tbody>
</table>

The real surface area of Pt-based catalyst membrane electrode was one of the important factors for the understanding of the characteristics of the electrode. Measurements were made on electrodes with 0.78 cm$^2$ in geometric areas. Figures 4(a) and (b) showed the CV results of different electrodes scanned between a potential range of -0.35 V and 1.60 V at a scan rate of 10 mV/s and room temperature in 0.5M H$_2$SO$_4$. From the charge of the oxidation of adsorbed hydrogen, the roughness factor (RF) and the ratio of the actual electrode area to the geometric area was calculated as listed Table 2 by assuming 210 mC for a real area of 1 cm$^2$ on a smooth Pt-electrode. The resistance of CMEs was measured using cyclic voltammetry and are given below in Table 2.
Table 2  Roughness factor (R.F.) and resistance ( R ) of carbon supported CMEs

<table>
<thead>
<tr>
<th>CME</th>
<th>Pt/C</th>
<th>Pt-Ru/C</th>
<th>Pt-Fe/C</th>
<th>Pt-Co/C</th>
<th>Pt-Ni/C</th>
<th>Pt-Cu/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.F.</td>
<td>465</td>
<td>318</td>
<td>702</td>
<td>118</td>
<td>352</td>
<td>100</td>
</tr>
<tr>
<td>R (mΩ/cm²)</td>
<td>260</td>
<td>280</td>
<td>290</td>
<td>266</td>
<td>266</td>
<td>318</td>
</tr>
</tbody>
</table>

The electrochemical oxidation methanol at CMEs with different supported materials (Carbon, Nafion® and Carbon-Nafion®) are shown in Figure 5. The current of Pt-Ru/C CME was higher than the current of Pt-Ru/Nafion®. It is due to that carbon supported catalysts have better electron conductivity. The resistances are 0.280, 1.00 and 106 W/cm² for Pt-Ru/C, Pt-Ru/Nafion® and Pt/C/Nafion® respectively. The Pt/C/Nafion® show the highest resistance. It was indicated that no electrochemical reaction occur on the surface of Pt/C/Nafion®.

STRUCTURAL STUDY OF PERFLUORINATED POLYMER ELECTROLYTE MEMBRANES (PPEMs)

All of the electrodes and membranes studied in this work have sulfonate (-SO₃) groups as the anionic functionalities attached to the backbone of the polymer electrolyte (shown below).

```
| [C-C] [C-C] | F₂ |
| [F₂ | F₂ | F₂ | F₂ | F₂ | F₂ |

n = number of repeat units
m = number of repeat units

F₂ = Fluorine
C = Carbon
O = Oxygen
H = Hydrogen
```

The presence of the water in the electrolyte facilitates or promotes proton transport. Without water, the proton conductivity of the membrane is insufficient to support adequate fuel cell operation in PEMFCs. Recent reports confirm that increasing the water content reduces the resistance to proton transport[17-20]. The thermal stability of Nafion® has been studied in detail using infrared spectroscopy, fourier transform infrared spectroscopy (FTIR) thermal gravemetric analysis etc. It is thermally stable up to 280 °C where the sulfonate groups begin to decompose[21]. Nafion is like polytetrafluoroethylene (PTFE) and serves as a binder and their contact with the electrode in PEFC enlarges the three phase boundary between the catalyst, gas and proton conducting membrane. A chronic concern in the engineering of fuel cell is to prevent poisioning of sulfur in these electrode catalysts and electrolyte membranes. Another source of sulfur in the fuel cell electrodes comes from the carbon support. Although, there has been an attempt to address the chemical state and surface morphology utilizing surface
analytical, X-ray and electrochemical techniques, its influence on the transport mechanism and electronic structure has not been completely understood. Another alternative technique to understand the electronic and geometric structure of these chemically modified materials is the X-ray Absorption Spectroscopy.

X-ray absorption spectra taken near the absorption edge of an atom in a given chemical environment provide detailed information on the electronic and/or geometric structure of the chosen atom on an atomic scale. XANES (x-ray absorption near edge structure) spectra give information about the valence of the excited atom, the electronegativity of the neighbor atoms, and the coordination geometry. From an analysis of EXAFS spectra the number and the type of the atoms in the first coordination shells and the radial distances of the next neighbors to the "central atom" can be obtained. X-ray absorption does not require any long range order and can thus be applied for the investigation of non crystalline materials e.g. polymers or doped proton exchange membranes. However, this technique has not been widely applied due to the difficulties to measure XAS at low Z elements which are normally in these polymeric systems. In an attempt to understand the electronic structure due to chemical modifications during electrochemical reactions, we have investigated the sulfur-K edge XANES in Nafion under different heat treatments and in treating with H$_3$PO$_4$.

Figure 6 shows the XANES spectrum of Nafion® 112, 117, 417, 450, and 115. The spectrum is dominated by a strong resonance at about 2480 eV with a shoulder on the high energy side. This energy position is typical for sulfur with valence IV. The presence of the two peaks are attributed to the two different types of oxygen in the sulfonate group. Two oxygen atoms have a double bond (about 1.4 Å) and one has single bond to the O-H group (about 1.53 Å). Since all of the Nafion® have sulfonate groups, the primary difference in XANES between the different Nafion® grades is the absorbance. Nafion® 117 has a far greater absorbance than the other grades from which can be implied that 117 has more sulfonate groups and a lower molecular weight than the other grades of Nafion®. It has been demonstrated that fuel cells with low molecular weight membranes show enhanced performance with increased voltage at a given current density and under relatively lower humidity. The irradiance from the XANES process (ref) can crosslink low molecular weight membranes. It was shown that this type of irradiation can increase water absorption Nafion® 117.

Figure 7 shows the XANES spectra of Nafion 115 and 112 dried at two different temperatures and time. Drying the samples (even at 110 °C) has little or no influence on the spectra. No significant differences in the spectra are observed which confirm the thermal stability of Nafion up to these temperatures. This is why Nafion has become a very popular PEM for low temperature (<100 °C) PEMFCs.

Figures 8 and 9 show the spectra before and after treatment with phosphoric acid on Nafion 112 and 117, respectively. The higher energy peak increased to about the height of the lower energy peak for both types of Nafion®. Also, the lower energy peak (2480 eV) shifted to a slightly higher energy for both Nafions®. The significance of this shift
could be due to the structure changes in the membrane after treatment with phosphoric acid. Because of the relatively high concentration of phosphoric acid, the presence of water is not as important as it is without the phosphoric acid. Without phosphoric acid, water is needed as the medium for proton transport. The water hydrates the Nafion®'s sulfonate groups and can function as the transporting agent for the protons produced at the fuel cell's anode. In the case of phosphoric acid treatment, the phosphoric acid replaces the water. It has 3 protons compared to water's 2. Phosphoric acid also has greater affinity for the Nafion® than the water. Therefore, the role of water in the structure of treated Nafion® diminishes and this role change is reflected in the higher energy peak of the XANES. Water still plays a role in the treated Nafion®. The water still hydrates the phosphoric acid, but the water is not the only medium for proton transport. The phosphoric acid and its hydrogen bonding abilities enhance the conductivity of the membrane. Therefore, changes in the water concentration inside the membrane is not as crucial as when the phosphoric acid is not present.

REFERENCES


CONCLUSIONS

- Electrochemical and structural characterizations were performed on traditional Nafion® type fuel cell proton exchange membranes.

- Evaluation of transition metal alloys as electro-catalysts instead of the generally accepted noble metal and alloy catalysts.

- Emphasis was placed on the cathodic oxidation of methanol crossover events instead of the anodic oxidation.

- The effect of methanol concentration in sulfuric acid, temperature, surface area of different carbon supported electro-catalysts were evaluated and matched with the existing electro-oxidation mechanisms.

- For the first time, the sulfur K-edge XANES in Nafion was measured using synchrotron radiation source.

- The phosphoric acid treated Nafion® exhibited a structural change due to the enhanced proton conduction.

- The current vs voltage characteristics for single cell fuel stacks were measured with similar membrane electrode assemblies(MEAs), will be published soon.
Pt + CH₃OH $\rightarrow$ Pt - CH₃OHₐds
Pt - CH₃OHₐds $\rightarrow$ Pt - COₐds + 4H⁺ + 4e⁻
M + H₂O $\rightarrow$ M - H₂Oₐds
M - H₂Oₐds $\rightarrow$ M - OHₐds + H⁺ + e⁻
Pt - COₐds + M - OHₐds $\rightarrow$ Pt + M + CO₂ + H⁺ + e⁻

PtOH $\rightarrow$ PtO + H⁺ + e⁻
PtO + H₂O + e⁻ $\rightarrow$ PtOH + H⁺
PtOH + H⁺ + e⁻ $\rightarrow$ Pt + H₂O
Energy [eV]

Absorbance [a.u.]

(a)

Nafion 112
- 70°C; 7h
- 110°C; 18 h

(b)

Nafion 117
- 60°C; 7 h
- 110°C; 18 h

Fig 8
Absorbance

Energy (eV)

2465 2470 2475 2480 2485 2490 2495 2500 2505

Fig 9

Nafion 112
after H$_3$PO$_4$ treatment

Nafion 117
After H$_3$PO$_4$ treatment

Nafion 117

Nafion 112
An Experimental Validation of the Polymer Electrolyte Fuel Cells Model

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Summer 1997

ABSTRACT
We studied Pt and a Pt-based alloy, Pt-Ru as electrocatalysts for anodes in Polymer Electrolyte Fuel Cells. In particular, we probed the effect of the presence of carbon monoxide in hydrogen on the performance of the cell. Optimal results were achieved by varying anode loadings and gas pressure. These experimental results were compared to a kinetic model of PEFC performance in the presence of CO developed by Springer, Zawodzinski and Gottesfeld. Good qualitative agreement was obtained.

INTRODUCTION
Fuel cells are energy conversion devices which convert chemical energy into electrical energy. Fuel cell use various fuels, including reformed fuels, which are chemically converted to hydrogen. Primarily, fuel cells are being explored as a potential source of power for electric vehicles. The operation of fuel cells require high power densities and high energy conversion efficiencies.

Of the many different types of fuel cells, the hydrogen/oxygen fuel cell is the most basic. Entering the anode feed stream, hydrogen is oxidizes to form 2 protons and 2 electrons. The protons cross the membrane and react with the oxygen at the cathode forming water, whereas the electrons are conducted from the cell into wire feeds in the form of electricity. In the case where the formation of water is not managed correctly, the cathode becomes flooded and hence it decreases the rate of gas molecules diffusing into the cell. Therefore in optimizing the fuel cell performance a gas-permeable, hydrophobic membrane is needed.

In Polymer Electrolyte Fuel Cells, Nafion is the most commonly used polymer electrolyte membrane. It allows the protons to pass through while simultaneously keeping the hydrogen and oxygen separate. This concept is basic, however very important in the performance of the fuel cell. Two catalyzed electrodes are hot pressed to the membrane by a membrane and electrode assembly (MEA). The MEA serves as the central part of the fuel cell.
There are advantages and disadvantages associated with PEFC. Some advantages include no corrosive liquids, easy fabrication and demonstration of longevity. While in contrast, the present disadvantages include expensive polymer electrolyte and the difficulty in proper maintenance of water management in the cathode.

A major emphasis of PEFC research is the development of low cost cell components for a fuel-cell system adequate for terrestrial transportation applications. A major fuel source is expected to be reformate gas, which contains both carbon dioxide and trace amounts of carbon monoxide in addition to hydrogen. It has been noted that the PEFC performance drops in the presence of CO. Recent works have explored this CO poisoning of the PEFC anode operating on reformate gas. This is due mainly to the adsorption of CO onto the catalyst surface to block sites for hydrogen oxidation. This is applicable to our investigative studies of Pt and Pt alloys, whose purpose is to decrease the surface deactivation.

We analyze the cell performance by looking at polarization plots of cell voltage versus current density. These performance curves for PEFC fed with CO mixtures in hydrogen in the anode feed stream are modeled. The basis of the polarization curves stems from four kinetic process occurring at the Platinum(Pt) anode catalyst. These processes are both chemical and electrochemical. They are described in detail by a model of the PEFC performance with reformate feed.

**THEORY**

The goal of the model was to obtain curves of PEFC performance in the presence of H₂/CO mixtures. In an attempt to verify this modeling we have shown several results for comparison.

This model developed by Springer, Zawodzinski and Gottesfeld predicts the performance of the fuel cell based on four kinetic processes occurring at the anode. It suggests we treat the anode loss as an electrode kinetics problem under the following conditions: (1) pure H₂ is the dry anode reactant gas, (2) the mass transport losses can be ignored, (3) the catalyst ionic resistance is low enough to ignore potential changes and (4) four chemical equations govern the interfacial kinetics. The chemical equations that govern these kinetics are listed in the equation section.

Mathematically, using a system of equations to represent these processes, the fraction of catalyst sites adsorbed and limiting currents were determined. Under the assumption that the transfer coefficient is 0.5, the model yields curves for current densities associated with both H₂ and CO/ H₂.

The calculated curves shown in the figures uses values of electrochemical and adsorption rate constants that reflect Pt/H₂ and Pt/CO systems near 80°C. Table 1 lists the values of base case parameters. These values describe high CO adsorption and a higher hydrogen electro-oxidation versus CO electro-oxidation at low anodic overpotentials. Figure 1 indicates the set of overpotentials versus current densities that fit these parameters while figure 2 shows the cell voltage as a function of current density.
EQUATIONS

The four equations below govern the kinetics that occur at the anode catalyst site. The first two equations are reversible and chemically represent [1] the adsorption of CO to the Pt sites and [2] the dissociative chemisorption of H₂ to the platinum. Equation [1] is responsible for the performance loss while in equation [2] the hydrogen on the Pt-H site becomes electrochemically oxidizes. This hydrogen oxidation process describes equation [3] which is ultimately responsible for generating the current. In equation [4] the adsorbed CO becomes electrochemically oxidizes to form CO₂. This becomes significant at high anode overpotentials because of the removal of CO from the catalyst sites, which allows for more hydrogen oxidation to occur.

\[
\begin{align*}
\text{CO} + \text{Pt} & \xrightleftharpoons[k_{fc}]{b_{fc}} \text{(Pt - CO)} \\
\text{H}_2 + 2\text{Pt} & \xrightleftharpoons[k_{fh}]{b_{fh}} 2(\text{Pt - H}) \\
(\text{Pt - H}) & \xrightarrow[k_{eh}]{e^-} \text{H}^+ + e^- + \text{Pt} \\
\text{H}_2\text{O} + (\text{Pt - CO}) & \xrightarrow[k_{cc}]{e^-} \text{Pt} + \text{CO}_2 + 2\text{H}^+ + 2e^- 
\end{align*}
\]

Mathematically, the model uses a steady-state balance of equivalent current densities to determine the θ_CO, the fraction of CO adsorbed and θ_H, the fraction of hydrogen adsorbed which are represented by equations[5] and[6]. It suggests the current that is produced originates from equation[7].

\[
\begin{align*}
\rho \dot{\theta}_\text{CO} &= k_\text{fc} P_{\text{co}} (1 - \theta_\text{CO} - \theta_\text{H}) - b_\text{fc} k_{\text{fc}} \theta_\text{CO} - k_{\text{cc}} \theta_\text{CO} e^{b_\text{cc}} = 0 \quad [5] \\
\rho \dot{\theta}_\text{H} &= k_{\text{fh}} P_{\text{h}} (1 - \theta_\text{CO} - \theta_\text{H})^2 - b_\text{fh} k_{\text{fh}} \theta_\text{H}^2 - 2 \theta_\text{H} k_{\text{eh}} \text{sinh} \left( \frac{\eta}{b_\text{h}} \right) = 0 \quad [6] \\
j_\text{H} &= 2 k_{\text{eh}} \theta_\text{H} \text{sinh} \left( \frac{\eta}{b_\text{h}} \right) ; j_\text{CO} &= 2 k_{\text{cc}} \theta_\text{CO} e^{b_\text{cc}} \quad [7]
\end{align*}
\]

In equation [7], j_H and j_CO are the current densities for the hydrogen and CO oxidation.

EXPERIMENTAL

The PEFC tested had active areas of 5 cm² with Nafion 105 used as the polymer electrolyte separator. Both sides of the membrane were catalyzed using preformulated inks. Experimental results consisted of 20 wt % Pt/C (Vulcan X C72R) with an anode loading of 0.33 mg/cm² and a cathode loading of 0.17 mg/cm². The Pt-Ru experimental results contained high and low loadings of Pt-Ru on the anode side with similar loadings for the cathode. The high loading contained 0.95 mg/cm² while the low had only 0.39 mg/cm². Each cathode contained roughly 0.17 mg/cm² of 20 wt % Pt/C.
These mixtures of inks each contained 5 wt % Nafion 105 by MEA. Both the anode and cathode were hot pressed on Nafion 105.

This MEA preparation method involved painting the inks on 5 cm² blanks. After each layer the inks were dried and weighed. This painting and drying process continued until a desired amount was reached. Next, we took the Nafion membrane, which had been treated in sodium hydroxide to convert it to the sodium form and dried it at 130°C on a hot plate. Labeling both sides of the membrane simplified our cell assembly. We placed the anode ink on the anode side of the membrane and the cathode on its respective side. Using two metal sheets, we placed the membrane and electrodes inside and hot pressed them together. Before attaching the MEA to the test station, we dropped it into a 0.5 M solution of H₂SO₄ to reprotoenate. Again we dried the membrane and electrode on a hot plate, however at 60°C.

The actual cell was not complete until it was properly attached. We attached all of the cell components systematically. We cut out gaskets, Teflon and ETEK uncatalyzed carbon cloth backings. Starting with the anode side, we placed the gaskets around the flow fields. Then we placed the carbon-cloth backing over the flow fields. Next, we added the Teflon sheet across the gasket and backing. Afterwards, we placed the MEA, anode flow fields. Similarly for the cathode side we added gaskets, backings and Teflon. To enclose the FC without leakage, we torqued each bolt 90 in-lbs.

We operated the FC at conditions similar to those used in the model. The cell temperature was set at 80°C. Our initial anode and cathode pressures were 30/60 PSIG, respectively, while the FC operated at 0.5V. Several hours was allowed for the cell to reach peak performance.

Data for the PEFC polarization curves were measured using the Hewlett-Packard 6060A electronic load. The curves were obtained using National Instruments Labview, a computer program linked to a Macintosh computer. Using Labview we were allowed to obtain polarization curves of voltage versus current densities. These curves allowed easy analysis of cell performance.

In conducting the actual experiment, our immediate concern was anode pressure and how it effects anode overpotentials in the presence of CO. By keeping most condition constant and varying only anode pressure and CO concentration we were able to test these effects. First, we set the anode pressure to the FC test station maximum of 60 PSIG, with all other conditions remaining stable. After allowing steady-state to be reached, a polarization curve was plotted. We next added 100 parts per million (ppm) of CO and allowed the cell to reach steady-state before running another curve. Immediately following its completion we cut the CO off and allowed the cell to once again reach a steady-state. A polarization curve was completed and then we added 10 ppm CO. Afterwards we completed a curve at 10 ppm CO. We repeated this process varying the anode pressure to 45, 30, 15, and 10 PSIG. This experiment was conducted for Pt/C on Pt/C, and Pt-Ru on Pt/C.

Each curve was logged. Difference curves between the neat H₂ and CO/H₂ curves were plotted using Labview. These differences are the anode excess overpotentials versus the
current. Based on these curves we analyzed the effect of CO concentrations in hydrogen on the cell's performance.

RESULTS/CONCLUSION

The model's prediction and the experimental results closely agreed. This suggests that solving the system of equations that govern these interfacial kinetics allow modeling of polarization curves for PEFC performance in the presence of both neat H₂ and CO/H₂ mixtures. Experimentally, we have shown the following: (1) the model and the experiment agrees qualitative, (2) the pressure dependence on the performance has profound effects, and (3) that it is possible to operate the PEFC in the presence of CO and be tolerant. Results of the modeling and the experiment are shown in the appendix.

ACKNOWLEDGMENTS

Special thanks to my mentors Drs. Rambau Bobba and Thomas Zawodzinski, Jr. also to the US Department of Energy Office of Advanced Automotive Technology, Los Alamos National Laboratory and Southern University A. & M. Physics Department for the support in this project.

REFERENCES


APPENDIX

LIST OF SYMBOLS

\( p \) = molar areal density

\( \theta_{\text{co}} \) = rate of adsorbed CO on platinum

\( \theta_{\text{h}} \) = rate of adsorbed hydrogen in platinum

\( b_{\text{c}} \) = ratio of backward to forward rate constants for CO

\( b_{\text{r},\text{h}} \) = ratio of backward to forward rate constants for hydrogen

\( k_{\text{c}} \) = forward constant ratio for CO

\( k_{\text{r},\text{h}} \) = forward constant rate for hydrogen

\( b_{\text{r},\text{h}} \) = effect Tofel slope for hydrogen

\( b_{\text{c}} \) = effect Tofel slope for CO

\( k_{\text{r},\text{e}} \) = rate of CO in electro-oxidation

\( k_{\text{r},\text{h}} \) = rate of hydrogen in electro-oxidation

\( P_{\text{h}} \) = partial pressure of hydrogen

### TABLE 1 - Base Case Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_{\text{c}} )</td>
<td>2x10^-5</td>
<td>atm</td>
</tr>
<tr>
<td>( b_{\text{r},\text{h}} )</td>
<td>0.5</td>
<td>atm</td>
</tr>
<tr>
<td>( k_{\text{c}} )</td>
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<td>A/cm²</td>
</tr>
<tr>
<td>( k_{\text{r},\text{h}} )</td>
<td>4</td>
<td>A/cm²</td>
</tr>
<tr>
<td>( b_{\text{r},\text{h}} )</td>
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<td>V/e-fold</td>
</tr>
<tr>
<td>( k_{\text{r},\text{e}} )</td>
<td>10^-9</td>
<td>A/cm²</td>
</tr>
<tr>
<td>( k_{\text{r},\text{h}} )</td>
<td>0.5</td>
<td>A/cm²</td>
</tr>
<tr>
<td>( P_{\text{h}} )</td>
<td>2</td>
<td>atm</td>
</tr>
</tbody>
</table>
Figure 1: Anode overpotential as function of current density for base case parameters in Table I for different CO concentrations in the anode feed stream.

Figure 2: Cell polarization curve for base case parameters in Table I for different CO concentrations in anode feed stream.
EXPERIMENTAL RESULTS

Figure 3: The anode overpotential as a function of current density for 10 ppm CO.

Figure 4: The anode overpotential as a function of current density for 100 ppm CO.
Figure 5: The anode overpotential as a function of current density for 10 ppm CO

Figure 6: The anode overpotential as a function of current density for 100 ppm CO
Figure 7: The anode overpotential as a function of current density for 10 ppm CO

Figure 8: The anode overpotential as a function of current density for 100 ppm CO
Figure 9: The anode voltage as a function of current density for CO concentrations. The curves shown has Pt on both the anode and the cathode.
Figure 10: The anode voltage as a function of current density for CO concentrations. The curves shown has Pt-Ru on the anode and Pt/C on the cathode.
Figure 10: The anode voltage as a function of current density for CO concentrations. The curves shown has a low loading Pt-Ru on the anode and Pt/C on the cathode.
SILVER BASED FAST ION CONDUCTING GLASSES

During this project duration, the PI Dr. Rambabu Bobba has initiated a collaborative effort with staff members at University of Pondicherry, Pondicherry, TN, India. As a result of this effort, Dr. N. Satyanarayana was brought here as an exchange visitor to work at Southern University. The intent was to develop sol gel synthesis technique to synthesize samples for fuel cell and battery application. Dr. Rambabu Bobba has presented this work at 11th International Conference on Solid State Ionics held in Hawaii, 11/16/1997-11/22/1997 and published this work in the Journal of Solid State Ionics. Primary Batteries were fabricated and characterized at Pondicherry University.

The studies on fast ion conducting (FICs) glasses are increasing due to their potential applications in various electrochemical devices. The FIC glasses not only have high ionic conductivity but also have many other advantages over their crystalline counterparts, such as, ease in preparation, wide selection of composition & glass forming region, miniaturization in the form of thin films, absence of grain boundaries, isotropic properties, negligibly small electronic conductivity, inert to atmosphere, high stability, etc., [1-3]. Hence, many FIC glasses have been synthesized in the form binary, pseudo binary and ternary to achieve high ionic conductivity. Recently, it has been demonstrated that further improvement in the conductivity could be achieved by adding one more component to the ternary systems, which are called quaternary FIC glasses [4,5].

On the other hand, the analysis and understanding of the experimental results of FICs have become a real task, because of the multicomponent and complex nature of the glassy matrix [5-7]. Recently, impedance spectroscopy has become a basic and ideal technique to characterize the FIC materials, where the impedance analysis can give the information about the bulk (d.c.) conductivity and also the electrical behavior (equivalent circuit of the FIC materials [7-9]). The analysis of the a.c. conductivity and dielectric results will give information about the various conduction species and their influence on the overall transport process in the glassy matrix [10-12]. Various compositions of silver based quaternary superionic conducting (SIC) [AgI-Ag2O-(SeO2 + P2O5 (SSP)] and AgI-Ag 2 O-(SeO2-V2O5) glass system were prepared and characterized. The highest conducting formers (F) composition and modifier (M) to former (F) ratio were fixed [13]. Hence, different dopant salt (AgI) content of SSV compounds were prepared by using the following expression.

\[
D\%AgI-(100-D)\%[M%Ag2O-F\%0.8SeO2+0.2V2O5]]
\]

where M/F = 2.25, D was varied from 20% to 70% in steps of 10. Analytical grade AgI, Ag2O, SeO2 and V2O5 chemicals were taken in different compositions, according to their molecular weight percentage. Each composition was melted in a quartz crucible at 550 °C and the molten liquid was poured into liquid nitrogen to form the glass. The obtained bulk compounds were grounded into a fine powders and were characterized by X-ray diffraction (XRD), Infrared (IR) and Differential Scanning Calorimetry (DSC) techniques.
A@- (1-X)%[M% Ag2O-F%(0.3SeO2 +0.7P2O5)] (X = 20 to 80% in steps of 10 and M/F = 2.25) system was prepared for various dopant salt (AgI) compositions by melt quenching technique. Analar grade chemicals of AgI, Ag2O, SeO2 and P2O5 were weighed and mixed thoroughly, according to their molecular weight percentages. The mixture was taken into a quartz crucible and melted at 500°C for about 30 minutes. The bulk compounds were obtained by quenching the molten liquid into liquid nitrogen. The obtained bulk compounds were made into fine powders using mortar and pestle.

X-ray diffraction spectra were recorded for 2θ values between 10 to 70 degrees at a rate of 2° per minute, for all the compositions of SSV system, using the Rigaku miniflex X-ray diffractometer with monochromatic Cu Kα radiation of wavelength of λ = 1.5418 Å. The peaks free X-ray diffraction spectra were observed for the 30 to 66.67% of AgI content in the SSV compounds and confirmed the glassy nature, whereas, 20 and 70% of AgI content showed the mixed nature (amorphous and polycrystalline). The Fig. 1 shows the glass forming region for different dopant salt content of SSV system. Fig. 3 show the XRD of SSP system. The absence of the peaks in the observed diffractogram spectra confirm the glassy nature and the existence of partial peaks in the diffractogram spectra were attributed to the mixture of polycrystalline and amorphous. The glass forming region for various dopant salt (AgI) compositions of the SSP system is shown in fig.1 and it confirms that the X = 20, 70 and 80% of dopant salt (AgI) compositions of the SSP system are mixed in nature (open circles) and all other compositions (X = 30 to 66.66%) are glassy in nature (solid circles).

The SSV glass samples of each AgI composition and spectral grade of KBr powder were mixed in 1:20 weight ratio and made in the form of thin pellets by using the KBr press. The IR transmittance (T%) spectra were recorded on the thin pellets (SSV:KBr = 1:20) in the region 400-4000 cm⁻¹, at room temperature (303 K), using the JASCO FTIR-5300 spectrophotometer. Fig.2 shows the typical IR spectrum of a particular AgI content in the SSV glass and it shows the following bands at 995, 900, 830, 755, 450, 417 cm⁻¹. The observed IR bands in SSV system are assigned by comparing with the reported IR bands in ternary vanadate, selenate glassy systems [3,14].

The band position 995 cm⁻¹ is assigned to the characteristic vibrations of the V=O in VO₃ groups. The 900 cm⁻¹ and 410 cm⁻¹ bands are respectively assigned to the stretching (ν₄) and bending (ν₃) modes of SeO₂ molecule. Similarly, the 830 and 450 cm⁻¹ bands are respectively assigned to ν₃ and ν₄ modes of SeO₄ molecule. Finally the 755 cm⁻¹ band is assigned to the ν₃ mode of VO₃⁻³ molecule. Further, it is found that the IR band positions are not changing with the AgI content in the SSV glass. This suggests that the SSV glass structure is not changing with the dopant salt (AgI) content, which is also in good agreement with the reported values [15]. Hence, from the IR results, it is concluded that the SSV glass is composed of ionic clusters of selenate, vanadate, silver and iodine.
Glass forming regions for various compositions of dopant salt (AgI) in Silver Silenophosphate (SSP) system. In figure ( ), represents glassy compound and (O) represent mixture of glass and poly crystalline.
Typical IR spectrum for particular dopant salt (AgI) content of SSV system.
Typical DSC Curve for the highest Conducting SSV. System.
Conductivity obtained at room temp as a function of dopant salt (AgI) in SSP system.
The DSC curves were recorded for all the dopant salt (AgI) content of SSV samples using differential scanning calorimeter (DSC) of Perkin Elmer make model (DSC-2). The SSV sample of 5 to 10 mg is heated at the rate of 1 degree C per minute and recorded the DSC curves for all the AgI content of SSV glasses. It is observed that the glass transition temperature (Tg) decreases from 75 to 52 degree C with AgI content in SSV system and the lowest Tg is observed for the highest AgI content in the SSV system. The typical DSC curve for the highest conducting SSV glass is shown in fig.3. The glass transition is a measure of strength of the glass and the decrease in Tg with AgI content suggest that more and more number of bonds destroy within the glassy network, in order to allow its rearrangement to form a thermodynamically stable phase [16].

Different dopant salt (AgI) compositions of SSV system were prepared and identified the glass forming region by recording the X-ray diffractogram spectra, where the 30 to 66.67% of AgI content of SSV system form glass. From the assignments of the observed IR bands, it is concluded that the SSV glass is composed of ionic clusters of selenate, vanadate, silver and iodine. Also, confirmed that the AgI is not interacting with the SSV glassy network, hence, structure of the glass is not changing, since the observed IR band positions are not changed with AgI content in the SSV glass. The decrease in Tg with AgI content in SSV glass of the DSC results is attributed to the formation of more and more loosen type of glassy network. Various compositions of the SSP glasses were prepared and the glass forming region was established from the X-ray diffraction spectra, where the 30 to 66.67% of AgI compositions form glass and the other compositions of SSP system show the mixed nature (polycrystalline and glass). From the electrical conductivity studies, the highest conducting (σ = 2.93 x 10⁻² S/cm) composition 66.67%AgI - 23.07%Ag2O -10.26% (0.3SeO2+0.7P2O5) of SSP system is fixed and it is found to be almost a pure ionic, since the electronic conductivity of the SSP glass is the order of 10⁻⁸ S/cm compared to the total conductivity (10⁻² S/cm).

REFERENCES:
CONCLUSIONS

The search for new and improved solid state ionic conductors and electrolytes continues in our laboratory. Along with improving infrastructure in our laboratory for material characterization, we have also contributed our effort in developing capability for research in electrochemical systems using the double crystal monochromator beam line (port 5A and 4B) for EXAFS investigations at Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge. Student participation has been the main thrust in this collaborative research project. Three undergraduate and three graduate students were given support through this project duration. A special emphasis was given on the development of materials for fuel cells. Based on our research finding we have arrived to a conclusion that the dopant cation size and its effect on the host crystal lattice structure are a major factor in determining the ionic conductivity of the solid electrolytes. In order to understand the precise role the dopant plays in modifying the major properties of the oxide, the primary information that is required is the exact location of the dopant in the host lattice. In the present study, we have investigated the effect of methanol concentration, temperature, surface area of different carbon supported cathodic catalysts (Pt, C, Pt/C, Pt-Fe/C, Pt-Co/C, Pt-Ni/C, Pt-Cu/C, Pt-Ru/C, and Pt-Ru/ Nafion®) using cyclic voltammetry. The effect of water content on the electronic structure of perfluorinated polymeric membranes (Nafion® 112, 115, 117, 417 and 450) using X-ray absorption near edge spectroscopy (XANES) has also been studied in this paper. Various compositions of silver based quaternary superionic conducting (SIC) [AgI-Ag2O-(SeO2 + P2O5 (SSP)] glasses were prepared by melt quenching technique. The nature of the compounds were confirmed by X-ray diffraction. Electrical and electronic conductivity studies were carried out to select the high ionic conducting composition of the SSP system for the fabrication of batteries. Different dopant salt (AgI) compositions in the AgI- Ag2O- SeO2 -V2O5 (SSV) system were prepared by melt quenching technique. All the prepared compositions of the SSV system were characterized by X-ray diffraction, IR and DSC.

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SOLID OXIDE FUEL CELLS

RESEARCH OF LITERATURE

by
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To Satisfy The Course Requirements For:
Special Problems 492

December 3, 1997
INTRODUCTION

What Is a Fuel Cell?

A fuel cell is a device that directly converts the chemical energy of reactants (a fuel and an oxidant) into low voltage d.c. electricity. It is similar to a battery in that it produces the electricity using chemicals, often just hydrogen and oxygen, without combustion or rotary machine. However, unlike the conventional batteries, it does not consume materials that form an integral part of or are stored within its structure, and it does not need to be recharged. It operates as long as it is fed with a suitable fuel and oxidant and the reaction products are removed. The reactants are stored outside the reaction areas (the electrodes) and are fed to the electrodes only when electric power generation is required. For most fuel cells, the oxidizing reactant is atmospheric oxygen. When its other reactant is exhausted, all that is required to resume operation is to refill the fuel tank. Because the fuel tank can be made as large as desired a fuel cell's period of operation can be made to be much longer than that of a conventional electrochemical primary battery.

There are several different types of fuel cells. A major distinguishing characteristic of different fuel cells is in the electrolyte used. For stationary power generation, the three major fuel cells are phosphoric acid (PAFC), molten carbonate (MCFC) and solid oxide (SOFC). This paper will focus on the solid oxide fuel cell.

Principle of Operation of a Fuel Cell

A fuel cell consists of a fuel electrode (anode) and an oxidant electrode (cathode) separated by an ion-conducting electrolyte. The electrodes are connected electrically
through a load by a metallic external circuit. In the metallic part of the circuit, electric current is transported by the flow of ions, an oxide ion ($O^{2-}$) in the case of the solid oxide system. In theory, any substance capable of chemical oxidation that can be supplied continuously (as a fluid) can be burned galvanically as the fuel at the anode of a fuel cell. Similarly, the oxidant can be any fluid that can be reduced at a sufficient rate. Gaseous hydrogen has become the fuel of choice for most applications, because of its high reactivity when suitable catalysts are used. Similarly, at the fuel cell cathode the most common oxidant is gaseous oxygen, which is readily and economically available from air for fuel cells for terrestrial applications. When gaseous hydrogen and oxygen are used as fuel and oxidant, a reaction takes place in the cell and water is produced.

At the anode of a hydrogen-oxygen fuel cell, incoming hydrogen gas ionizes to produce hydrogen ions and electrons. At the cathode, oxygen gas reacts with migrating hydrogen ions from the electrolyte and incoming electrons from the external circuit to produce water. The overall reaction that takes place in the fuel cell is the sum of the anode and cathode reactions; in the present case, the combination of hydrogen with oxygen to produce water. This overall reaction takes place at much lower temperatures than the conventional combustion of the two gases. Instead of energy being released as heat, as is the case when hydrogen is burned with oxygen, part of the free energy of reaction is released as electrical energy. The theoretical standard free energy of formation of liquid water from gaseous hydrogen and oxygen at 1 atm pressure and 25°C is 1.229 V. In theory, the hydrogen-oxygen fuel cell should be capable of generating d.c. electrical energy at 1.229 V. (1) In practice, however, on account of electrode polarization and other irreversibilities, under net flow of current the terminal voltage will be lower than
this ideal value. In any event, it can be seen that as long as hydrogen and oxygen are fed
to the fuel cell, the flow of electrical current will be sustained by electronic flow in the
external circuit and ionic flow in the electrolyte.

**Fuel Cell Uses and Benefits**

The challenge in fuel cell development for practical applications has been to
improve its economics through the use of low-cost components with acceptable life and
performance. Engineering, materials improvements, and manufacturing processes now
are developing to produce fuel cells with sufficiently high power, acceptable lifetimes,
and affordable costs. Fuel cells can be made in a huge range of sizes. They can be used
to produce quite small amounts of electric power, for devices such as portable computers
or radio transmitters, right up to very high power for electric power stations.

Several benefits of fuel cells include new markets, energy security, cleanliness and
efficiency, and economic growth for America. Fuel cell power system markets could
exceed $3 billion world wide by the year 2000. U.S. energy dependence is higher today
than it was during the "oil shock" of the 1970's and oil imports are projected to increase.
Passenger vehicles alone consume 6 million barrels of oil every single day, equivalent to
85% of oil imports. If cars used fuel cells, oil imports could be cut by 1.5 million barrels
every day. Fuel cells could dramatically decrease oil imports, reduce urban air pollution,
reduce the trade deficit and produce American jobs. Fuel cells could create new markets
for American steel, electronics, electrical and control industries, helping to maintain
American technological leadership. (2)
SOLID OXIDE ELECTROLYTE FUEL CELLS

As their name implies, solid oxide electrolyte fuel cells (SOFCs) utilize a solid oxide as the electrolyte. When this material is heated to about 1000°C, it becomes sufficiently conductive to oxide ions (while remaining nonconductive to electrons) to serve as a solid-state electrolyte.

Let's examine the basic principles of operation of a high temperature SOFC operating on hydrogen fuel and oxygen oxidant. At the cathode, oxygen reacts with the incoming electrons from the external circuit, ionizing to form oxide ions, which migrate to the anode through the zirconia electrolyte. At the anode, hydrogen reacts with these oxide ions to produce water vapor, which is accompanied by the liberation of electrons for the external circuit. The overall process is simply the reaction of hydrogen with oxygen to produce water. Depending on the actual composition of the fuel, water vapor, and oxidant, the open circuit voltage of a SOFC is usually 0.8V-1.0V. The driving force for the SOFC is seen to be the difference in the oxygen partial pressure on either side of the electrolyte. (3)

Features of Solid Oxide Fuel Cells

There are several features of SOFCs that make them very attractive for utility and industrial applications. First the very high operating temperature (~1000°C) ensures that all fuel compositions, when combined with water vapor when necessary, will oxidize rapidly and spontaneously to thermodynamic completion if sufficient air is provided on the cathode side. The high temperature of reaction, does not require expensive catalysts, and permits the direct processing of the fuel cell in the fuel cell itself. Solid oxide
systems are able to attain at least 96% of the theoretical voltage at open circuit any losses being due to minor crossleaks and to the effect of small electronic conductivity of the electrolyte. (3)

High temperature operation and a tolerance to impure fuel systems may make solid oxide systems especially attractive when combined with coal gasification plants. The heat released in the fuel cell reactions can be efficiently transferred and used for coal gasification or hydrocarbon reforming. In consequence, no fuel need be burned to proved the heat of reforming.

Because the solid oxide electrolyte is normally very stable, no electrolyte migration problems under cell operating conditions exist. In addition, the composition of the electrolyte is not a function of fuel or oxidant composition. Because no liquid phases are present, there are no three-phase interfaces to maintain, no problems with pore flooding and no catalyst wetting problems. Solid oxide cells also have a good tolerance to overload, underload and even short-circuiting.

Another advantage inherent in a SOFC is that cell component can at least in principle be fabricated into a variety of self-supporting shapes and configurations that may not be feasible with cells employing liquid electrolytes. Through the use of innovative designs, the self-supporting nature of the solid oxide electrolyte makes it potentially feasible to achieve very high power densities. The potentially high power-to-weight and power-to-volume ratio for such SOFC systems may eventually enable their use in mobile power sources as well as in those for stationary applications. (3)

Since high-temperature water electrolysis is both thermodynamically and kinetically better than low-temperature electrolysis, so cells can be operated in reverse, as
high-temperature water electrolyzers capable of operating at current densities in excess of 500mA/cm² at cell voltages in the order of 1.3 V. This makes solid oxide systems attractive for use as energy storage devices and for peak power leveling applications.

State-of-the-Art Solid Oxide Fuel Cells

Westinghouse SOFC

The conventional design for a SOFC battery has been one in which a number of narrow cylindrical cells are joined end-to-end, and electrically connected in series to build up a stack of cells of a desired output. Westinghouse Electric Corporation has now developed a new design in which the electrical connections and power take-offs use low cost metallic components. In this new design, each tube consists of a single cell. (1)

Japanese SOFC

In Japan, solid oxide electrolyte fuel cells of conventional thin-film internal anode tubular are being developed by the Electrochemical Laboratory as part of the Moon Light Project. The Japanese originally tested bell-and-spigot systems, but owing to the difficulty of fabrication this layers of electrolyte, they later switched to thin layer type cells on porous alumina support tubes, the this layers being applied by a flames spray process. (1)
Monolithic SOFC

Argonne National Laboratory (ANL) has been working on a flat-plate SOFC of a radically new design. The Argonne cell, termed a monolithic fuel cell, employs the this ceramic layer components of existing SOFCs in a strong lightweight honeycomb structure that promises to give much higher energy and power densities than conventional configurations.

Conclusion

The goal of the collaboration between the Lawrence Berkeley Lab (LBL) and the Electric Power Research Institute (EPRI) is the development of a commercial thin-film solid oxide fuel cell. EPRI has enlisted the skills of an entrepreneurial start-up company, Ceramatec, to facilitate transfer of the LBL technology to manufacturing. In this way, the unique capabilities of LBL team in the area of thin-film SOFCs are combined with the manufacturing talents of Ceramatec in planer SOFC technology. To date, development efforts are ahead of schedule with technical performance exceeding initial expectations. Commercialization of this technology looks promising. (2)

Westinghouse is developing the technology under a cooperative agreement with the U.S. Department of Energy. Under its DOE program, Westinghouse recently initiated a new phase of development arrived at producing mega-watt-class power plants with unprecedented fuel-to-electrical energy conversion efficiencies of 60 to more than 70 percent, reached by combining pressurized SOFC generating units with gas turbine-generators. (5)
Argonne National Laboratory is developing solid oxide fuel cells operating in the 500 and 800 C range. To decrease the operating temperature of the SOFC from the conventional 1000 C, new materials need to be explored. Argonne is investigating novel oxide/electronic conductors for this type of SOFC. Auxiliary high-temperature sealant materials for the SOFC are also being developed to seal cell edges and the stack-to-manifold junctions. (4)
References


This is a report on the installation and operation of the fuel cell test station. The fuel cell test station was installed by Globetech, Inc. on June 21-23. The station was tested using a Nafion 115 Pt/Ru (1 mg/cm²) membrane electrode assembly (MEA). Due to the lack of a special Hydrogen regulator (on order from Lincoln Big 3), it was not possible to start the test station until July 16.

The purpose of procuring the test station was to study a wide variety of polymer membranes as well as different catalysts for the direct oxidation of methanol fuel cell. Literature survey has shown that, though highly active, the Platinum electrocatalyst gets quickly poisoned by CO formation during oxidation of methanol. A Pt/Ru catalyst has proved to be more stable against CO poisoning. It is our plan to investigate Pt/Ru as well as ternary catalysts for improving the life and efficiency of a direct oxidation of methanol fuel cell (DMFC).

In addition to investigating catalysts we propose to study different proton conducting polymeric membranes. The Nafion membranes currently used are not suitable for use with methanol. They have a high methanol permeability which results in methanol loss across the membrane.

The initial step was to familiarize myself with operation of the fuel test station. This included understanding the effect of back pressure, gas flow rate and humidifier temperature. The test station was delivered and installed by Globe Tech. The fuel cell with MEA#1 was assembled and the conditioning of the MEA was carried out under the supervision of Globe Tech.

MEA #1
During the first experimental run, I found that the thermocouple had slipped out of the fuel cell resulting in fuel cell temperature reaching 146°C. The actual operating temperature of the cell was 75°C. I was told by Globetech that Nafion has a temperature limit of 90°C and that the membrane had probably been destroyed. I decided to continue operating the same MEA and found that I was getting oscillatory but high current output. During several subsequent runs the current output oscillated in the range 100-600 mA/cm² at 10-30 psig back pressure and 0.300 volts. After more than 24 hours of intermittent operation over six days, the membrane failed. When the fuel cell was opened, I found that the teflon tubing had become narrow (hour glass shape) near the o-rings between the copper plate and the graphite block. This could have contributed to the failure of the membrane.

MEA #2
The second MEA (MEA #2) was conditioned according to the procedure provided by Globetech. In the initial run, the conditions were same as those for MEA #1 and the current output obtained was lower than that from MEA #1. Increasing back pressure to 10 psig resulted in an unexpected drop in current output and increased oscillations. When the back pressure was reduced to 0 psig the current output returned to its original level. Hydrogen flow rate was increased to 300 cc/min to bring it up to the stoichiometric value for Oxygen (150 cc/min). Increasing the back pressure to 10 psig again resulted in drop in current and increased oscillations. Leak check on all external fittings was negative. It was felt that water accumulation in the cell could be a cause of the
increased oscillations and so the cell was placed along one corner so as to position the outlet directly below the inlet. This would result in all the water flowing towards the outlet instead of collecting at the bottom. Even this new position, increasing back pressure from 0 to 10 psig and then to 30 psig resulted in increased oscillation of the current. The fuel cell was pressure tested on the station and there was a 10 psig drop in pressure from 72 psig in 30 minutes. This indicated a leak but it was not clear whether the leak was in the fuel cell or test station. The cell was disassembled and then reassembled. There was no pressure drop in 20 minutes at 55 psig and it was assumed that all leaks had been stopped. Operating the fuel cell at increased back pressure (10 psig) however, resulted in oscillation as well as a drop in current output. This seemed to indicate a leak. The fuel cell was operated intermittently for several days and each time increase in back pressure resulted in increased oscillations and drop in current output. The teflon tubing again had hour glass shaped constrictions near the o-rings.

Since the inadvertent overheating of MEA #1 had resulted in increased current output, I decided to try to duplicate the conditions to see if thermal treatment would increase current output. The backpressure was increased to 20 psig and the fuel cell heated to 145 C and then allowed to cool to the operating temperature of 75 C. The fuel cell was operated for 6.6 hours at 20 psig back pressure and had reached a current output of 460 mA/cm^2. The back pressure was increased to 30 psig and the fuel cell operated for 1.5 hours. At the end of the run the fuel cell output was 560 ± 30 mA/cm^2. Although there was oscillation, the current output had increased considerably after the heat treatment. When the cell was operated the day after the heat treatment, current output at 30 psig reached only 330 mA/cm^2 compared to 550 mA/cm^2.

Apparently, the effect of the heat treatment is temporary and when the fuel cell was operated the next 2 days under the same conditions of temperature and gas flow rate, current output at 20 psig backpressure was 165 mA/cm^2 and at 30 psig it was 330 mA/cm^2. In order to see if a second heat treatment would improve the current output, the fuel cell was heated up but the MEA failed during the process. MEA #2 failed after 56.5 hours of intermittent operation.

MEA #3 was conditioned overnight according to the prescribed procedure. The fuel cell was operated for several hours to compare the performance of the new MEA with MEA #2. The current reached 320 mA/cm^2 at 0 psig. When the cell was operated the next day, the current output reached only about 200 mA/cm^2 at 0 psig back pressure. On increasing the back pressure to 10 and the 30 psig, the current began to oscillate just like the current output of the previous MEAs. MEA #3 was also given heat treatment to see if its the oscillations would reduce and its current output would go up. After heat treatment, current output at 10 psig was higher (260 mA/cm^2 and rising) than current output before treatment (220 mA/cm^2). At 30 psig, the current had exceeded 435 mA/cm^2 and as expected the oscillations had increased. When the cell was restarted the next day, current output at 10 psig was low (200 mA/cm^2 versus 260+ on the previous day). I decided to give a second heat treatment because drop in current indicated that the effect of the treatment was temporary. The cell was heated up to 119 C and the temperature maintained at 118 C for about 4 minutes. The cell was then allowed to cool to 75 C, the operating temperature. There was only a slight improvement in current output but there was a definite increase in oscillations. The next day, the heat treatment (up to 144 C) was repeated and the fuel
cell allowed to operate overnight. The membrane failed at some point in the night. The data could not be recovered because the computer stopped saving data due to insufficient memory. The upgraded version of the software will allow data acquisition for long periods of time. This upgrade will be available to us free of cost.

MEA #3 was operated intermittently for 33 hours over 5 days.

MEA #4
I had noticed that in the case of all three MEAs the current output took hours to reach a stable value at each back pressure. A possible reason for this could be under-conditioning. Usually catalysts and chromatography columns are conditioned at temperatures higher than operating. I decided to condition the MEA #4 at 30 C above recommended conditions.

Comparison of recommended and new conditioning temperatures (°C)

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Gas flow rates were maintained higher than recommended. Anode 200 cc/min and cathode 150 cc/min.

After conditioning the MEA overnight, the fuel cell was operated at the conditions shown above. The current reached a stable value of 300 mA/cm² (0 psig back pressure) within minutes. Even after 6 hours of operation there was no variation in the current output. When the cell was restarted the next day, the current quickly reached a value of 200 mA/cm² and became stable. On the third day also the current quickly reached 200 mA/cm² and remained stable until the back pressure was increased. As soon as the back pressure was increased, the current began to drop indicating a leak. This was confirmed by Ed Miller (Globe Tech) and Steve Noding (Dow Chemicals).

I disconnected the fuel cell from the test station and connected the inlet of the anode side to the inlet of the cathode side with (1/8” dia.) teflon tubing. I, then, plugged the anode outlet and connected the Nitrogen tank directly to the cathode outlet. The fuel cell was then pressurized up to 60 psig. The teflon tubing connecting the inlets of anode and cathode is for equalizing the pressure in the two halves of the cell. The pressurized cell was then lowered into a bucket of water. Gas bubbles indicating leaks began appearing between the two gaskets. The torque wrench (0-250 ft-lb) was replaced with a new one (0-250 in-lb) to allow the required torque (60 in-lb) to be applied much more accurately. However this did not help in sealing all the leaks. Freshly cut gaskets as well as teflon gaskets provided by Steve Noding were tried but the leaks did not stop. Globe Tech is mailing thicker gaskets which may help seal the fuel cell better.
It appears that constriction of the teflon tubing occurs even at room temperature. This was discovered during my attempts to assemble a fuel cell without any membrane. The gaskets were placed between the graphite blocks and the cell tightened to the required torque. After disassembling the fuel cell, I found that the new teflon tubing had constrictions very near the place where it passes through the o-ring. I intend to replace the section of the teflon tube inside the cell with stainless steel tubing.

Conclusions and Recommendations

The fuel cell test station was operated with four Nafion 115 MEAs (1 mg/cm² Pt/Ru catalyst). The current output was found to be almost same for all MEAs. Inadvertent heating of the fuel cell to 146°C resulted in higher current output indicating that short term heating of the Nafion membrane may be beneficial even though the temperature for continuous operation should not exceed 90°C. Each of the MEAs was heated to 146°C at least once resulting in improved current output. The effect of the heat treatment was temporary as current output dropped with prolonged operation of the fuel cell.

Placing the fuel cell along one corner helped in slightly reducing the oscillations. Leak check of the fuel cell by immersing it in water indicated several leaks which could be the main cause of the oscillations. Two different types of gaskets were tried, however, the leaks have not been eliminated. A thicker gasket has been requested from Globe Tech.

The constriction of the tubing appears to be due to the pressure applied on it by the o-ring. Replacing the teflon tubing with stainless steel will solve the problem. This has not been tried yet because the major leaks were between the gaskets and not between the copper plate and the graphite block.

At this stage it is not possible to comment on the current output of Pt/Ru versus Pt catalyst. The fuel cell test station appears to be functioning well and as soon as the leaks in the fuel cell have been eliminated, a Pt MEA will be operated. This will enable us to compare the results from this test station with those provided by Globe Tech.

Safety Requirements for Fuel Cell Test Station

The fuel cell station is primarily being used for operating fuel cells with polymer membrane electrolytes. The fuel cell is an equipment which is used to generate electricity by carrying out an oxidation-reduction reaction across a polymeric membrane. The reactants used until recently were oxygen and hydrogen. From the point of safety and cost, research is now being conducted on utilizing methanol in place of hydrogen.
In order to come up to the level of current research we plan to operate the fuel cell with hydrogen and oxygen using different types of membranes, catalysts and then replace hydrogen with methanol.

The use of hydrogen and oxygen as reactants necessitates several safety precautions. This is especially important in this case because the fuel cell has to be operated for several hours continuously. In fact, when the new membrane is being conditioned, the fuel cell is operated continuously for 24 hours. Even though the fuel cell test station automatically shuts down in case of power failure or loss of pressure, the use of flammable gases requires several other safety precautions.

1. The exhaust gases which contain unreacted hydrogen and oxygen must be vented outside the building. This will prevent the accumulation of gases in the room which can be an explosion hazard. The simplest way would be to vent the gases into a chemical hood. The hood is also required for the muffle furnace which will be used for preparing the membranes. The exhaust duct for the two hoods in the computer room (Rm 123) passes through the roof of the lab (Rm 123) and the hood can be connected to it.

It is important to note that the presence of the band saw and other machines next to the fuel cell test station constitute a fire/explosion hazard. A spark from the machine could ignite any accumulated hydrogen. If the fuel cell equipment is to remain in this lab (Rm 123), there should be a wall between the lab and the machine shop. The wall should isolate the lab completely to prevent flammable gases from leaking into the machine shop.


3. First aid and eye wash kit.

4. Fire extinguisher in the lab

These are some of the necessary requirements at this time. I do not know if Southern University labs have to conform to OSHA regulations.

Saleem Hasan
These measurements are taken on nafion 117 operating in a humidified environment. These measurements are consolidating that there is a maximum flow, cell temperature beyond which there is no appreciable deviation in current density. Even though the current is stabilizing after a long time, it is not appreciable.

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The membrane performance is observed over an extended period of time with a gradual decrease in cell voltage. It is again observed that there is no appreciable change in current density beyond certain limits for both gas flow rate and cell temperature. It seems to be that at an ideal temperature of 70 degC at which point there is no appreciable change in properties of nafion membrane, catalysable gas quantity could be determined and approximately equivalent to 25 cc/min/cm². The membrane performance as shown could be described as one with a steady increase in current density with a decrease in voltage.
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MEGLO1

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Pt/Ru on C with 3M methanol

Current

Time

Pt/Ru on C with 3M methanol

Series1

Page 9
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11597  18.76  0.215  0.545  -7.744 -4.386  75 1 1 1 0
11657  18.86  0.215  0.547  -7.747 -4.386  75 1 1 1 0

Pt/Ru on C GlobeTech

\[ \begin{align*}
\text{Voltage} & \quad 0.214 & 0.2145 & 0.215 & 0.2155 & 0.216 \\
\text{Current} & \quad 0 & 5 & 10 & 15 & 20
\end{align*} \]

Pt/Ru on C GlobeTech

\[ \begin{align*}
\text{Current} & \quad 0 & 5 & 10 & 15 & 20 \\
\text{Time} & \quad 0 & 2000 & 4000 & 6000 & 8000 & 10000 & 12000
\end{align*} \]
STRUCTURE OF A PROTON EXCHANGE MEMBRANE
NAFION

Nafion® 105, 110, 112, 115, 117, 417 and 450

\[
\begin{align*}
\text{[} & \text{C—C]_m} \\
& \text{F}_2 \\
\text{O—C—C—SO}_3\text{H}
\end{align*}
\]

SULFUR IN PROTON EXCHANGE MEMBRANE

X-RAY ABSORPTION NEAR EDGE STRUCTURE (XANES)

* Investigation of the structure (F-K and S-K edge)
* Systematic investigation of chemically modified materials
* In Situ Investigations during electrochemical reactions
11th International Conference on Solid State Ionics (SSI-11)
Honolulu, Hawaii, USA
November 16–21, 1997

Extended Abstracts
International Society for Solid-State Ionics
in collaboration with
The College of Engineering
University of Hawaii
Honolulu, Hawaii, USA
METHANOL CROSSOVER IN DMFCs: A STUDY OF ELECTROCHEMICAL AND STRUCTURAL PROPERTIES OF CATHODIC ELECTRODES AND MEMBRANES

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The direct methanol fuel cells (DMFCs) using polymeric (or proton) electrolytic perfluorinated ionomeric membranes (such as Nafion®) are promising candidates for the application of portable power sources and transportation purposes. They are attractive alternatives to hydrogen-air fuel cells because of their inherent high energy densities and the low cost of the methanol as a fuel. The catalytic activity of methanol oxidation in an acidic environment using unsupported carbon platinum (Pt) and platinum based binary alloy electrodes such as Pt-Ru, and Pt-RuOₓ have been well studied in ambient and at elevated temperatures. However, the degradation of commonly used electrode catalysts (Pt, Ag, and others) and the corrosion of carbon substrates are making commercialization of fuel cells using present day technologies economically problematic. Furthermore, the methanol crossover from the anode to cathode results in consumption of fuel and impacts the performance of the cathode causing the cell to operate at a lower overall efficiency. The crossover rate is largely determined by the electrochemical, thermal and structural activity of electrode catalysts and permeability of the membrane. Perfluorinated ion conducting polymers with low equivalent weight (i.e. Nafion® 117) possess high ionic conductivity and are permeable to methanol. Nafion® membranes with higher equivalent weight have lower methanol permeability and reduced ionic conductivity. The development of membranes with low methanol permeability with high ionic conductivity is critical. The DMFCs can have high performance due to higher catalyst loadings, but the dense catalyst layer structure permits enhanced transport for a large number of active sites. However, methanol is relatively electrochemically inert. The kinetics of the methanol oxidation is slow. Though extensive work was conducted on platinized electrodes for both the oxidation and the reduction reactions, the mechanism involving the methanol cross over issue in DMFCs is not well understood. The goal of this work is to correlate the catalyst's electrochemical and electronic properties, structure and its oxidation state with the performance of proton exchange membrane(s) (i.e. Nafion®) for DMFCs. In the present study, focus will be on the electrochemical (i.e. cyclic voltammetry and in situ current and potential step coulometry) investigations of different cathodic catalysts (Pt, C, Pt/C, Pt-Fe/C, Pt-Co/C, Pt-Ni/C, Pt-Cu/C, Pt-Ru/C, and Pt-Ru/Nafion®) and XANES measurements of F, S-K edge of sulfonic acid membranes such as Nafion® 117 under different conditions.

The cathodic electrodes, except those composed of Pt black, contain 20% Nafion® 117, and were cast onto Teflon® impregnated carbon paper. The membrane electrode assemblies (MEA) used in this work were prepared by Globe Tech Inc., College Station, TX. The electrochemical investigations of these catalysts for the oxidation of hydrogen
and the reduction of oxygen were carried out in the Solid State Ionics laboratory using an EG&G PAR Model 270 potentiostat/galvanostat and a frequency response analyzer model 1025. The performance of the MEA under fuel cell conditions was measured using a Globe Tech Fuel Cell workstation. The Nafion® samples were pretreated using different precursor chemicals such as nitric and phosphoric acid. The XANES spectra of the F and S-K edge on the pretreated Nafion® samples were obtained by our Universität Bonn collaborators at the Center for Advanced Microstructures and Devices (CAMD).

The cyclic voltammograms showed a higher current response when Pt-Ru/C is the catalyst rather than Pt/C (Figure 1). The Pt catalysts showed a higher current response for cathodic oxygen reduction than the Pt-Ru/C catalysts. In general, the Pt-Ru/C catalysts showed greater electrochemical properties when compared to the Pt catalysts. The effect of the alloying of Ru on a carbon substrate facilitated the removal of carbon monoxide from its surface. Incorporating these catalysts on Nafion® has an increased current density which is believed to be due to the enhanced proton conductivity (i.e. proton is the main ionic charge carrier). The investigation of the inexpensive transition metal alloys (i.e. Pt-Fe, Pt-Co, Pt-Ni, Pt-Cu) as electro-catalysts will also be reported.

The resistance of the Nafion® membrane increases as the temperature increases due to the loss of water and the resulting decreased current density of the fuel cell. The structure of the Nafion® allows water to be gained or lost and the rheology of the ionomer. The F and S-K edge of these sulfonic acid membranes showed differences in the XANES spectra (Figure 2). These spectral differences revealed that the molecular structure of these membranes depends upon the membrane's pretreatment (e.g. phosphoric acid [Figure 2]). The acidic pretreatment effected the rheology and the molecular structure of the inomer (i.e. Nafion® 117) and contributed to the enhancement of proton conduction.

Acknowledgement: This work is supported by the US Department of Energy and National Science Foundation. B. Rambabu acknowledge the support from FETC (DE-FG22-95MT95016), SEA Sync beamline (DE-F605-95ER 45549), NSF-ARI and LEQSF MS program grants.
Fourth Annual
Historically Black Colleges and Universities/
Private Sector Energy Research and Development
Technology Transfer Symposium

AGENDA
APRIL 2–3, 1996
Breaking Out of the Paradigm:
Minority Institutions—Showcases of Excellence and Quality

Exhibitors
Piedmont Natural Gas Company
Honeywell Technologies
Federal Information Exchange
U.S. Department of Energy, Office of Fossil Energy
Southern University
Los Alamos National Laboratory
Rocky Mountain Oil Field Testing Center
Sandia National Laboratories

Cosponsors
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North Carolina A&T State University
U.S. DOE, Office of Economic Impact and Diversity
Monday, April 1, 1996

1:00 PM—7:00 PM
Guilford Ballroom G

Setup of Posters and Exhibits

3:00 PM—7:00 PM
Outside Guilford Ballroom

Registration—Holiday Inn Four Seasons

Tuesday, April 2, 1996

7:30 AM—4:30 PM
Speaker Audio-Visual Preview Room

7:30 AM—8:30 AM
Guilford Ballroom G

Pre-Meeting Break

7:30 AM—4:30 PM
Student Poster Presentations/Exhibit Room

8:00 AM—4:00 PM
Outside Guilford Ballroom

Registration

Opening Plenary Session

8:30 AM—10:00 AM
Guilford Ballroom E

Welcoming Address and Introduction of Keynote Speaker

Dr. Sun W. Chun
Director, Pittsburgh Energy Technology Center,
U.S. Department of Energy

Keynote Speaker

Patricia Fry Godley
Assistant Secretary for Fossil Energy,
U.S. Department of Energy

Opening Remarks

Corlis S. Moody
Director of the Office of Economic Impact and Diversity,
U.S. Department of Energy

Dr. Edward B. Fort
Chancellor
North Carolina A&T State University

Dr. Jasper D. Memory
Vice President for Research, General Administration,
The University of North Carolina

Katherine LeBlanc
White House Executive Director,
White House Initiative on Historically Black Colleges and Universities

Alfred Ramirez
White House Executive Director,
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FOURTH ANNUAL HISTORICALLY BLACK COLLEGES AND UNIVERSITIES/
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Saleem Hasan, Jerry LeBlanc, Vijay K. Rayanki, Timothy George and B. Rambabu
Materials Research Instrumentation Laboratory
Department of Physics
Southern University A&M College
Baton Rouge, Louisiana 70813.

Introduction

In 1973, the oil price quadrupled and the world became aware of its total dependence on petroleum. Resources of fossil fuels are decreasing and the complexity of power generation and distribution is increasing. The need for mobile power systems is also attaining greater significance. The growing concerns about environmental pollution have made the search for alternative and viable energy resources even more urgent. The US Department of Energy has been consistently striving to explore new technologies such as Solid State Ionics (SSI). Application of SSI ranges from small batteries for transportation (1), to high power batteries for energy storage systems (2), electrochromic windows for energy conservation (3) and sensors for chemical pollution detection (4-5). All electrochemical devices which contain at least one solid electrolyte i.e. a solid with unusually high diffusion coefficients and conductances for specific ions, are referred to as SSI technologies. As compared to traditional power generation systems, the ability of fuel cells for direct conversion of chemical energy into electricity offers significant advantages (6). Solid Oxide Fuel Cells (SOFCs), operated at 900-1000 ºC have the advantages of rapid reaction kinetics without the need for expensive noble metal electrodes. The use of solid ceramic materials in SOFCs makes power and heat co-generation an attractive option and also eliminates the corrosion and liquid electrolyte management problems associated with other types of fuel cells (7-9). However, the high operating temperature has placed considerable constraint on the materials requirements, which also increases the price of the cell manufacture. To overcome these problems, one can use a combination of ceria based electrolytes and stainless steel bi-polar plates operating on either natural gas or methanol fuel cells. We have recently initiated a project to study the structural and electrical properties of solid electrolytes for SOFCs with the support from Pittsburgh Energy Technology Center and Morgantown Energy Technology Center for DOE. We have also been investigating structure and rechargeability relationships in Li/FeS$_2$ and Li/SPE/FeSZ secondary rechargeable batteries using Synchrotron Radiation based experiments at Center for Advanced Microstructures and Devices (CAMD).

The operating principle of batteries and fuel cells is essentially the same. Solid electrolytes are used in both the devices. In each of these, mixed conductors are required for electrodes and purely ionic conductors for solid electrolytes. In addition to SOFC research, we are also initiating a research project on Direct Oxidation of Methanol Fuel Cells (DMFCs) for transportation applications for the Department of Defense (DOD). In this paper we review in brief the materials and design considerations of electrochemical cells and present our effort in developing the research infrastructure for characterization of solid electrolytes in the Department of Physics at Southern University A&M College, Baton Rouge.
Electrochemical Cells

Electrochemical cells are devices that convert chemical energy into electric power; the electric current delivered to an external load between its two electrodes is compensated by the ionic current through an electrolyte inside the cell between its two electrodes. The internal resistance of the electrochemical cell is

\[ R = \frac{L}{(\sigma_i A)} + R_{\text{int}} + R_e \]

where \( L/A \) is the thickness/area ratio of an electrolyte, \( R_{\text{int}} \) is the resistance to ionic transfer across the reactant-electrolyte interface and \( R_e \) is the internal resistance to collection of the electronic current within the electrodes. The operating voltage is limited by the open circuit voltage \( (V_{oc}) \)

\[ V = V_{oc} - IR \]

\[ V_{oc} = \frac{(\mu_a - \mu_c)}{(-nF)} \]

where \( (\mu_a - \mu_c) \) is the difference in the electrochemical potential of the anode and the cathode, \( n \) is the number of electrons involved in the chemical reaction of the cell, and \( F \) is Faraday's constant. A low voltage, \( V \leq 4\text{V} \), in an electrochemical cell means that the high power \( P=I^2V \) requires a high current \( I \) through the cell. A low internal \( I^2R \) loss and a high maximum power \( P_{\text{max}} = I_{\text{max}} V_{\text{max}} \) require, in turn, a small resistance \( R \). Since the electrolyte conductivity is generally low, a small \( R \) demands a small \( L/A \) ratio; but a practical lower limit to the size of \( L/A \) is set by \( R_e \), which increases with \( A \). In addition to optimizing \( \sigma_i \) and minimizing \( L \) of the electrolyte, the designer of a power cell must have metallic electrode current collectors. The interfacial resistance \( R_{\text{int}} \) must also be minimized. If the reactants are solids, a solid electrolyte introduces a solid-solid interface that may rupture with changing volumes of the solid reactants during repeated discharge/recharge cycles. Loss of interfacial in area not only increases the resistance for internal transport across the electrode-electrolyte interface but also lowers the capacity of the cell as segments of the electrode become disconnected from the electrolytes. Therefore liquid or elastomer electrolytes are preferred where the reactants are solids.

In polymer electrolyte fuel cells (PEFC), a thin organic proton exchange membrane plays the dual role of electrolyte and the gas separator. The resistance of the organic membranes depends on its thickness and on the resistivity of its material. The resistivity in turn is a function of temperature and of membrane hydration. However, the membrane water management under fuel cell operating conditions is complex and depends on many parameters such as current density, temperature, gas flows, water partial pressures, and cell design (10). In both SOFCs and PEFCs the reactants are fed to the catalytic electrodes and the reaction products are continuously discarded in the exhaust. In a fuel/electrolysis cell, the reactants are gaseous or liquid and chemical reaction takes place at a three phase interface between reactant, electrolyte and catalytic current collector; the current collector is a source/sink of electrons that facilitates dissociates chemisorption or associative desorption of a molecular species and creates or accepts the ionic species transferred to/from the electrolyte. For example a prototype fuel/electrolysis cell reaction in acid is

\[ 2H_2 = 4H^+ + 4e^- \]  \hspace{1cm} \text{(anode)}

\[ 4H^+ + 4e^- + O_2 = 2H_2O \]  \hspace{1cm} \text{(cathode)}
where the reactions progress from left to right in the fuel cell, from right to left in the electrolysis cell. In this case a protonic electrolyte is used, and the anode and cathode current collectors chosen are metallic catalysts for the particular electrode reaction. In a solid oxide fuel cell (SOFC), for example, a solid oxide ion conductor such as zirconia is used as the electrolyte and metallic oxide current collectors catalyze the reaction (11):

\[
2H_2 + 2O^{2-} = 2H_2O + 4e^- \quad \text{(anode)}
\]

\[
4e^- + O_2 = 2O^{2-} \quad \text{(Cathode)}
\]

Unfortunately, the oxide ion conductivity \( \sigma_{O^2-} \) is not high enough in the solid electrolyte below an operating temperature \( T_{op} = 1000 \) C, whereas use of liquid, aqueous electrolyte restricts \( T_{op} \) to an upper limit of about 100 C. The search for \( H^+ \) or \( O^{2-} \) solid electrolyte membrane that would permit operation in the range \( 400 < T_{on} < 800 \) C is required.

Hydrogen generated from reformed hydrocarbons is used as the fuel in \( H_2/O_2 \)-air polymer electrolyte fuel cells. An alternative approach is to use the hydrocarbon directly in the fuel cell, as for example the direct electrochemical oxidation of methanol (12). The Direct Methanol Fuel Cell (DMFC) can operate on either acid, alkaline or polymer electrolyte. Esso and Shell studied methanol oxidation (anode) catalysts extensively and found that a Platinum/Ruthenium system was among the most active of those tested. The direct methanol fuel cell is capable of converting methanol into electrical energy without intermediate thermal steps. Unlike other fuel cells, there is no need for an external reformer to first convert the fuel into hydrogen. Eliminating this step results in considerable saving in weight and cost. In principle, it should be possible to build very simple, battery like devices capable of being refueled with a liquid fuel (3). A direct methanol air fuel cell operating at or near ambient temperature would be an ideal small generator for fixed or portable applications. Direct methanol fuel cells have also been considered as auxiliary power supplies for internal combustion engine vehicles, since a fuel cell could generate power much more efficiently than the engine driven alternators. The performance of the DMFC anode is determined by a wide range of parameters, including catalyst formulation, nature of the catalyst substrate, and the overall electrode structure. It is evident that the problem of poor catalytic activity remains the main barrier to the success of the direct oxidation of methanol fuel cell. Previous studies and Arrhenius plots (4) indicate that acceptable power densities should be obtainable at modestly elevated temperatures. Problems that have to be overcome include: migration of methanol to the cathode, where it is oxidized non electrochemically (yielding no power) or simply evaporates into the exhaust air stream of the cathode and be lost. Methanol migration may be substantially reduced, but probably not eliminated, by incorporating ion exchange membrane separators (13-15).

The DMFC based on a solid electrolyte allows higher operating temperatures and thereby increased catalytic activity compared to conventional cells with a liquid electrolyte. For solid state fuel cells with integrated methanol reforming and a working temperature of 200-300 C, the main problem is the stability and conductivity of the solid electrolytes. A solid state methanol fuel cell with an operating temperature of 100 C looks promising in terms of electrode current density (6), electrolyte corrosion and electrolyte conductivity. Investigations of proton conducting materials have included intercalates with species like acidic metal oxides and organoamines in host structures like zeolites Y and X, transition metal phosphates.
Polymer Electrolyte Fuel Cells (PEFC) technology (7) has been preferred over other fuel cell technologies because it offers high power densities, excellent tolerance to high levels of CO₂ in the fuel stream and thus capability to use reformed organic fuels and low temperatures (100 °C). This makes possible a fast startup sealing, reduces corrosion and improves the lifetime of the fuel cell. One of the important areas for further research is the stability, conductivity and methanol compatibility of the solid polymer electrolyte. The membrane currently being used in methanol fuel cells is the perfluorinated sulfonate membrane Nafion. This membrane was originally developed for the chlor-alkali industry and methanol diffusion through it is high especially at the high operating temperatures for direct methanol oxidation fuel cells. The diffusion coefficient for methanol in Nafion is of the order of 10⁻⁵ cm²/s. In order to make commercially viable DMFCs it is essential to develop a solid polymer electrolyte membrane with proton conductivity greater than 10⁻³ (Ohm cm)⁻¹ which is practically impermeable to methanol.

We are initiating a research effort on DMFCs and will concentrate initially on the proton conducting compounds such as zirconium phosphates and Tin-Mordenite (H-zeolite containing Sn(IV)-oxide clusters) for fuel cell applications. The initial effort will include the preparation and characterization of these membranes. Our goal is to understand the electrode stability and electrolyte compatibility with methanol.

**Electrolytes**

An electrolyte is an ionic conductor and an electronic insulator that should not react with the reactants of the cell other than to accept/donate the working ions from/to the electrodes. An electrolyte may be liquid or a solid. Liquid electrolytes require the addition of a separator that maintains the separation of the two electrodes and yet is permeable to the working ions. The separator also immobilizes the liquid electrolyte. The principle is the same whether the immobilizing agent and the separator is the polymer of a proton exchange membrane, the oxide of a particle hydrate, or a permeable fiber. A solid electrolyte itself acts as a separator. The reactants of an electrochemical cell may be gaseous, liquid or solid. Solid electrolytes are useful where the reactants are gaseous or liquid. Liquid or elastomer electrolytes are to be preferred where the reactants are solids. Most emphasis in the field of polymer electrolytes has been put on the improvement of the performances of materials based on polyethylene oxide. There is now a visible tendency to use plasticised electrolytes in place of conventional salt/polymer complexes. Composite polymer electrolytes consisting of at least 35 mol% poly(vinylidene fluoride) (PVDF) and mixtures of propylene carbonate (PC) and dimethyl formate, lithium salts (LiAsF₆, LiN(CF₃SO₂)₂ or LiC(CF₃SO₂)₃ are some of the electrolytes worth investigating for secondary battery applications. A non-aqueous electrolyte allows consideration of electropositive Group-A metals as the anode. However, the cation released by the anode to the electrolyte, not a proton or an OH⁻ ion, can be expected to be a working cation in a non-aqueous electrolyte. The most mobile ions would be monovalent, and the monovalent Group-A metals are alkali metals. The lightest of the alkali metals is lithium, so it is logical to explore cells with Li⁺ as the working ion in the liquid electrolyte and elemental lithium as the anode. Unfortunately, elemental lithium reacts with the known Li⁺ ion electrolytes to form a passivating surface film. Although Li⁺ ions can be transported across the film into the electrolyte on discharge, competition between transport across the film and plating on to fresh surface on recharge tends to favor the latter, which leads to the formation of dendrites that grow across the space separating the two electrodes. After
a limited number of discharge/recharge cycles, the dendrites make contact with the cathode and short circuit the cell. Although, limited success has been achieved in controlling dendrite formation on recharge of a lithium anode cell, this problem has motivated the exploration of intercalation electrode systems (16-17).

**Intercalation Electrodes**

The term insertion and intercalation refer to the addition of a species to a host structure with retention of the major structural features of the host. The intercalation is a special case of insertion in which no strong chemical bonds of the host are broken during the reaction. The classification scheme used for electrode reactions is summarized below. An example of each is also shown.

**Electrode Reactions**

\[
\begin{align*}
\text{Insertion} \\
\text{Intercalation} \\
\text{Other} \\
\end{align*}
\]

In this paper we will discuss one specific battery system Li-anode/solid polymer electrolyte/intercalated cathode material such as FeS₂. We have performed synchrotron based radiation experiments such as EXAFS and NEXAFS at Center for Advanced Microstructures and Devices (CAMD) to understand the structural integrity and rechargeability relationships in Li/FeS₂ and Li/SPE/FeS₂ system. Battery R&D organizations have been pursuing a large number of candidate systems for use in electric vehicles for the past 2-3 decades (18). One of the best candidates to be used in the cathode system in future EV (polymer electrolyte) batteries is FeS₂ (19). It is cheap and abundant. The Li/FeS₂ cell was invented at Argonne National Laboratory and was first reported in the early 1970s. It makes use of a molten salt electrolyte which is a mixture of alkali metal halides containing high concentrations of lithium ions, a lithium alloy negative electrode (usually Li-Al), a positive electrode of FeS₂. The earlier versions of this cell were operated at 450 C, but recent changes in the composition of the electrolyte have allowed the operating temperature to be decreased to 400 C. The LiAl/LiCl-LiBr-KBr/FeS₂ cells and Li₂FeS₂ battery systems have achieved higher performance than other rechargeable batteries that operate at ambient conditions, this being the main reason for the acceptance of the higher operating temperature. The lifetime and performance information on these two systems revealed that the specific energy and specific power of single, unsaturated cells are very attractive, being about 200 Wh/kg and above 200 W/kg, respectively.
Earlier work with the FeS$_2$ electrode made use of both discharge plateaus: the conversion of FeS$_2$ to Li$_2$FeS$_2$ followed by the conversion to Li$_2$S and Fe. The Li/SPE/FeS$_2$ batteries operate over a moderate temperature range of 100-140 C; therefore common, commercially available, low cost hardware, materials, insulators, scales and current collectors can be used. The electrolytes consist of PEO, a thermodynamically stable anion and high surface area oxide matrix. The high surface area oxide matrix improves the mechanical strength, immobilizes the molten phases and seems to help in achieving low and stable interfacial resistance. It is expected that Li/SPE/FeS$_2$ battery will meet the power density and energy density requirements for electric vehicles. In addition, it has safety and manufacturing advantages over other lithium and sodium batteries. The other positive electrode materials that have received most attention in recent years are MnO$_2$, V$_6$O$_{13}$, and organodisulfides. The energy storage in organo-disulfides is believed to take place by the scission and formation of S-S bonds coupled with the movement of Li$^+$ ions into and out of the polymer matrix. Polymer electrolytes have a low ionic conductivity (less than 10$^{-3}$ ohm$^{-1}$ cm$^{-1}$ ) at room temperature and are generally used in the thin sheet form. Typically, the electrolytes are tens of micrometers thick with a total thickness of 250 micrometers. The Li/polymer/V$_6$O$_{13}$ have delivered a specific energy of 150 Wh/kg, specific power 400 W/kg and these energies could provide a range of 200-300 miles. In general 400 W/kg is required for electric vehicle applications. To improve the performance of the lithium battery based on a polymer electrolyte, major efforts are needed in the areas of cell scale up, overcharge and overdischarge tolerance, battery design, heat removal and other battery engineering issues. The aim of this project is to develop in situ techniques to understand the relationship between the electrochemical properties and the structural changes that occur during the charge-discharge cycles of the Li/SPE/FeS$_2$ system.

Conventional X-ray Diffraction (XRD) measurements are of limited value to understand structural changes in these electrochemical systems which are often noncrystalline and amorphous. The rather recent application of EXAFS to the in situ study of electrochemical systems has made it possible, for the first time, to explore basic concepts in the structure and electronic properties of materials under conditions which closely resemble those found in practical devices. Compared to other spectroscopic methods such as IR, Raman, Mossbauer etc., EXAFS and NEXAFS spectroscopy has the advantage of providing information about the inter-atomic bonding and coordination geometry with high element selectivity. While it is quite feasible to carry out many X-ray experiments using other sources, the experimental problems posed by electrochemical measurements are most easily overcome by working with a synchrotron X-ray beam which is many orders of magnitude greater in intensity. The plane grating monochromator beamline (port 4A) and double crystal monochromator beam line (port 5B) at CAMD are ideally suited for the in situ experiments proposed in this project. The beam line operates in the 2-18 keV range with up to 4 m rad of dipole radiation from the CAMD storage ring. The monochromator maintains a fixed exit beam and a fixed positions of the beam on the two crystals using mutually perpendicular elastic translations. With the ring operating at 1.5 GeV and 160 mA, Si(220) crystals provide a flux of $3 \times 10^9$ photons/s/mrad at 8 keV, with an energy resolution of 2 eV, to the experimental hutch. The beam line is equipped with an EXAFS end station.

We have acquired the UWXAFS software for XAFS data analysis. It will be used for determining first and more distant coordination shell parameters. The UWXAFS 3.0 package analyzes the data by removing background using a new, improved, automated algorithm and then fits the data either to FEFF calculations in R space or to isolated shells of data standards in k space. Our students have learnt the utility of a similar software used to analyze the XAFS data available at CAMD. We have made an attempt
to understand, in detail, the Fe K absorption edge structures of FeS₂. The Fe K absorption spectra of FeS₂ are similar to the one reported earlier in the literature (J. Appl. Phys. 17, 184 (1978), J. Chem. Phys. 80(3), 1047-1049, 1984). The pyrite type FeS₂ has a grouping of iron atoms and S₂ pairs that can be considered similar to NaCl. Its crystals are cubic with four molecules in a cell of dimensions a₀ =5.40667 Å. In the pyrite structure each iron atom is surrounded by six sulfur atoms at the corners of a nearly regular octahedron with the Fe-S distance of 2.26 Å, while each sulfur atom is bound to another sulfur atom and to three iron atoms. The bonding throughout the structure is wholly covalent. The X-ray valence band emission and absorption spectra give information about the density of states in the valence and conduction bands, respectively. For example, the sulfur K emission and K absorption spectra of the metal sulfides reflect the distributions of p like states in the valence and conduction bands, respectively and the sulfur L₂,3 emission, and L₂,3 absorption spectra reflect the distribution of the s and d like states. The K absorption edges consist of a step like structure and are interpreted in terms of energy band structure for these sulfides. The absorption spectra provide an interesting insight into the bonding roles of various sulfur orbitals. X-ray Photoelectron (XPS), UV photoelectron (UPS), X-ray emission (XES), Mossbauer spectroscopy, magnetic data, and SCF-X scattered wave MO studies on FeS₂ are available. All these studies clearly show the Fe²⁺ to be in low spin singlet state and the shortness of the S-S distance indicates that the anions are actually disulfide S₂²⁻ rather than sulfide ions. A comparative study was made to draw MO diagrams for valence type orbitals in high spin quintet, transition state (2t₂g)³ (3e₉)¹ (2t₂g)² and low spin singlet state of FeS₆¹⁰⁻ with different R(Fe-S) distances.

The problem of localization and mobility of lithium ions in the pyrite structures is still an open question and the charge transfer mechanism during the oxidation process is not well understood. From a crystallographic point of view, the question arises about whether the mobile lithium ions are in "tetrahedral" (Li-S₄) or "octahedral" (Li-S₆) environment or both. From an electronic point of view, removal of lithium from Li₂FeS₂ structure is to be accompanied by an oxidation process of the starting phase. Mossbauer spectroscopy studies indicate a strong isomer shift decrease, consistent with the oxidation of Fe²⁺ iron encountered in Li₂FeS₂ to Fe³⁺ in LiFeS₂. From a band structure point of view this corresponds to lowering of the iron d band level. It is difficult to imagine that oxidation beyond the LiFeS₂ composition would result in further oxidation of Fe³⁺ since d molecular orbitals of more oxidized iron ion would certainly overlap the S²⁻ anionic bond. It is hence assumed that holes will be created in that band with the possible formation of S₂²⁻ pairs. For better insight into the structural and electronic properties, we are planning to measure the FT-IR spectrum of various LiₓFeS₂ samples. We have installed a Nicolet FT-IR spectrometer in our laboratory.

Previous IR studies on LiₓFeS₂ samples show the monoclinic distortion of FeS₂ is due to the formation of the S₂²⁻ pairs that may destroy the assumed original rhombohedral arrangement of the sulfur atoms. As indicated in the contract, the emphasis of the project is to acquire sulfur K edge spectra in pyrite using our EXAFS system. The energy associated with K edge of sulfur is much lower than that of the first row transition metals and therefore one has to take special precautions to acquire sulfur K edge XAFS data and the analysis of the data. We have obtained for the first time, K edge of the sulfur spectra using our spectrometer.

The investigation of the mechanism of discharge in the high energy density battery system Li/FeS₂ using ⁵⁷Fe Mossbauer Spectroscopy and in situ Fe K edge of the XAS study of lithium insertion in pyrite has been conducted. These studies revealed the formation of Fe₁₋ₓS and the electrochemical reduction of
FeS$_2$ exhibits superparamagnetism. A substantial reduction in the amplitudes of the Fe-S and Fe-Fe backscattering was observed as the amount of intercalated Li in FeS$_2$ lattice was increased from 0 to 2 Li$^+$ equivalents. In addition, XANES revealed a rounding of the otherwise highly structured edge of FeS$_2$ as the amount of inserted lithium was increased. We have attempted to construct an electrochemical cell which consists of a thin lithium anode, a separator and a thin FeS$_2$ cast electrode arranged in a sandwich type configuration using a solution of trifluoromethane sulfonate (trflate) in a mixture of dimethoxyethane/dioxolane as the electrolyte. The geometry provides an optimal condition for achieving a highly uniform current distribution so that the lithium incorporation (or cell discharge) will occur homogeneously over the entire FeS$_2$ electrode.

Ceria based Solid Electrolytes

The host lattice of ceria is most compatible with a wider range of trivalent dopants compared to zirconia, hafnia, and thoria and proved to be an excellent oxygen ion conductor because of its stable defect structure at elevated and intermediate temperatures and pressures (19-20). The dopant ionic radii and its effect on the host crystal lattice structure are a major factor in providing mixed ionic and electronic conductivities which are desirable in some application such as electrode/electrolyte interfaces. We are studying the structure and the ionic conductivity of ceria doped with all naturally occurring rare earth elements to explore the suitability of these materials for fuel cell applications. The dopant cation size and its effect on the host crystal lattice structure are a major factor determining the ionic conductivity of solid electrolytes. In order to understand the precise role the dopant plays in modifying the properties of the oxide the primary information that is required is the exact location of the dopant in the host lattice. However, in many systems this problem cannot be resolved by conventional diffraction techniques. For example, the concentration of the dopant may be very low (less than 1 mol%), the dopant may be indistinguishable from the host (as in atoms with similar atomic numbers), the dopant may introduce complex disorders into the lattice or the material may be amorphous. It is therefore important to use experimental techniques like EXAFS to obtain complete structural information. Trivalent rare earth ion doping increases the concentration of oxygen vacancies result an increase in the ionic conductivities. Among the trivalent cations, anomalous behavior has been reported for Y$^{3+}$, Sm$^{3+}$, Gd$^{3+}$ and La$^{3+}$, yielded highest ionic conductivities. The cations of different ionic radii than that of Ce$^{4+}$ were chosen for our XAS investigations and compared with the ac impedance measurements.

Materials Research Instrumentation Laboratory

The Department of Physics has been developing a "Materials Research Instrumentation Laboratory" to train undergraduate and graduate students in applied materials research and to execute funded research projects from state and federal agencies as well as private industry. The specific projects to be investigated in this laboratory include the preparation and characterization of solid state electrolyte membranes and electrocatalysts for direct oxidation of methanol fuel cells (DMFCs), fiber optic chemical sensors (FOCS), rare earth doped fiber amplifiers (EDFAs), ferroelectric single crystals for optical memory devices, fast ion conducting glasses, heterostructure magnetic thin films, and piezoelectric crystals for high temperature superconductivity studies. Our goal is to strengthen our instrumental capability for conducting cutting edge research and providing high quality results in the ongoing DOE, ONR, AFSOR, NASA, NSF and LEQSF funded projects. In addition, we intend to integrate the proposed instruments and projects with ongoing in situ structural characterization studies using the
synchrotron radiation source at Center for Advanced Microstructures and Devices (CAMD), a multimillion dollar facility available in Baton Rouge. The principal investigators have been actively involved in the development of a new beam line for Science and Engineering Alliance Institutions (SEA) to facilitate materials science research in Historically Black Colleges and Universities (HBCUs). The DOE's Office of Energy Research has provided partial funds ($600 K/two years) and also promised to provide funding for a period of 5 years at a level of $6.7 M to SEA institutions for the design, construction and operation of a separate beamline that will enable us to utilize the entire spectral range of the CAMD storage ring.

The following instruments are available at our laboratory:

**Galvanostat/Potentiostat** is designed for integrated amperometry, dc amperometry, conductivity and cyclic voltammetry modes of detection. When the time constant of the EMF cell is sufficiently low, it will be possible to follow the intensity of a product or intermediate formed in an electrochemical reaction as a function of applied potential. AC impedance spectra will be measured using the Princeton Applied Research Model 273A potentiostat and Solartron model 1255 frequency response analyzer using PAR M383 software. This is a very effective combination for electro-catalysis studies and particularly useful for the investigation of electrode-electrolyte materials to be used in solid state fuel cells.

**Workstation for proton exchange membrane (PEM) fuel cells:** The workstation will be used to monitor the operation of fuel cells. It includes independent microprocessor based temperature controls for both fuel and oxidizer. Initially we will acquire ready-made fuel cells for testing and evaluation. The system will allow us to determine conventional rate constants over a wide range of temperatures and pressures, for a variety of catalytic systems. The workstation will also be used to investigate a wide range of electrolyte materials.

**Differential Scanning Calorimetry (DSC).** The DSC measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature. Such measurements provide quantitative and qualitative information about physical and chemical changes that involve exothermic or endothermic processes, or changes in heat capacity. DSC is used to characterize polymers, glasses and other organic materials, but is also applicable to metals, ceramics and other inorganics. The DSC can be used to study 1. glass transitions, 2. melting and boiling points, 3. crystallization time and temperature, 4. percent crystallinity, 5. specific heat and heat capacity, 6. oxidative stability, 7. rate and degree of cure, 8. thermal stability, and 9. electrochemical reactivity.

**Thermogravimetric Analyzer (TGA)** measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and predict their thermal stability at temperatures up to 1200°C. TGA experiments provide important information that can be used to select materials, predict product performance and improve quality. The technique is particularly useful for determining 1. composition of multicomponent systems, 2. thermal stability of materials, 3. oxidative stability of materials, 4. decomposition kinetics, and 5. the effect of reactive or corrosive atmospheres on materials.

A glove box for sample preparation under inert conditions and an FT-IR spectrometer have been recently installed in our laboratory for solid electrolytes research.
Conclusions

The search for new and improved solid state ionic conductors and electrolytes continues in our laboratory (22-24). We have focused on design aspects of electrochemical cells and discussed the characteristics of electrolytes and electrode materials for fuel cells and lithium batteries. We have obtained the K absorption spectra of Fe and sulfur in FeS₂ (pyrite). The energy associated with K edge of the sulfur is much lower than that of the first row transition metals. Investigations show that sulfur K absorption spectra of sulfur and FeS₂ are similar to each other and lie almost in the same energy region. Our observed K absorption spectra of FeS and Fe₂S₃ are alike in the main features but are fairly different from that of FeS₂. The absorption peaks were assigned to the spectroscopic transitions and tentative explanations were provided based on the band calculations and molecular orbitals of the S²⁻ ion. Along with a brief description of the existing instrumentation in our laboratory, we have also reported our efforts in developing capability for research in electrochemical systems using the double crystal monochromator beam line (port 5A and 4B) for EXAFS investigations at Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge. Two graduate and two undergraduate students are involved in utilizing the experimental resources discussed in this report. Their participation has been encouraged in all our projects and their contribution has been a vital component of our research.

Acknowledgments

This work is sponsored by the Pittsburgh Energy Technology Center for the US Department of Energy under grant number DE-FG22-95MT95016. We also acknowledge the DOE for supporting our effort in utilizing the synchrotron radiation source for the characterization of solid electrolytes for batteries and developing the beam line for SEA institutions under grant number DE-FG05-95ER45549. B.Rambabu thanks Dr. Kennedy Reed, LLNL for providing financial assistantships to his undergraduate students through a DOE grant DE-FG03-95SF20799. The electrochemical research instrumentation was acquired with the State of Louisiana (MS funds # 1324) funds to develop the graduate program in Physics at Southern University.

References

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B.V.R.Chowdary and Radhakrishna (world scientific, Singapore, 1980
Experimental Facilities for Fuel Cell and Battery Materials Research at SUBR

* Impedance Spectroscopy (EG&G E'Chem Research Station PAR model 273A Galvonostat/Cyclic Voltameter)

* Fuel Cell research station (Globe Tech)

* FT-IR Spectroscopy (Nicolet 7000 series) dual beam spectrometer

* DSC and TGA techniques

* Materials Testing System for Mechanical properties

* Scanning Electron Microscopy

* Transmission Electron Microscopy

* Optical Spectroscopy Techniques

* X-Ray Diffraction

* Center for Advanced Microstructures and Devices (CAMD)

* EXAFS has proven to be a unique technique for studying the structure of various systems such as crystalline or amorphous solids, super ionic conductors, spin glasses, solid solution surfaces, catalysts, and biological systems regardless of their degree of crystallinity. EXAFS is structure sensitive and under favorable conditions gives valuable information about the position as well as the type and the number of near neighbors of the absorbing atom. The distance determination is limited to 4 Å.
XRD PATTERN FOR A Li/FeS$_2$-cell

CELL RECHARGE OF A Li/FeS$_2$-cell
CAMD Facility Layout
X-Ray Lithography Sector  Basic Sciences Sector

 Beam Lines
1A Micromachining X-Ray Lithography 1 (EXLM1)
1B Micromachining X-Ray Lithography 2 (EXLM2)
4A Plane Grating Monochromator (PGM)
4B Toroidal Grating Monochromator (TGDM/4m)
4C Spherical Grating Monochromator (SGM)
6A X-Ray Microscopy Probe (XMP)
6B Double-Crystal Monochromator (DCM)

Design parameters of the CAMD Storage Ring

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam energy (GeV)</td>
<td>1.2/1.5</td>
</tr>
<tr>
<td>Beam current (mA)</td>
<td>400/165</td>
</tr>
<tr>
<td>Bending magnet radius (m)</td>
<td>2.928</td>
</tr>
<tr>
<td>Critical wavelength (Å)</td>
<td>9.5/4.9</td>
</tr>
<tr>
<td>Critical energy (keV)</td>
<td>1.3/2.6</td>
</tr>
<tr>
<td>Estimated beam half life (hr)</td>
<td>8</td>
</tr>
<tr>
<td>Harmonic number (bunches)</td>
<td>92</td>
</tr>
<tr>
<td>Radiative power (W/mrad)</td>
<td>4</td>
</tr>
<tr>
<td>Injection energy (MeV)</td>
<td>200</td>
</tr>
<tr>
<td>Injection time (min)</td>
<td>≤ 2</td>
</tr>
<tr>
<td>Natural emittance (m-rad)</td>
<td>2 x 10^{-7}</td>
</tr>
</tbody>
</table>

October 1994
Figure 1.3.1 CAMD Beamline Layout
Fe K-edge X-ray Absorption Data for FeS$_2$
Sulfur K edge X ray Absorption Spectra of FeS2
Li$_{0.9}$Co$_{0.2}$ @ Co K edg
EXAFS Data Analysis

The EXAFS oscillations, after separation from the background absorption, are described by an equation of the form:

\[ \chi(k) = \sum_j N_j/kR_j^2 |f_j(\pi)| \exp(-2\sigma_j^2k^2) \times \exp(-2R_j/\lambda) \sin(2kR_j + \psi_j + \delta) \]

\[ \chi(k) = \text{Normalized absorption coefficient as function of photoelectron momentum } k \]

\[ N_j = \text{Number of atoms (all of the same type) with back scattering factor } f_j(\pi) \text{ at a distance } R_j \text{ from the central atom} \]

\[ \sigma_j = \text{Debye-Waller factor expressing the mean square variation in } R_j \]

\[ \delta \text{ and } \psi_j = \text{phase factors of the photoelectron wave} \]

\[ k\chi(k) = \text{Fourier transform with respect to } \sin(2kR) \]

EXAFS Software: UWXAFS 3.0, FEFF (University of Washington)
CONCLUSIONS

The design of a solid electrolyte provides an excellent illustration of materials science and engineering. General considerations lead to several quality criteria, but final specification depends upon the practical application, including the physical state of any reactants in an electrochemical cell and the operating conditions.

Lithium incorporation results in an uniaxial expansion of the cavity. The strength of the bonding and the direction of the expansion appears to be a major factor in determining the extent of lithium intercalation before the catastrophic rupture of Fe-S bonds.

The importance of the study of electrolyte-electrode interfacial reactions in battery and fuel cell materials using the synchrotron radiation based techniques such as EXAFS, XANES were discussed. We have obtained the Fe and S K absorption spectra in Li/FeS$_2$ battery system, Mn and Co K absorption spectra in spinel structures, K absorption of rare earth dopants in ceria for the first time using our EXAFS spectrometer.

Materials Research Instrumentation Laboratory at Southern University A&M College, Baton Rouge is equipped with state of the art research equipment for the preparation and characterization of solid electrolytes for fuel cell and battery applications.
ACKNOWLEDGEMENTS

We acknowledge the technical support and assistance from the Center for Advanced Microstructures and Devices (CAMD) for the successful completion of the ongoing US Department of Energy and State of Louisiana (MS program) funded projects on solid electrolyte materials.

B. Rambabu thank Drs. Venkat R. Venkatraman (METEC), Kennedy Reed (LLNL), Kim Kinoshita (LBL) and Diola Bagayoko (Timbukutu Academy) for their encouragement and support for the development of the "Materials Research Instrumentation Laboratory" in the Department of Physics at Southern University.
Science and Technology at CAMD
The 1996 Workshop
April 8-9, 1996
Baton Rouge, Louisiana

Program

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JOHN SCOTT
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The J. Bennett Johnston Sr.
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We are pleased to have you at the 1996 Science & Technology Workshop at CAMD. The workshop consists of four sessions of platform presentations and a poster session. We hope it will be a productive and pleasurable event!

Program

Monday, April 8, 1996

12:00-1:00  Registration

1:00-1:05  Opening Remarks  Yuli Vladimisky

1:05-3:00  Session 1  Chair: John Scott

1:05-1:30  Status of CAMD  
(Volker Saile)

1:30-1:55  Status of the synchrotron at CAMD.  
(H.Bluem, B.Hartline, R.Bailey, L.Oliszewski)

1:55-2:20  Status of the beamlines at CAMD.  
(J. Scott, E. Morikawa, P. Schilling, P.Sprunger, J.M.Klopf)

2:20-2:45  Cooperative research at CAMD: Importance for Louisiana universities.  
(G. Findley, F. Watson, Jr)

2:45-3:05  The science and engineering alliance (SEA): History, mission and interactions with CAMD.  
(P.J.Ebert, R.Gooden, R.L.Shepard)

3:05-3:30  Coffee Break

3:30-5:10  Session 2  Chair: Harish Manohara

3:30-3:50  LTU - Louisiana's Key Player in Micromachining  
(M. Vasil)

3:50-4:10  HI-MEMS Alliance program  
(C. Khan Malek)

4:10-4:30  Industrial applications of synchrotron radiation at ELSA.  
(J.Hormes)

4:30-4:50  Monotonicity and logical analysis of data: A mechanism for evaluation of mammographic and clinical data.  
(B.Kovalerchuk, E. Triantaphyllou, J. Ruiz)

4:50-5:10  Imaging soft x-rays with opaque spheres.  

5:30-7:30  Poster session  Chair: Gina Calderon
Tuesday, April 9, 1996

8:00-8:30 Coffee & Doughnuts

8:30-10:00 Session 3 Chair: Gina Calderon

8:30-8:55 Molecular photoionization as a probe of coupling between nuclear and electronic degrees of freedom.
(R. Rao, E. Poliakoff)

8:55-9:20 Soft x-ray fluorescence experiments at the TULANE/NIST/TENNESSEE beamline at CAMD.
(A. Moewes, D. Ederer, T. Eskildsen, E. Morikawa)

9:20-9:55 Front end capability for the Anorad x-ray exposure tool.
(D. Young, M. Feldman)

10:00-10:30 Coffee Break

10:30-11:50 Session 4 Chair: Michael Klopf

10:30-10:55 Structural studies of cathodes and electrolytes for fuel cell and battery applications.
(B. Rambabu, V. Young, T. Wang, S. Mattox, P. Schilling)

(L. O. Ferreira, S. Moehlecke)

11:20-11:50 To be announced.

11:50-12:00 Closing Remarks & Adjourn Yuli Vladimirsky
CHARACTERIZATION OF SOLID STATE BATTERIES MADE UP OF SILVERSELENOPHOSPHATE GLASS SYSTEM

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OBJECTIVES

1) TO SYNTHESISE DIFFERENT DOPANT SALT (AgI) COMPOSITIONS OF SILVERSELENOPHOSPHATE \{AgI-Ag_2O-(SeO_2_+P_2O_5_)} (SSP) SYSTEM

2) TO CONFIRM THE NATURE OF SSP SAMPLES

3) TO SELECT THE HIGH IONIC CONDUCTING COMPOSITION OF SSP GLASS - MEASURING IONIC & ELECTRONIC CONDUCTIVITIES

4) TO FABRICATE SOLID STATE PRIMARY BATTERIES - THE HIGH IONIC CONDUCTING SSP GLASS WITH DIFFERENT CATHODE MATERIALS (I+C), (I+C+SE) AND (I+C+SE+TM(B)AI)

5) TO DETERMINE CHARACTERSTICS OF BATTERIES MADE UP OF SSP GLASS AND ESTIMATE THEIR PERFORMANCE
MATERIAL PREPARATION, CHARACTERIZATION
AND FABRICATION OF SOLID STATE PRIMARY (SSP)
BATTERIES

PREPARATION TECHNIQUE: Conventional melt quenching method

FORMULA: X%AgI - (100-X)% [M%Ag2O -F%(0.3SeO2 +0.7P2O5)]
M/F=2.25 & X IS VARIED FROM 20 TO 80 IN STEPS OF 10%.

Chemicals: AgI, Ag2O, SeO2 and P2O5

Crucible: Quartz

Temperature: 550 °C

Duration: 30 minutes

Quenched: Liquid Nitrogen Temperature (77K)

CHARACTERIZATION: X-ray diffraction

MAKE: Rigaku miniflex X-ray diffractometer
Radiation: CuK monochromatic radiation (λ=1.5418 Å)
Range: 10 to 70 degree
Scan rate: 2 degree per minute
Nature: Peak free spectrum confirmed glassy nature

ELECTRICAL CONDUCTIVITY

The electrical conductivity is measured on pressed pellets of SSP samples at 1KHz using two probe a.c. conductivity bridge (Elico make model CM82T)

* FABRICATION OF SOLID STATE PRIMARY BATTERIES

* CHARACTERIZATION OF BATTERIES