DEVELOPMENT OF MATERIALS FOR SOLID STATE
ELECTROCHEMICAL SENSORS AND FUEL CELL APPLICATIONS

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SUMMARY

The intent of this project was two fold: 1. to develop new ionically conducting materials for solid state gas phase sensors and fuel cells and 2. to train students and create an environment conducive to Solid State Ionics research at Southern University. We have investigated the electrode-electrolyte interfacial reactions, defect structure and defect stability in some perovoskite type solid electrolyte materials and the effect of electrocatalyst and electrolyte on direct hydrocarbon and methanol/air fuel cell performance using synchrotron radiation based Extended X-ray Absorption Spectroscopy (EXAFS), surface analytical and Impedance Spectroscopic techniques. 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. We have measured the K edge of the EXAFS of these dopants to determine the local structural environment and also to understand the nature of the defect clustering between oxygen vacancies and trivalent ions. The analysis and the data reduction of these complex EXAFS spectra is in progress. Where as in the DOMFCs, we have attempted to explore the impact of catalyst loadings on the performance of direct oxidation of methanol fuel cells. Our initial measurements on fuel cell performance characteristics and EXAFS are made on commercial membranes Pt/Ru/Nafion 115, 117 and 112. The performance of the DOMFCs 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 the following goals: 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 DOMFCs. Also, we have prepared a comprehensive review article entitled " Ionic Optodes and aqueous ion sensing " and submitted for publication in the journal " Analytica Chemica Acta"

The funds of this project along with the other ongoing US DOE and NSF grants have significantly contributed to the development of Solid State Ionics materials research and also for the establishment of MS program in Physics with materials science and applied physics option in the Department of Physics at Southern University. During this project duration, the PI **Dr. R. Bobba** has acquired research grade equipment for materials research and graduate education: 1). fuel cell test station, 2). PAR 273A Galvanostat/Potentiostat, 3). Impedance Analyzer, 4). Differential Scanning Calorimeter (DSC 10), 6). high temperature furnaces and 7. HVC Scanning Tunneling Microscopy (STM) and UV-VIS-NIR Absorption and Fluorescence Spectrometers.

Financial award
deleted.

HUMAN RESOURCES

Technical Personnel

1. Dr. Rambabu Bobba, Project Director
2. Ms. Venitia Yang, Undergraduate Student (Physics Major)
3. Timothy George, Undergraduate Student (Physics Major)
4. Charles Lejune, Undergraduate Student (Engineering Major)
5. Jaymes A. Baker, Undergraduate Student (College of Sciences)
6. Dr. Josef Hormes, Universitat Bonn, Germany, LSU-CAMD.

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1. Dr. Kennedy Reed, Project Director, RCS program for HBCUs, LLNL, CA

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1. Dr. Robert Ford, Vice Chancellor for Research and Strategic Initiatives
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U.S. DOE Oakland Operations Office Project Administration

1. James H. Doron, EEO
2. Ms. Arlene Coleman, Contracts Specialist
3. Ms. Maria C. Hernandez, Contracting officer

LABORATORY RESOURCES

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 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

5. PROJECT OBJECTIVES, AND MATERIAL ISSUES

This project was initially designed to involve students in research projects that are of interest to federal funding agencies and also to fully utilize the EXAFS end station in the double crystal monochromator (DCM) beam line (port 5A and 4B) at CAMD, Baton Rouge. The goal was to enhance the experience that our undergraduate students gain during summer research employment at Lawrence Livermore National Laboratory. A collaboration with Southern University, Baton Rouge, and the Center for Advanced Microstructures and Devices (CAMD) was subsequently established as a part of the LLNL Research Collaborations program for HBCUs. Three undergraduate African American students were trained and provided rigorous training in the utilization of Synchrotron Radiation in materials research. As a result of this effort, the students have enhanced their academic experience by integrating the special projects with the existing experimental research program in Materials Science. Three specific projects related to the development of ionically conducting materials for gas phase sensors and fuel cells have been executed during this project duration. Every student was given an opportunity to work directly with the instrument, provided provision to prepare and characterize the materials and finally asked to submit a report and present their work during the group meetings. All these three students were given an opportunity to present their work in the national conferences include National Society of Black Physicists and DOE_FETC Fossil Energy HBCU conferences and workshops. One of the student in the project has submitted an abstract to present the paper in the 10th International Conference on Solid State Ionics held in National University of Singapore. So this report present the effort of these undergraduate students and their contributions in the projects entitled: 1. Ceria based Solid Electrolytes 2. Effect of ionic radius and their influence on the structural properties of rare earth trivalent cationic dopants in ceria 3. Characterization of porphyrin pathalocynanine 4. Catalysts and MEAs for polymer electrolyte fuel cells and 5. Ionic Optodes.

5.1: NEED FOR DEVELOPMENT OF SENSORS AND FUEL CELLS

Modern human life has been supported by science and technology and by consuming huge amount of energy. 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. . Solid Electrolytes have been used in battery, sensor and fuel cell applications. The operating principle of these devices, in particular batteries and fuel cells are the same. Currently much attention is being focused on materials for two specific applications, lithium batteries and fuel cells. In each of these mixed conductors are required for electrodes and purely ionic conductors for solid electrolytes. 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 .

5.2 THE ROLE OF SOLID ELECTROLYTES IN SENSORS AND FUEL CELLS

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. 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. Solid electrolytes are useful where the reactants are gaseous or liquid.

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 particular to the electrolyte. Electrochemical reaction occurring 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 monophasic 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 polarization effects during the charge carrier flowing.

Solid State Ionic (SSI) sensors are electrochemical devices that are used to determine the concentration of the particular species which are usually found in gases or liquids. Some of the outstanding advantages of the SSI sensors are that the EMF response can be measured with high precision. Nevertheless, the performance of the device is related to the selection of the two essential cell components: the solid electrolyte and the reference electrode. In principle any gas or solid mixture which does not react with the cell components and which establishes a constant chemical potential is suitable reference electrode. However the reference potential should be as close as possible to the measured one and the reference electrode must exhibit diffusion process which are rapid enough to maintain a constant chemical potential at the electrode-electrolyte interface. In this project we have attempted to understand the electrode-electrolyte interfacial reactions using the advanced X-ray Absorption Spectroscopy technique.

To date variety of SSI chemical sensors have been studied in detail, and several are commercially available. Much of the development was devoted to oxygen SSI sensors. The sensors that are based on a solid O^{2-} ion electrolyte. We have attempted to use the ceria based electrolyte. For example they are currently being used to determine the oxygen partial pressure in automobile exhaust systems, molten steel, food packing --. These sensors are able to cover a wide range of oxygen pressures and satisfy a large variety of applications. For low oxygen partial pressures and relatively high temperature the reference electrode are often made with liquid metal embedded in the corresponding oxide ion pellet. High oxygen pressures require the use of gaseous reference electrode. We have used the rare earth dopants in cerium oxide as a material of our choice in this project.

Figure 1 illustrates the various fuel cell types (alkaline, phosphoric acid, solid polymer, molten carbonate, solid oxide) and the phenomena of catalysis process which take place in these systems.

	Fuel (Anode: Fuel Oxidation)	$e^- \rightarrow$ Load	Oxidant (Cathode: Oxidant Reduction)	
60-120 °C	Alkaline $H_2 + OH^- \rightarrow 2H_2O + 2e^-$	$\leftarrow OH^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	First Generation
200	Phosphoric Acid $H_2 \rightarrow 2H^+ + 2e^-$	$H^+ \rightarrow$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	
60-100	Solid Polymer $H_2 \rightarrow 2H^+ + 2e^-$	$H^+ \rightarrow$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	
650	Molten Carbonate $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$	$\leftarrow CO_3^{2-}$	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$	Second Generation
900-1000	Solid Oxide $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ $CO + O^{2-} \rightarrow CO_2 + 2e^-$ $CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$	$\leftarrow O^{2-}$	$O_2 + 4e^- \rightarrow 2O^{2-}$	
	(Electrolyte)			

The most basic type of fuel cell is a hydrogen/oxygen fuel cell. As shown in the above figure, the hydrogen stream enters the anode chamber where it is oxidized on the anode, forming two protons and two electrons. The electrons are conducted out of the cell to a wire and used as electricity. The protons cross the cell separator and react with the oxygen at cathode forming water which exits out of the cathode chamber. The two reactions are shown below.

In a polymer electrolyte fuel cell, the cell separator is a polymer film which allows the protons to pass through it, but blocks the hydrogen or oxygen from passing. So, a Direct

Methanol Polymer Electrolyte Membrane Fuel Cell (DMFPEFC) is simply a fuel cell which reacts methanol and water at the anode, protons and oxygen at the cathode, and uses a polymer electrolyte to separate the two. The advantage of a DMFC over a traditional H_2/O_2 fuel cell is not in the fuel itself , but in the fuel cell support system. Obtaining pure hydrogen for the hydrogen/oxygen fuel cell involves a process called cracking where methane , methanol or some other fuel is broken down using heat, pressure and a catalyst of some sort. This process requires lot of energy , causing the overall efficiency of the H_2/O_2 fuel cell to drop significantly. With a DMFC , this process is avoided so even through the DMFC is not as efficient as the H_2/O_2 fuel cell, it is hoped that the overall efficiency will be equal or greater.

Normally, the fuel gas used in low temperature fuel cells is hydrogen. Hence, a PEM fuel cell system also contains fuel gas production and purification units. When hydrogen gas is produced by natural gas steam reforming , the product gas contains fractions of carbon monoxide poisons the catalyst layer of the fuel cell membrane. Purification units are used to eliminate carbon monoxide from the feed gas. Once , hydrogen is produced, it is difficult both to store and transport. The most satisfactory approach seems to be to electro-oxidize a liquid fuel at anode. Methanol is the only liquid fuel that has any substantial electroactivity and can be directly oxidized to carbon dioxide and water on catalytically active anodes in a direct methanol fuel cell (DOMFCs). However, the fundamental limitations in the practical utilization of such fuel cells has been the existence of electrochemical losses at both the anode and cathode, leading to poor overall conversion efficiencies[6]. The most commonly employed polymer electrolyte membrane “ Nafion “. However, for this application Nafion has low permeability towards methanol which leads to a mixed potential at the cathode, and thereby reduces the overall potential. Development of membranes which have greater permeability towards methanol would significantly increase the usability of the fuel cells.

In a fuel cell using a proton exchange membrane (PEM), the membrane acts as a separator and as the electrolyte. The heart of the fuel cell is a membrane electrode assembly consisting of two catalyzed electrodes bonded to either side of a proton exchange membrane (PEM) similar to that used in the low temperature hydrogen-oxygen fuel cells. However, the energy conversion proceeds through charge transfer reactions taking place at gas diffusion electrodes, since fuels and oxidant are gas and their solubility into electrolyte in polymer electrolyte fuel cells is very low. Obviously, the performance of the fuel cells depends upon the structural and electrochemical integrity of the gas diffusion electrodes and the PEMs.

The conductivity of the PEM is very dependent on the degree of hydration. During operation, water molecules move from the anode to the cathode which results 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. Also, 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, as well. The conductivity of a perfluoro-membrane is influenced by the molecular structure, since in the acid form it has a dual functionality. The perfluoro-portions of the polymer chain achieve a crystallinity akin to that of polytetrafluoroethylene (PTFE), and reflect the physical properties of the material; whereas the sulphonated regions of the polymer align in a non crystalline manner and are associated with water molecules. This gives rise to concept of ionic clusters and of segregated core shell structures with in the polymer membrane [11]. In general these membrane structures are a continuum but in reality they contain a nano dimensioned highly localized ionic interface with amorphous sulphonic acid rich regions , surrounded by crystalline , water proof , gas permeable PTFE regions.

The PEM has been traditionally been Nafion 117, 115 or 112. Other perfluorosulfonated ionomers (PFSI) such as perfluorosulfonic acid (PFSA) with branched polymer backbone have been investigated. The PFSA's 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

5.3 Ceria based Solid Electrolytes (C. Lejune, T. George, J. Hormes and R.Bobba)

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. 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. Figure 1 show the conductivity and AC impedance measurements of rare earth dopants in ceria. (Experimental data was obtained from Drs. Bravan Balazas and Robert S. Glass at LLNL)

* Oxide conducting solid electrolytes for SOFCs

* Proton conducting solid electrolytes for SOFCs

Ce/Nd - Overview

Ce/Nd - Overview

5.4 Characterization of Catalysts and Membrane Electrode Assemblies(MEAs) for Proton Exchange Membrane Fuel Cells(PEFCs) and Solid Oxide Fuel Cells(SOFCs). (R.Bobba, J.Baker, Vinitia Yang, T. Page)

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-RuO_x 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 polymer electrolyte fuel cells (PEFC), a thin organic proton exchange membrane nafion 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. In both SOFC 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 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.

Conventional X-ray Diffraction (XRD) measurements are of limited value to understand structural changes in these electrochemical systems because they 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 3×10^9 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 the XAFS data analysis 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.

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 Universitat Bonn collaborators at the Center for Advanced Microstructures and Devices (CAMD).

We have measured the XANES and EXAFS Pt-L 111 edge of the following samples: Pt-Ru/Nafion 112, Pt-Ru/Nafion 115, Pt-Ru/117. Figures 2-4 the XANES spectra are shown

in comparison with the specimen of a pure Pt metal foil which is always measured simultaneously with the actual samples for better energy calibration. All spectra are treated in the standard way concerning background conditions (from higher edges) and normalization to the edge jumps. Figure 4 and 5 show the derivative spectra. Significant differences are seen in these spectra. The intensity of the peak is directly correlated to the number of empty d states of the Pt in the alloy as is observed transition is assigned to 2p-5d transition. As the transition to these samples is higher than for the pure metal the number of d holes has to be larger. The difference in the spectra may be due to the formation of Pt-Ru alloy or the Pt in the Pt-Ru samples is oxidized. It would be interesting to compare if there is a correlation between the observed peak and the performance as a catalyst. The data reduction and analysis are in progress.

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 Universitat Bonn collaborators at the Center for Advanced Microstructures and Devices (CAMD).

The cyclic voltammograms for methanol oxidation show a higher current response when Pt-Ru/C is the anode catalyst rather than for Pt/C. The Pt/C catalysts showed a higher current response for cathodic oxygen reduction at the cathode than the Pt-Ru/C catalysts (Figure 6). In general, the Pt-Ru/C catalysts showed higher electro-oxidation properties when compared to the Pt catalysts. The alloying of Ru on a carbon substrate facilitated the removal of carbon monoxide from its surface.

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 F and S-K edge of these sulfonic acid membranes showed differences in the XANES spectra (Figure 7-10). These spectral differences revealed that the molecular structure of these membranes depends upon the membrane's pretreatment (nitric or phosphoric acid). The acidic pretreatment of the perfluoro-membranes, and the resulting interaction of water with the perfluoro-polymer effected the molecular structure and contributed to the enhancement of proton conduction.

5.5 Characterization of Porphyrin -Catalyzed Oxidation of Trichlorophenol (V. Yang and R. Bobba)

Ms. Vinitia Young has undertaken a special project to investigate polychlorophenols to explore the development of sensors.

Pt/Ru on Nafion 112

Energie (eV)

1

Pt/Ru on Nafion 115

Pt/Ru on Nafion 117

Energie (eV)

Pt/Ru on Nafion

Energie (ev)

SULFUR IN PROTON EXCHANGE MEMBRANES

An example for a XANES analysis

Problems:

- **Transport mechanisms are not completely understood**
- **For technical fuel cells specifications have to be improved**
- **Chemical modifications during electrochemical reactions**

Tasks:

- **Investigation of the structure (F-K and S-K edge)**
- **Systematic investigation of chemically modified materials**
- **In situ investigation during electrochemical reactions**

WHAT IS NAFION ?

Nafion = Tetrafluoroethylene-Sulfonyl-fluoridevinyl Ether Copolymer is a permselective film for cations but not for anions, for use in electrochemical processes

A copolymer of tetrafluoroethylene with about 10 - 20 mol% of

5.6 Ionic Optodes and aqueous ion sensing (Kevin C. Langry (LLNL) and R. Bobba)

During this project duration the PI Dr. Rambabu Bobba has developed a manuscript entitled " Ionic Optodes and its aqueous ion sensing " and submitted for publication. This is a collaborative work with the staff scientists at LLNL. We have reviewed transduction schemes used in fiber optic sensors for monitoring aqueous ionic species and examined some critical concerns that may hinder the commercial acceptance. The complete manuscript of this review article is enclosed in the later sections.

6. Materials Research Instrumentation Laboratory, Department of Physics, SUBR

The **Department of Physics at Southern University and A&M College (SUBR)** in Baton Rouge is the project site for NSF-RCMS, "Timbuktu Academy", and NSF-ARI. projects. Most likely it will be the project site for NSF-CREST- Materials Research and Technology- Center for Excellence . Southern University A&M College is the main campus of the system of **historically Black colleges and universities (HBCUs) in Louisiana.** With the recent "**Higher Education Desegregation Settlement in Louisiana**", the university is now developing Ph.D. programs in Materials Science, Mathematics and Science Education, Biomedical Sciences, Public Administration and Public Policy and Urban Forestry. In mid 1995, the Louisiana Board of Regents gave its approval for the development of MS in Physics with Materials Science and Applied Physics options at Southern University . Seventeen minority graduate students are enrolled in the fall of 1996 i.e first batch of freshmen in the graduate program. Over 12 students chose experimental materials science as an option to develop graduate theses.. We are now in the process of vigorously updating our experimental research base by upgrading existing instruments and acquiring new ones in order to provide the necessary infrastructure and creating an environment conducive to high quality graduate research.

A 2000 square foot room (100 ft X 20 ft, room #123) and 1600 square foot room (40 ft X 40 ft, Room # II4) 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 #II4, James Hall).

The specific projects to be investigated in our 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 etc.), 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 providing quality returns to 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, which is just 6 miles away from Southern University. 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(\$600K/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 in 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 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.

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. 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 of materials, and 5. the effect of reactive or corrosive atmospheres on materials.

Scanning Tunneling Microscope (STM): 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

A Glove Box for sample preparation under inert conditions and FT-IR spectrometer have been recently installed in our laboratory for solid electrolytes research.

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 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.

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 projects. Three undergraduate students were given support through this project duration. A special emphasis was given on the development of materials for sensors and 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. We have also found that the obvious differences and commonalties that distinguish as well as to share the solid state devices and fiber optic sensor technologies for detecting analytes in host media.

ACKNOWLEDGMENTS

The PI Dr. Rambabu Bobba acknowledge the support of U.S Department of Energy, the Center for Advanced Microstructures and Devices (CAMD) at Baton Rouge, the Lawrence Livermore National Laboratory (LLNL) and the Southern University administration . The project staff appreciates the continued technical support from the RCS program at LLNL for historically Black colleges and universities.

Preliminary Report
on the
PORPHYRIN-CATALYZED OXIDATION OF TRICHLOROPHENOL

Submitted to
Dr. Rambabu Bobba
Project Director and
Associate Professor of Physics
Southern University
Baton Rouge, Louisiana

By
Venitia O. Young
Physics/Premed Student
July 25, 1996

INTRODUCTION

Chlorinated aromatic compounds have contaminated the environment as a result of pollutants in industrial wastes which are discharged into lakes and rivers. Chemical spills into the soil also contaminate ground water. Polychlorophenols are major pollutants of the pulp mill industry. Despite the useful application as a wood preservative for marinas, pentachlorophenol transfers from the wood to waters resulting in severe contamination. In addition, toxic chlorinated solvents and pesticide wastes also pollute the environment. Efforts have been made by scientists to find a chemical catalyst that will degrade aromatic pollutants with very little expenditure of energy at room temperature and pressure. Currently, the main method for destruction of chlorinated aromatics is incineration, where chemicals are burned. However, this method results in pollution of the air requiring large quantities of energy for burning and expensive pollutant control equipment. Biodegradation has also been tried in dechlorination of aromatics by using bacteria and fungi. The disadvantage is that high concentrations of chlorinated compounds are toxic to these organisms.

In this study, a porphyrin-catalyzed process is used for converting toxic and chlorinated phenols in industrial effluents to compounds which are less toxic. It has been demonstrated that hemin can catalyze oxidation of 2,4,6-trichlorophenol (TCP, a major pollutant in paper mill effluents when wood pulp is delignified by chlorine bleaching) with t-butyl hydroperoxide (TBHP) as the oxidizing agent. Batch experiments of a reaction mixture were used to demonstrate this new method of degradation of toxic compounds. Trichlorophenol was used as a model compound for actual wastes from paper mills which are complex mixtures of a variety of chlorinated aromatics in aqueous solution.

PROCEDURE

The Gas Chromatograph (GC) was used for analysis of TCP concentrations and to determine the extent of oxidation of TCP. Since TCP is found in aqueous solution (i.e., in rivers, lakes or industrial waste water), all the reactions were conducted in aqueous solution. It is not possible to analyze aqueous solutions in the GC, so TCP was extracted with hexane. A 5ml sample of 600 PPM TCP solution was added to an equal amount of hexane. The mixture was shaken vigorously and then allowed to settle into a hexane and water layer. A 1 μ l sample was taken from the hexane layer and injected into the GC, generating a graph of area versus time. Each peak on the graph represents a compound in the solution, and in this study, there are usually two peaks- one for hexane and one for TCP with a retention time of approximately 17.0 minutes. The peak area corresponding to the 600 PPM TCP solution was 17,761 (refer to figure 1).

Bulk quantities of a buffered solution [1.38g of NaH_2PO_4 monobasic and 14.15g of K_2HPO_4 dibasic in 200ml of distilled water; pH of 8.2], a 600 PPM 2,4,6-trichlorophenol solution [60mg TCP in 100ml buffer solution], a catalyst solution [52.6ml of 242.3 μ M hemin solution (i.e., 8.34mg hemin in 50ml of buffer solution) and 1.0g NaHCO_3 to help dissolve the hemin in buffer], and an oxidant solution [0.1ml TBHP in 9.9ml distilled water] were prepared for use in the reaction mixtures. Reactions were conducted in the phosphate buffer at room temperature and were monitored by GC [PTE-5 capillary column]. 25ml of the 600 PPM TCP solution were taken in a 125ml erliemeyer flask, and 4 ml of hemin solution were added. In this reaction mixture, the initial concentrations of TCP and hemin were 517.24 PPM and 33.42 μ M, respectively. After adding 1ml of TBHP solution, a sample of 5ml was taken for hexane extraction and GC analysis. The peak area for TCP was 8232, approximately one half of the peak area for the TCP solution without TBHP. This means that only 50% of the TCP reacted with the TBHP. 3ml of the TBHP solution were added to the reaction mixture 1ml at a time every 3 minutes to see if TCP would be oxidized even more. The mixture

was stirred with a magnetic bar and heated to slightly above room temperature. As a result the TCP peak area reduced to 5305. After adding another 1ml of TBHP solution, the TCP peak area reduced to 4454. Finally after adding 3ml of TBHP solution to the reaction mixture, the TCP peak area reduced to 1957 (refer to figure 2). The drop in TCP peak areas after each successive addition of TBHP proves that TBHP does oxidize TCP. A control solution [25ml of 600 PPM TCP solution in buffer and 6ml TBHP solution, without catalyst] was prepared for comparison with reaction mixtures which contained catalyst to prove that hemin accelerates the reaction.

RESULTS AND DISCUSSION

After all TBHP solution additions, extractions, and GC analyses, the final concentration of TCP was 141.87 PPM. The reaction resulted in a 72.6% conversion in 20 minutes. Controls which did not contain the porphyrin, resulted in a 10% conversion. The porphyrin-catalyzed oxidation of 2,4,6-trichlorophenol with t-butyl hydroperoxide as the oxidizing agent is a viable process.

FUTURE PLANS

This study will continue through Fall 1997 and will be used as my honor's thesis. Beginning September 1996, I will conduct experiments to find a characteristic wavelength for TCP. I hope to find concentrations of TCP at different time intervals, and the rate of reaction at different temperatures and concentrations of catalyst. I will observe how the hemin and other catalysts work on pentachlorophenol and actual waste samples.

Figure 1. Initial Peak Area of TCP

Hexane

Figure 2. Final Peak Area of TCP

TABLE 1
GC CONDITIONS

COLUME (PTE-5)

Length: 30m
Diameter: 0.32 mm
Film thickness: 1um

OVEN CONDITIONS:

Initial Tem 100 C
Iso Time 1 5 min
Ramp Rat 10 C/min

DETECTOR:

Type: FID
Range: 10 E-11

Final Tem 200 C
Iso Time 2 5 min
Ramp Rat 0 C/min

INJECTOR:

Temperat 250 C

CARRIER GAS:

Type: Nitrogen
Flow Rate: 7 ml/min

TCP RETENTION TIME: 17.0 MIN

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