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NOVEL SOLID STATE PROTON-CONDUCTORS
BASED ON POLYMERIC NON-OXY ACIDS

Progress Report for the Period November 1, 1988 -
January 31, 1992

By

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January 1992

Work Performed Under Contract No.: DE-AC21-88MC25169

For

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By

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FINAL REPORT

NOVEL SOLID STATE PROTON-CONDUCTORS BASED ON POLYMERIC NON-OXY ACIDS

(Period November 1, 1988 - January 31, 1992, Contract # DE-AC21-88MC25169)

SUBMITTED BY

CENTER FOR ELECTROCHEMICAL SYSTEMS AND HYDROGEN RESEARCH
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TO

U.S. DEPARTMENT OF ENERGY
MORGANTOWN ENERGY TECHNOLOGY CENTER
MORGANTOWN, WEST VIRGINIA 26507-0880

JANUARY 31, 1992

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NOVEL SOLID STATE PROTON-CONDUCTORS BASED ON POLYMERIC NON-OXY ACIDS

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NOVEL SOLID STATE PROTON-CONDUCTORS BASED ON POLYMERIC NON-OXY ACIDS

EXECUTIVE SUMMARY

The objectives of this project were to prepare and characterize novel solid state proton-conductors and to evaluate these compounds as fuel cell electrolytes. The thrust was on the synthesis of new proton-conducting "model" and "polymeric" compounds, based on acid functions of the type $(R_fSO_2)_2NH$ and $(R_fSO_2)_2CH_2$ in appropriate fluorinated carbon structures, their physico-chemical characterization (Infra-red, Nuclear Magnetic Resonance, Differential Scanning Calorimetry, and X-ray Diffraction), and evaluation as candidate fuel cell electrolytes for use at elevated temperatures. This project consisted of four tasks (i) Synthesis of Proton-Conducting Polymer Electrolytes; (ii) Physical and Chemical Characterization of Proton-Conducting Polymer Electrolytes; (iii) Electrochemical Characterization of Proton-Conducting Polymer Electrolytes; and (iv) Evaluation of Proton-Conducting Polymer Electrolytes for Fuel Cells. The first two tasks were carried out on a sub-contract with Clemson University; the third task was performed at Texas A&M University, the Contractor; and the fourth task was sub-contracted to ElectroChem, Inc. The accomplishments on these tasks may be summarized as follows:

1. SYNTHESIS OF PROTON-CONDUCTING POLYMER ELECTROLYTES (CLEMSON UNIVERSITY)

Methods were developed for the synthesis of ionene polymers of the type

$CF_3SO_2[NSO_2(CF_2)_4SO_2]_nNSO_2CF_3$ by step-reaction polymerization. Plans to prepare isoelectronic carbon ionenes (CH_2 in place of NH) were unsuccessful due to experimental difficulties. In order to obtain pure polymers of reasonable molecular weight, considerable development was required to prepare the critical difunctional monomer

$MeSi^{Na}_2NSO_2(CF_2)_4SO_2^{Na}_2NSiMe_3$ in pure form and to successfully carry out the polymerization reaction with the other monomer $FSO_2(CF_2)_4SO_2F$. This work was aided considerably by carefully studying the reactions to form model compounds

$CF_3SO_2[NSO_2(CF_2)_4SO_2]_nNSO_2CF_3$ ($n = 0,1,3$).

A reaction sequence was ultimately developed using acetonitrile as solvent to control the end groups in the polymer and to give an ionene polymer with an average molecular weight of 10,000-30,000. These materials could be purified after acidification with an ion exchange resin, by treatment with hydrogen peroxide to remove hydrocarbon impurities. Higher degrees of polymerization can probably be achieved using higher reaction temperatures. The ionene polymers obtained represent the first examples of polymers of this type containing very strong Bronsted acid groups in the polymer main chain or backbone.

2. PHYSICAL AND CHEMICAL CHARACTERIZATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES (CLEMSON UNIVERSITY)

The many intermediates and products obtained in this work were fully characterized by spectroscopy (IR, NMR) and their thermal stabilities examined by DSC. Structures of

selected model compounds were characterized by single-crystal x-ray diffraction. The

perfluoroalkyl sulfonimides of the type $R_fSO_2\overset{H}{[NSO_2(CF_2)_xSO_2]_n}\overset{H}{NSO_2}R_f$ are all thermally stable to at least 300°C. Most of the compounds in acid form are very soluble in water and all react exothermically with water. Multifunctional compounds show equal acidity for all acidic protons in water. The ionene polymer in acid form dissolves in H₂O to give a clear solution. In the sodium form, it exhibits a colloidal behavior in H₂O due to an unknown mechanism of aggregation. Large particles are present by light scattering. In acetone, the sodium form gives a regular solution.

Structures of metal derivatives of these compounds by x-ray, show a common feature in the formation of extended solids containing fluorocarbon and ionic domains. The ionic domains result from extensive interaction between the metal with the nitrogen and the sulfonyl oxygens.

3. ELECTROCHEMICAL CHARACTERIZATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES (TEXAS A&M UNIVERSITY)

The microelectrode technique was used for the electrochemical investigations on the acids because it has the advantages of (i) minimizing mass transport and ohmic overpotentials in the experiments to determine electrode kinetic parameters; (ii) being unique in yielding mass transport parameters (diffusion coefficient and solubility) by a single transient measurement; and (iii) being able to carry out experiments with very small quantities of "precious" electrolytes - the electrolytes prepared under stringent conditions at Clemson University. Three types of studies were carried out using aqueous electrolytes (concentration 0.1 M) - cyclic voltammetry, pseudo-steady state current vs. potential, and transient current vs. time measurements. Sulfuric acid was used as the control electrolyte. The experimental studies revealed the following results:

(i) adsorption of the organic acids or of impurities on the microelectrode cause a deformation of the cyclic voltammograms and reduction in the electrochemically active surface area of the electrodes, as compared with the results in sulfuric acid;

(ii) only a one section Tafel slope ($b = 120$ mV/decade) was observed for oxygen reduction on platinum in the organic acid, whereas in sulfuric acid there is an additional linear region with a 60 mV/decade Tafel slope at lower current densities. The single Tafel region behavior is again due to the adsorption of the organic species on the electrode. However, the exchange current densities (i_0) in the organic acids were nearly of the same order as in sulfuric acid. Further the diffusional limiting current densities were higher in the organic electrolytes than in sulfuric acid; and

(iii) the solubility of oxygen is higher in the organic acids than in sulfuric acid, but the diffusion coefficient is lower in the former acids.

These experimental studies were carried out in dilute electrolytes to overcome the problem of contamination of microelectrodes but the results show the promising behavior of these electrolytes in terms of good electrode kinetics performance and lower mass transport problems.

4. EVALUATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES AS ELECTROLYTES FOR FUEL CELLS

The evaluation of the proton-conducting polymers as additives to phosphoric acid fuel cells was conducted in single cells with high surface area electrocatalysts (state-of-the-art fuel cell electrodes) and an immobilized silicon carbide matrix. Experimental results in the phosphoric acid fuel cell (single cell) served as the base line. The monomeric and dimeric sulfonimides exhibited similar open circuit potentials to that in phosphoric acid, while the tetrameric and polymeric ($n = 40$) acid depressed it by 100 mV. However,

the latter two electrolytes showed better fuel cell performances than the former three electrolytes at the normal operating current densities of fuel cells. Cells containing these two acids also demonstrated excellent stability over 100 hrs of operation. There is some evidence that the lower molecular weight acids may be getting reduced at the anode and poisoning the anode. The fuel cell experiments demonstrate the benefits of improving their performance by addition of the tetrameric or polymeric acid to phosphoric acid.

NOVEL SOLID STATE PROTON-CONDUCTORS BASED ON POLYMERIC NON-OXY ACIDS

TASKS, INVESTIGATORS AND AFFILIATIONS

TASK 1: SYNTHESIS OF PROTON-CONDUCTING POLYMERIC ELECTROLYTES

TASK 2: PHYSICAL AND CHEMICAL CHARACTERIZATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES

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TASK 3: ELECTROCHEMICAL CHARACTERIZATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES

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TASK 4: EVALUATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES FOR FUEL CELLS

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NOVEL SOLID STATE PROTON-CONDUCTORS BASED ON POLYMERIC NON-OXY ACIDS

1. INTRODUCTION

1.1 Objectives

The objectives of this project were to prepare and characterize novel solid state proton-conductors and to evaluate these compounds as fuel cell electrolytes.

1.2 Background

The "energy crisis" in 1973 awakened the United States in respect to its strong dependence upon imported oil, and to the rapid depletion of fossil fuel reservoirs. Thus, during President Richard Nixon's second term in the White House, energy research and development programs were activated under the umbrella of the newly created Energy Research and Development Administration, which later incorporated the U.S. Atomic Energy Commission. There was a further boost to the energy programs when the Energy Research and Development Administration was elevated to the level of the U.S. Department of Energy during President Jimmy Carter's administration. The main themes of the Department of Energy were to (i) reduce the dependence upon imported oil, by energy conservation, improved energy conservation efficiency, and advanced methods of energy conversion; (ii) develop efficient methods for the recovery of hydrocarbon fuels from primary energy sources such as coal and oil shale; enhanced oil recovery - offshore, secondary and tentative oil recovery; and (iii) develop methods for the utilization of renewable energy resources.

Of relevance to this project is the initiation of the Fuel Cell Program by ERDA in 1976, which had as its main objective the more efficient, direct conversion of chemical energy of fuels such as natural gas, naphtha and coal to electrical energy. The other advantages of fuel cells are (i) its modular construction which makes these types of power plants (kW to MW levels) relevant to a wide variety of applications (peaking, load-leveling, and base-load power generation by electric utilities, remote power sources, and stand-by power sources); (ii) high energy density, considerably superior to batteries, and hence a more attractive power source for electric vehicles; (iii) environmentally clean (minimal problems of emission of toxic chemicals into the atmosphere and of noise pollution); and (iv) the good prospects for developing on-site integrated energy and cogeneration systems for the production of electric and heat energy.

Several programs are underway under the auspices of the U.S. Department of Energy, Electric Power Research Institute and Gas Research Institute to develop advanced fuel cells for peak-shaving, spinning-reserves and intermediate and base-load power generation, on-site integrated energy and cogeneration systems and power sources for electric vehicles (1). The types of fuel cells which are most appropriate for one or more of these applications are the ones with phosphoric acid, molten carbonate, solid oxide and solid polymer acid electrolytes. Apart from the U.S., Japan is foremost in fuel cell research, development and demonstration. There are several other countries in the world (Canada, Germany, Netherlands, Italy, India, Korea) which are also actively engaged in fuel cell R&D. Several publications (books, chapters in books, review and original articles in journals) cover the progress in fuel cell technologies (2-5).

This project "Novel Solid State Proton-Conductors Based on Polymeric Non-Oxy Acids" is an off-shoot of the "Phosphoric Acid" and "Solid Polymer Acid Electrolyte Fuel Cell" programs. The thrust is on the synthesis of new proton-conducting "model" and "polymeric" compounds, based on acid functions of the type $(R_fSO_2)_2NH$ and $(R_fSO_2)_2CH_2$ in appropriate fluorinated carbon structures, their physiochemical

characterization (stability, conductivity, oxygen reduction kinetics) and evaluation as candidate fuel cell electrolytes for use at elevated temperatures.

1.3 Technical Approach and Scope of Work

This project consists of four tasks:

- (i) Synthesis of monofunctional and polyfunctional perfluoroalkyl sulfonimides;
- (ii) Physico-chemical characterization of the acids;
- (iii) Investigations of electrode kinetics of oxygen reduction on platinum in these acids; and
- (iv) Evaluation of the acids as electrolytes for fuel cells.

The synthesis and physicochemical characterization of the acid was carried out by Professor Darryl DesMarteau and coworkers at Clemson University. Clemson University was the major subcontractor on this project and 62.5% (including indirect costs to Clemson University) of the DOE budget was provided for this work. The oxygen reduction kinetic studies were carried out at Texas A&M University. The budget allocation (direct costs) for this task was 7% of the total budget. The evaluation of acids as electrolytes for fuel cells was carried out by Dr. Vinod Jalan and coworkers at ElectroChem, Inc., under a subcontract with Texas A&M University. The budget for this task, including overhead to ElectroChem, Inc., was 17.9% of the total budget from the U.S. Department of Energy.

2. SYNTHESIS OF PROTON-CONDUCTING POLYMER ELECTROLYTES

2.1 Background

Based on promising electrochemical evaluation of perfluoroalkylsulfonyl derivatives of nitrogen and carbon of the type $(R_fSO_2)_2NH$ and $(R_fSO_2)_2CH_2$ (6,7), the goal was to prepare polymeric compounds incorporating these acid functions. Ionene

polymers of the type $[O_2\overset{\overset{H}{|}}{S}NSO_2(CF_2)_x]_n$ and $[O_2SCH_2SO_2(CF_2)_x]_n$ were planned. Based on methodology that had been developed under GRI sponsorship (8), extensions of the following reaction types to step reaction polymerization seemed feasible.

Nitrogen

Monofunctional

(1)

Difunctional

Carbon

Monofunctional

Difunctional

Using the appropriate carbon and nitrogen difunctional monomers as shown above, the desired, long-chain, ionene polymers were in principle obtainable. Such polymers would represent a new class of ionene polymer and the only known examples of polymers containing a very strong Bronsted acid group as part of the polymer backbone or main chain. Many unusual properties might be expected for such materials, including the possibility of very high proton-conductivities, useful in electrochemistry. Our goals were achieved in the case of nitrogen, but the carbon analogues proved impossible using the planned methodology. Early results with carbon indicated that the Grignard reactions could not be controlled in a step-reaction polymerization. Only intractable mixtures were obtained and it became clear that all available resources would be consumed in pursuing this avenue without any guarantee of a successful outcome. The carbon acid polymers were therefore abandoned.

2.2 Synthesis of Model Compounds

The planned synthetic strategy gave early indications of success with nitrogen but a host of experimental problems were encountered in our hope of quickly arriving at the goal of pure ionene polymers. Without pure polymers, electrochemical evaluation would be uncertain and perhaps the wrong conclusions would be reached regarding the efficacy of these materials in electrochemical applications. A decision was made to look closely at the

synthesis of known compound $\text{[CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{]}_2$ and to prepare the next member

of the series $\text{CF}_3\text{SO}_2\text{[NSO}_2\text{(CF}_2\text{)}_4\text{SO}_2\text{]}_n\text{NSO}_2\text{CF}_3$ with $n = 3$.

2.2.1 $\text{[CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{]}_2$

The original synthesis of $\text{[CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{]}_2$ was accomplished, as indicated under the background, but sublimation from sulfuric acid requires a temperature which results in the contamination of the acid with H_2O and sulfuric acid. Since we knew that the polymer would not be obtainable in the same manner, ion exchange using Amberlite IR-120 was investigated as a means of acidifying the compound. This led to acid samples contaminated by organic matter. Investigation revealed that the dioxane being used as a solvent was almost impossible to remove completely from the sodium salt. The strong coordination between the sodium and the dioxane was reasoned to be a result of coordination of both oxygens of the dioxane to the sodium atoms in the extended solid structure of the difunctional compound, because no such strong coordination is observed between $(\text{CF}_3\text{SO}_2)_2\text{NNa}$ and dioxane. This has not been confirmed in the case of

$\text{(CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{)}_2$ but exactly this behavior has been shown for the cesium salt of

the homologue $\text{[CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{]}_3$ (see later discussions and section 2.2.3).

At this point, investigation of alternative solvents for the reaction was begun. Finally, acetonitrile was found to be a very effective solvent in place of dioxane for all steps

of the reaction. It can be removed by heating under vacuum and subsequent treatment of the compound by IR-120 gave the acid in a nearly white form. This could be further purified by treatment with 30% H₂O₂ to remove organic contaminants. Details of this work are contained in the MS Thesis of Mark S. Gillette, Clemson University, August, 1991 (9).

2.2.2. The Tetrafunctional Acid

The tetrafunctional acid was synthesized to provide a model for the polymeric ionene. It was necessary to know if such a compound would have only two types of CF₂ groups in the ¹⁹F NMR. Early work on the polymer gave more than two signals of this type and it was not known if this was due to impurities or was a true property of the polymer. It was reasoned that the tetrafunctional compound could be prepared pure and extrapolation of observations on this material to the polymer would be valid.

The route to this compound involved the following reaction sequence:

After many trials leading to mixtures of the desired compound with

$\text{CF}_3\text{SO}_2\overset{\text{Na}}{\text{NSO}_2}(\text{CF}_2)_4\text{SO}_2\overset{\text{Na}}{\text{NSO}_2}\text{CF}_3$, it was found that the reaction proceeded readily in a stepwise fashion in CH₃CN using only 0.2 molar excess of FSO₂(CF₂)₄SO₂F. Once pure monomer was available, the next step proceeded in excellent yield.

The preparation of pure disilyl compound was often difficult and incomplete silylation of [H(Na)NSO₂CF₂CF₂]₂ was a common problem. In the end, the use of CH₃CN as solvent for the silylation was found to be effective if pure (H₂NSO₂CF₂CF₂)₂ was used to prepare (H(Na)SO₂CF₂CF₂)₂. Details of this work are contained in Reference 9.

2.2.3 Other Difunctional Compounds and Derivatives

In this project, the main emphasis was on $\text{R}_f\text{SO}_2\overset{\text{H}}{\text{NSO}_2}(\text{CF}_2)_x\text{SO}_2\overset{\text{H}}{\text{NSO}_2}\text{R}_f$ where $x = 4$ and $n = 1, 3$ and $\gg 3$, and $\text{R}_f = \text{CF}_3$. There is of course the flexibility to vary R_f and x and even the nature of (CF₂)_x. Resources did not permit an in-depth investigation of these factors, but some efforts were made to vary R_f and x . The emphasis on $\text{R}_f = \text{CF}_3$ and $x = 4$ was due to the ready availability of the starting materials from the 3M Company.

The acid $[\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2]_2$ and its Ag(I) derivative are described in detail in Reference 9.

The synthesis and properties $(\text{C}_4\text{F}_9\text{SO}_2\text{NSO}_2(\text{CF}_2)_x)$ ($x = 1,2$) and its Cs derivatives are given in Reference 9.

The synthesis and properties of $(\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2)_2$ are described in detail in Reference 9.

The variation of x was further demonstrated in the synthesis of $(\text{CF}_2\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2)_2$. For this purpose the telomer $\text{I}(\text{CF}_2)_2\text{I}$ was first converted to the 1,6-disulfonyl fluoride.

The overall yield of this reaction is ~70%. The main problem was the separation of NaI before chlorination. If not removed, I_2 is formed and interferes in subsequent steps. The best procedure on a small scale is to selectively chlorinate at low temperature to form $\text{I}_2 + \text{NaCl}$ without oxidizing the sodium sulfinate. This proved successful but it was easy to over chlorinate in larger scale reactions. Selective solvent extraction using acetone to remove NaI was effective in separating the NaI from the sulfinate.

Details on the synthesis and properties are contained in Reference 9.

2.3 The Ionene Polymer $\text{CF}_3\text{SO}_2[\text{NSO}_2(\text{CF}_2)_4\text{SO}_2]_n\text{NSO}_2\text{CF}_3$

In a step reaction polymerization of the type

$$\text{FSO}_2(\text{CF}_2)_4\text{SO}_2\text{F} + \text{Me}_3\text{SiNSO}_2(\text{CF}_2)_4\text{SO}_2\text{NSiMe}_3 \xrightarrow{\text{Na}} [\text{NSO}_2(\text{CF}_2)_4\text{SO}_2]_n$$

, it is well known that high molecular weights are difficult to obtain and that long reaction times are necessary to achieve a high degree of polymerization. In the ideal situation starting with stoichiometric amounts of the difunctional monomers, one would expect an equal number of end groups of the type $\text{FSO}_2(\text{CF}_2)_4\text{SO}_2\text{N}^{\text{Na}}$ — and

$\text{Me}_3\text{SiN}(\text{SO}_2(\text{CF}_2)_4\text{SO}_2\text{N})_{\text{Na}}$. With no side reactions, one could expect values of the

number average degree of polymerization $\bar{X}_n$ to be of the order a few hundred if the extent of reaction is high.

In this system we had to deal with the fact the $\text{Me}_3\text{SiN}-\text{SO}_2$ end group is easily converted to $\text{H}(\text{Na})\text{NSO}_2-$, which will limit chain length and probably interfere with electrochemistry. Very anhydrous conditions were necessary and we were reluctant to run the reactions at temperatures greater than 80-90°C out of fear of destroying the

$\text{Me}_3\text{Si-N-SO}_2-$ functions. Obtaining a pure polymer of reasonably high molecular weight proved to be a big challenge. Forming a polymer is trivial but controlling the polymerization to give a well defined material is anything but trivial.

After much effort by trial and error, a successful process was developed. We used a small molar excess of $\text{FSO}_2(\text{CF}_2)_2\text{SO}_2\text{F}$ to favor having only $\text{FSO}_2(\text{CF}_2)_4-$ end groups,

with the recognition that this would decrease $\bar{X}_n$. In an ideal situation, $\bar{X}_n = 200$ using a 1 mol% excess of one of the monomers. We had to sacrifice molecular weight in order to obtain a well characterized material. For nearly the entire project, we were unable to produce a pure polymer, having only two types of CF_2 groups as expected from the results of the tetrafunctional acid. In future work, we are confident that much higher molecular weights and pure polymers can be obtained. Unfortunately, this project ended just when we finally had the necessary experience and understanding of the system to make good materials.

The polymer was prepared by the following sequence. Further details are contained in Reference 9.

The polymer acid at this point contains some $\text{CF}_3\text{SO}_2\text{NH}_2$ and $(\text{CF}_3\text{SO}_2)_2\text{NH}$. These can be removed by grinding to a powder and heating under vacuum at 150-180°C. The removal of the impurities was monitored by ^{19}F NMR and found to be difficult,

presumably due to physical entrapment in the polymer. Both $\text{CF}_3\text{SO}_2\text{NH}_2$ and $(\text{CF}_3\text{SO}_2)_2\text{NH}$ have ~1 torr vapor pressure at 22°C.

At this point, the polymer has a light brown coloration but it should be white. We believe this is due to traces of organic contaminants. A white material can be obtained by heating the polymer with 30% H_2O_2 at 40-45°C for 24-48 h.

The best sample obtained at the end of this work had $\bar{X}_n = 80$. This is lower than desired but is a function of the excess $\text{FSO}_2(\text{CF}_2)_2\text{SO}_2\text{F}$ and a low extent of reaction

caused by the 80°C reaction temperature. It may also be due to the loss of the $\text{Me}_3\text{Si-N-}$

during the polymerization, but we could not detect $\text{HNSO}_2(\text{CF}_2)_4^-$ endgroups by NMR.

The value of $\bar{X}_n$ was determined by endgroup analysis by ^{19}F NMR. Integration of the CF_3 signal and comparing to the CF_2 signals gives a simple determination of $\bar{X}_n$.

3. PHYSICAL AND CHEMICAL CHARACTERIZATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES

The characterization of intermediates and target compounds was mainly by IR, NMR, DSC and x-ray in some cases. ^{19}F NMR was the single most valuable probe in monitoring the reactants and products. The high sensitivity and wide dispersion of ^{19}F NMR chemical shifts obtained in a modern FT/NMR system make this a very powerful tool. Details of the IR and NMR studies can be obtained from Prof. Darryl DesMarteau.

DSC was used to determine melting points and decomposition temperatures. All

acids of the family $\text{R}_f\text{SO}_2[\text{NSO}_2(\text{CF}_2)_x\text{SO}_2]_n\text{NSO}_2\text{R}_f$ are stable to at least 300°C. Most exhibit sharp melting points, which increase as the functionality increases and to lesser degree as the size of R_f increases. The ionene polymer melts at ~320°C, but it also decomposes near the same temperature. Representative DSC scans are obtainable by communication with Prof. Darryl DesMarteau.

All these acids dissolve exothermically in H_2O to give highly acidic solutions with a pH of 1-2. Titration of multifunctional acids with NaOH in water shows no differentiation in the proton acidities. A typical strong acid - strong base titration curve is observed in each case. For the tetrafunctional acid the equivalent weight, by titration, was very close to the theoretical value. For the ionene polymer, there is a buffering effect and/or equilibrium problems and accurate equivalent weight was difficult to attain by titration. The average value of n was always lower by this method than by NMR.

The Na-form of the polymer in water gives a milky solution indicating the formation of large aggregates. An estimate of the average particle size by light scattering gave a value in water of 271 nm while a clear solution in acetone was only 5 nm. The milky solution retains the same appearance even after standing for one year at room temperature.

Several x-ray structure determinations were made in the course of this work. Efforts to obtain suitable crystals of the tetrafunctional acid or its salts were not successful. The polymer is microcrystalline and obtaining crystals for x-ray would be improbable due

to the fact that the material is expected to contain a fairly broad distribution about $\bar{X}_n$.

The structures of metal salts are fascinating examples of layered and extended solids (10,11). In the solid state it is a general phenomenon that the solids contain regular ionic

and fluorocarbon domains. As can be seen in the case of $[\text{CF}_3\text{SO}_2\text{N}^{\text{Ag}}\text{CF}_2]_2$, the layers are

not bonded to one another (11). In $(\text{CF}_3\text{SO}_2\text{N}^{\text{Cs}}\text{SO}_2\text{CF}_2\text{CF}_2)$ the layers are held together by strong bonding with interactions along all axes to give an extended solid, which still contains regular fluorocarbon and ionic layers (10). In the case of

$\text{CF}_3\text{SO}_2\text{N}^{\text{Cs}}\text{SO}_2(\text{CF}_2)_6\text{SO}_2\text{N}^{\text{Cs}}\text{SO}_2\text{CF}_3 \cdot \text{dioxane}$, the structure is similar but the dioxane neatly fits in the fluorocarbon domain coordinated at each end between ionic layers (10). Although not the subject of this work, these solids are considered of interest as potentially useful materials. For further details on views of the structures and packing in the solid state, the reader is referred to Prof. Darryl DesMarteau.

4. ELECTROCHEMICAL CHARACTERIZATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES

4.1 Rationale for Investigations at the Pt Microelectrode/Electrolyte Interface

The main purpose of this study is to determine effect of the proton-conducting polymer electrolytes on the electrode kinetic parameters for oxygen reduction at a platinum electrolyte. It is this electrode reaction which predominantly contributes to the efficiency loss in low temperature ($T < 200^\circ\text{C}$) fuel cells. Apart from the electrode kinetic parameters, it is also essential to have knowledge of the diffusion coefficients and solubilities of oxygen in these electrolytes. An elegant microelectrode technique was previously developed to determine the electrode kinetic parameters for oxygen reduction and the mass transport parameters for oxygen in the electrolyte (12). The rationale for the microelectrode method is that mass transport and ohmic overpotentials can be greatly minimized and hence the half-cell potential vs. current density relation can be obtained over a considerably wide range of current densities. Though it is possible to obtain such data over nearly the same current density range using the rotating disc electrode technique, the microelectrode technique has the additional advantage of being useful to determine the diffusion coefficients and solubilities of oxygen in the electrolyte. Another reason for using the microelectrode technique in the present work was that only small quantities of the proton-conducting polymer electrolytes were prepared by Clemson University and even smaller quantities were available for the electrochemical characterization. Thus, it was necessary to design an experimental set-up which minimizes the volume of the electrolyte.

4.2 Experimental

4.2.1 Electrochemical Cell and Instrumentation

The cell (Fig. 1) consists of a three electrode configuration and is connected to a PAR 273 potentiostat (EG&G Princeton). A lock-in amplifier is connected in series to perform high frequency ac impedance experiments for conductivity measurements. The cell is thermostated using a water bath. The working electrode was a 100 μm -diameter platinum wire (Aesar), sealed in a capillary tube. Electric contact with the microelectrode was made with Woods' metal (Johnson Matthey). The bore of the capillary was sealed with Torr-Seal® (Varian Associates) epoxy. The working electrode face was polished with 600 grit carborundum paper and then with 10 μm , 0.3 μm and 0.05 μm alumina

Figure 1: Schematic of the cell with the microelectrode for oxygen reduction kinetic studies

(Buehler). The electrode was then sonicated in 1:1 reagent grade nitric-sulfuric acid mixture and rinsed in several portions of water. The reference electrode was a dynamic hydrogen electrode (DHE). In the DHE, hydrogen and oxygen are electrolytically generated at two platinum electrodes in contact with the acid. H₂ and O₂ were generated by applying a current of 10 mA/cm² to the platinum wires by means of a 9 V battery connected in series with a 5.1 mW resistor. The hydrogen evolving electrode was then used as the reference electrode. The electrodes of the DHE were platinized by galvanostatic cathodic deposition from a mM chloroplatinic acid bath. The counter electrode consisted of a perforated platinum foil (Aesar) (5 mm x 8 mm x 0.254 mm) spot-welded to a glass-sealed, 0.5 mm-diameter platinum wire. A gas sparging tube maintained a blanket of gas during the course of an experiment

4.2.2 Experimental Procedures and Analyses

Experiments were carried out on the Pt microelectrodes in (i) 0.1 M H₂SO₄; (ii) 0.1 M of the monomeric acid; and (iii) 0.1 M of the polymer acid (n = 40). The acids were cleaned in three stages: (i) heat treatment to 75°C with 30% H₂O₂ for 3 hours; (ii) addition of platinum black to decompose H₂O₂ in the electrolyte and bubbling H₂ gas for 30 minutes, followed by filtration of the mixture through a Whatman 40 filter paper and then through an Anapore (0.2 µm) membrane filter to remove the Pt particles; and (iii) preelectrolysis at 1.7 V/RHE for six hours. The cyclic voltammetric technique was used to ascertain the purity of the acids. This technique also yielded the electrochemically active surface area of the microelectrode.

Slow-scan voltammetric experiments were then conducted to determine the pseudo-steady state potential vs. current density plot for oxygen reduction; ultra high pure oxygen (Linde) was used in these experiments. The mass-transfer corrected Tafel plots were then constructed from which the Tafel parameters (exchange current density, i₀, and Tafel slope, b) for oxygen reduction were calculated.

For the determinations of the diffusion coefficients (D) and solubilities (C) of oxygen in electrolytes, a chronoamperometric method was used. The oxygen reduction reaction was driven at the diffusion controlled rate by applying a potential step from an initial potential of 1.1 V/RHE to a final potential of 0.4 V/RHE. During a time window, spanning from 0.07 to 10 s, the current (i) vs. time (t) plot was recorded. The data were analyzed according to the Cottrell plot (i vs. t^{1/2}). The expression, which has been derived for the transient behavior of the limiting current density as a function of current density, is:

$$i = \frac{nF\pi^{1/2}D^{1/2}Cr^2}{t^{1/2}} + \pi nFD C r \quad (9)$$

The slope and the intercept of the plot yield D^{1/2}C and DC respectively from which D and C can be independently calculated.

4.3 Purity of Electrolytes and Electrochemically Active Surface Areas from Cyclic Voltammograms

The cyclic voltammograms (CV) on the Pt microelectrode in sulfuric acid, and the monomeric and polymeric acids are shown in Fig. 2a and 2b. The CVs were recorded after repeated scanning between 0.05 and 1.6 V/DHE for 4 hours. The surface electrochemical processes (hydrogen adsorption and desorption and oxide formation and reduction) are clearly resolved in sulfuric acid (Fig. 2a). The roughness factor, calculated from the coulombic charges for hydrogen adsorption and desorption, is 5.2 (the assumption is that

Figure 2: Cyclic voltammograms at the Pt/acid interface in a N_2 saturated atmosphere (scan rate 100 mV/s)

for a smooth surface with a roughness factor of unity, the coulombic charge for these processes is 220 $\mu\text{C}/\text{cm}^2$).

In the case of the imide acids, there are deformations of the CVs (Fig. 2b) and reductions in the roughness factors, which observations can be attributed to organic contamination of the electrodes. Adsorption of the organic super-acids and/or of impurities can cause reduction in the electrochemically active surface area. The electrochemically active surface area of Pt in these acids corresponds to a reduction in roughness factor by about 5, as compared with the results in sulfuric acid. Organic contamination is also responsible for the sloping oxide formation regions in the CVs. The effect of organic contamination is much greater with the polymeric than with the monomeric acid.

4.4 Electrode Kinetic Parameters for Oxygen Reduction at Pt Microelectrode/Electrolyte Interface

The pseudo-steady current vs. potential plots for oxygen reduction on Pt in H_2SO_4 and the monomeric and polymeric acids are shown in Fig. 3a-c. The pseudo-steady state plot was recorded during scanning of the potential between 1.1 and 0.3 V/DHE at a sweep rate of 1 mV/s. In the case of the measurements in H_2SO_4 , there is negligible hysteresis (forward and reverse scans), which is indicative of a high degree of purity of the electrolyte. However, the hysteresis in the pseudo-steady state current vs. potential plots is quite significant for oxygen reduction on Pt in the monomeric and polymeric fluorinated sulfonimides. This behavior is again indicative of organic contamination, as was seen in the CVs. An interesting observation is that the diffusional limiting current densities are higher in the monomeric and polymeric acid than in sulfuric acid. The higher diffusional currents are indicative of higher solubilities of oxygen in the former acids.

The mass transfer-corrected Tafel plots for oxygen reduction on Pt in the three acids were constructed from the data in the pseudo-steady current vs. potential plots and are shown in Fig. 4. As expected, oxygen reduction on the Pt microelectrode in sulfuric acid reveals a two-section Tafel plot. The results are well in agreement with previous ones on macro or microelectrodes. The low Tafel slope (60 mV/decade) at low current densities is a result of oxygen reduction at an oxygen covered platinum electrode, under Temkin adsorption conditions for the intermediates in the reaction. The 120 mV/decade Tafel slope, at higher current densities represents the region in which oxygen reduction occurs on the free metal surface, under Langmuir adsorption conditions. With the proton-conducting polymer electrolytes, the Tafel plots revealed only a single linear region with a slope of 120 mV/decade. The generally accepted view is that the first electron transfer step,

is the rate-determine step in this region. The Tafel parameters for oxygen reduction on Pt in the three acids are presented in Table 1. The exchange current densities, calculated from the Tafel plots in the region where the Tafel slope is 120 mV/decade, are approximately equal in the three cases. It must be noted that because of the impurities in the acids or organic contamination by these acids, dilute electrolytes (0.1 M) were used in the microelectrode studies. A method to overcome the effects of organic contamination with higher concentrations of the acids is by investigations on high surface area electrodes (for example, fuel cell electrodes - see section 5).

4.5 Diffusion Coefficients and Solubilities of Oxygen in Electrolytes

The current (i) vs. time (t) transients, recorded as described in subsection 4.2.2 for the Pt microelectrode in the three electrolytes are presented in Fig. 5a-c. These plots were used to construct the corresponding i vs. $t^{1/2}$ plots (Fig. 6). The slopes and intercepts of

(A) 0.1 M H_2SO_4

(B) 0.1 M monomeric acid

Figure 3: Pseudo steady-state current vs. potential plot on Pt electrode in an O_2 saturated electrolyte (scan rate 1 mV/s)

(C) 0.1 M polymeric acid

Figure 3: Pseudo steady-state current vs. potential plot on Pt electrode in O_2 saturated electrolyte (scan rate 1 mV/s)

Figure 4: Mass transfer corrected Tafel plots at the Pt/acid interface: (a) 0.1 M H_2SO_4 , (b) 0.1 M monomeric acid, and (c) 0.1 M polymeric acid

TABLE 1
Electrode Kinetic Parameters for Oxygen Reduction
at a Platinum Microelectrode/Acid Interface

Acid	Tafel slope mV/decade	Exchange Current Density A/cm ²
0.1 M Sulfuric Acid	-69	7.21×10^{-10}
	-121	7.15×10^{-8}
0.1 M Monomeric Acid	-118	1.32×10^{-8}
0.1 M Polymeric Acid	-125	2.49×10^{-8}

these plots were used to calculate the diffusion coefficients and solubilities (c) of oxygen in the electrolytes, according to Equation 10. The values of D and C in these electrolyte are found in Table 2. The solubility of oxygen is higher in the proton-conducting polymer electrolyte than in sulfuric acid. On the contrary, the diffusion coefficient is lower in the former acid. However, from a mass transport point of view, the product of D and C is the more important parameter to determine its effect on fuel cell performance and it may be expected that the increase of C will be considerably greater than the decrease of D with increasing concentration of the acid, as evidenced from the results in trifluoromethane sulfonic acid (12) and Nafion® (13).

TABLE 2
Mass Transport Parameters for Oxygen in Acid Electrolytes

Acid	Diffusion Coefficient cm ² /s	Solubility mole/cm ³
0.1 M Sulfuric Acid	9.2×10^{-6}	2.5×10^{-6}
0.1 M Monomeric Acid	8.8×10^{-6}	3.8×10^{-6}
0.1 M Polymeric Acid	3.5×10^{-6}	7.4×10^{-6}

5. EVALUATION OF PROTON-CONDUCTING POLYMER ELECTROLYTES FOR FUEL CELLS

5.1 Rationale for Single Cell Investigations

The level of purities of the compounds has been a major concern in evaluating these electrolytes by more fundamental techniques, such as, microelectrodes or rotating electrodes. The ratio of the catalytic surface to the electrolyte volume in such techniques is very small, and even very low levels of impurities can have large effects on the

(A) 0.1 M H_2SO_4

(B) 0.1 M monomeric acid

Figure 5: Current vs. time plot following a potential step on Pt electrode in an O_2 saturated electrolyte

Figure 5: Current vs. time plot following a potential step on Pt electrode in an O_2 saturated electrolyte

Figure 6: Current vs. $t^{-1/2}$ plots for O_2 reduction in Pt electrode: (a) 0.1 M H_2SO_4 , (b) 0.1 M monomeric acid, and (c) 0.1 M polymeric acid

electrochemical behavior. Our approach is to evaluate these electrolytes in a complete fuel cell using an immobilized matrix and very high surface area catalyst--the net effect being a very large ratio of the catalytic surface to the electrolyte volume. Under such conditions, the low levels of impurity would not affect the fuel cell performance. A phosphoric acid fuel cell was constructed and tested prior to the evaluation of the new electrolytes in a fuel cell. This was done in order to achieve a set of parameters that could be used for comparison with these new electrolytes. Parameters of interest include current density, internal resistance, cell potential, and decay rate.

Since many properties of the new electrolytes are not well established, tests were carried out both in molten salt as well as in aqueous solutions. In the molten state, the performance of the fuel cell was scanned from the melting temperature to above 200°C. In the aqueous state, performance of the fuel cell was evaluated from room temperature to above 200°C. If warranted, the best performing electrolyte could be tested under pressurized conditions. Our current test facility (Fig. 7) is capable of running PAFC up to 150 psig.

5.2 Experimental

The fuel cell used in this study consisted of machined graphite blocks with inlet and outlet connections, fluid plenums, and stainless steel current collector/load distribution plates held in place by bolts covered with PTFE for insulation (Fig. 8). The 10% Pt/Vulcan XC-72 electrodes were used; Pt loadings were 0.5 mg/cm² for the cathode and 0.4 mg/cm² for the anode. Both of these electrodes were coated with a 75 micron thick layer of SiC, using the doctor-blade technique. A thin layer of 100% phosphoric acid was sandwiched between the anode and cathode to make a complete cell package. The anode fuel gas was hydrogen and the cathode oxidant was pure oxygen. The performance of the cell was tested at 190°C. The cell potential and internal resistance were monitored as a function of current density using a potentiostat, interfaced with a microcomputer. The internal resistance was measured via a current interruption module, built into the fuel cell evaluator.

The following four acids were supplied by Clemson University to ElectroChem:

monomeric acid	(CF ₃ SO ₂) ₂ NH	m.p. 48°C
dimeric acid	((CF ₃ SO ₂) ₂ NH) ₂	m.p. 175°C
tetrameric acid	((CF ₃ SO ₂) ₂ NH) ₄	m.p. 248°C
polymeric acid	((CF ₃ SO ₂) ₂ NH) _n n = 40	m.p. 320°C decomp.

Each of these acids was incorporated into a fuel cell, evaluated and compared with a phosphoric acid fuel cell. Each cell was evaluated both at 190°C and at 75°C.

5.3 Results and Discussion

The open circuit voltage (OCV) for each cell tested is presented in Table 3. This table shows that the low molecular weight compounds studied (i.e., monomeric acid and dimeric acids) have OCVs very similar to that of a cell containing 100% phosphoric acid. However the OCVs of the high molecular weight compounds (tetrameric and polymeric acids) are depressed by about 100 mV. Despite this depression of the OCVs, in both tetrameric and polymeric acid cells, the performance of these cells at high current density was superior to that of the other three cell systems (Fig. 9 and 10). In fact at 190°C and 200 mA/cm², the iR corrected voltages of the stabilized polymeric and tetrameric acid cells was 20-30 mVs higher than the 100% phosphoric acid fuel cell (Table 3). Although the

Figure 7: Photograph of fuel cell test facility

Figure 8: Components of single cell test fixture for performance evaluation of new fuel cell electrolytes

TABLE 3
Open circuit voltage and steady state voltage at 200 mA/cm² in single cells

Liquid Electrolyte	OCV	190°C		75°C	
	mV	mV w/o iR	mV	mV w/o iR	mV
Phosphoric acid	950	732	688	657	609
Monomeric acid + H ₃ PO ₄	961	728*	659	---	
Dimeric acid + H ₃ PO ₄	988	732*	676	623*	536
Tetrameric acid + H ₃ PO ₄	824	759	723	641	592
Polymeric acid + H ₃ PO ₄	871	749	706	665	615

* after anode polarization

low molecular weight compounds had initially high OCVs, their performance deteriorated with time when a load was applied. This deterioration in performance also resulted in a depression of the OCV (961 mV → 661 mV). This apparent load and time effect could be reversed by polarization of the anode. In fact, immediately after polarization, the iR corrected voltage at 190°C and 200 mA/cm² was very similar to that for the phosphoric acid cell (Table 3). The above information suggests that the anode was being poisoned either by these low molecular weight compounds or by some impurities which had not been removed.

Comparison of Tafel plots at 190°C and 75°C (Fig. 9 and 10) show that the performance of all five acids is much better at higher temperatures. However, at 75°C only cells containing either phosphoric acid, polymeric acid or tetrameric acid can sustain a reasonable cell voltage at higher current densities (i.e., 100 mA/cm²). Only after anodic polarization was a good voltage obtained for low molecular weight acids under these conditions (Table 3).

Figure 11 shows the iR corrected voltage when the temperature was decreased from 190°C to 75°C. As can be seen from this figure, the performance of tetrameric, polymeric and phosphoric acid cells are very similar under these non-stabilized conditions. The performances of monomeric and dimeric acid cells are much lower, especially at the lower temperatures. In fact, these low molecular weight acids have problems sustaining a 200 mA/cm² current density below 100°C.

The cell resistance with the lower molecular weight acids is higher than that with the higher molecular weight acids. Also the low molecular weight acid cells have a resistance which appears to increase with decrease in temperature. However the resistance of the high molecular weight acids is not affected by temperature (Fig. 12). This resistance effect could be the result of electrode poisoning caused either by the formation of a high electrode morphology. This poisoning effect appears to be more acute at lower temperatures. The phosphoric acid cell is shown here to have a high cell resistance.

Figure 9: iR corrected plots of cell potential vs. current density in H_2/O_2 fuel cells with phosphoric acid and the proton-conductor electrolyte additives as electrolyte, temperature 190°C.

Figure 10: iR corrected plots of cell potential vs. current density in H_2/O_2 fuel cells with phosphoric acid and the proton-conductor electrolyte additives as electrolyte, temperature 75°C.

Figure 11: Dependence of iR corrected cell potential on temperature in H_2/O_2 fuel cell with phosphoric acid proton conductor additive as electrolyte

Figure 12: Dependence of cell resistance on temperature in H_2/O_2 fuel cell with phosphoric acid and the proton-conductor additive as electrolyte

Of all the acids studied during this time period, the cell which contain either tetrameric or polymeric acid appeared to be the most promising. Therefore these cells were allowed to run for approximately 100 hours at 200 mA/cm². Figure 13 shows a plot of iR corrected voltage vs. time for the tetrameric acid cell. It can be seen that these cells are very stable over a 100 hour period.

The polymeric acid was tested without any H₃PO₄. Aqueous solution of this material was used to cast thin films on the anode and the cathode. Figure 14 shows the resistance of this material as a function of temperature. The significant increase in resistance at 100°C is probably due to the loss of water from the thin film.

6. CONCLUSIONS

Four fluorinated sulfonimides of the type (R_fSO₂)_nNH were synthesized and characterized. The four compounds are strong polyfunctional acids with all acid groups of equal strength. The acids are stable up to 320°C, as shown by differential scanning calorimetry. The tetramer melts at 248°C and the polymer at 320°C.

The microelectrode technique was used to determine the electrode kinetic parameters for oxygen reduction on platinum in these acids and also to obtain the diffusion coefficients and solubilities of oxygen in these acids. Hydrogen peroxide pretreatment and preelectrolysis were essential to remove the organic impurities. However, there was a deformation of the cyclic voltammograms due to adsorption of the acids or of impurities. The electrode kinetic parameters for oxygen reduction in sulfurimides were similar in values to those in sulfuric acid. The transient electrochemical studies revealed that the solubilities of the oxygen in these electrolytes was higher than in sulfuric acid, but the diffusion coefficients were somewhat lower.

The fluorinated sulfonimides were tested as additives to phosphoric acids in H₂/O₂ fuel cells. Impurities lower the open circuit potentials but the fuel cell performances at the higher current densities are better in the presence of these super-acids.

7. ACKNOWLEDGEMENTS

This work was carried out under the auspices of the U.S. Department of Energy (Contract # DE-AC21-88MC25169). The investigators are grateful to Mr. William Huber, Technical Program Manager, for helpful discussions and suggestions. Acknowledgements are also due to (i) Dr. Bo Yang, presently at Nalco Chemical Company, Naperville, Illinois, who carried out the preliminary investigations on the electrolyte (Task 3); (ii) Mr. Jean-Guy Le Helloco, Visiting Research Associate at Texas A&M University from Rhone Poulenc, France, who assisted in the analysis of results (Task 3); and (iii) Ms. Judith Hickson for the arduous task of word-processing of the report.

Figure 13: Time dependence of iR corrected voltage in H_2/O_2 fuel cell with phosphoric acid electrolyte and proton conductor additive, temperature $190^\circ C$, current density 200 mA/cm^2

Figure 14: Resistance of proton conducting polymer, as a recast thin film vs. temperature

8. REFERENCES

1. T.J. George and M.J. Mayfield, "Fuel Cells - Technology Status Report", Report # DOE/METC-90/0268 (DE 9000686) U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV (1990).
2. S.S. Penner (ed.), Assessment of Research Needs for Advanced Fuel Cells, Pergamon Press, New York (1986).
3. S. Srinivasan, "Fuel Cells for Extra-terrestrial and Terrestrial Applications", *J. Electrochem. Soc.*, **136**, 41C (1989).
4. A.J. Appleby and F.R. Foulkes, Fuel Cell Handbook, Van Nostrand-Reinhold, New York (1989).
5. K. Kinoshita, F.R. McLarnon and E.J. Cairns, "Fuel Cells - A Handbook", Publication # DOE/METC-88/6096, U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV (1988).
6. M. Razaq, A. Razaq, E. Yeager, D.D. DesMarteau and S. Singh, *J. Applied Electrochem.*, **17**, 1057 (1987).
7. M. Razaq, A. Razaq, E. Yeager, D.D. DesMarteau and S. Singh, *J. Electrochemical Soc.*, **136**, 385 (1989).
8. D.D. DesMarteau, "Novel Fluorinated Acids for Phosphoric Acid Fuel Cells", Final Report, Gas Research Institute (Contract #5084-260-1086), September (1989).
9. M.S. Gillette, M.S. Thesis "Synthesis of Perfluro-bis-Sulfonimides", Clemson University, Clemson, SC, August 1991.
10. D. DesMarteau, W.T. Pennington, K.S. Sung, S.Z. Zhu and R. Scott, "Novel Layered Structures in Metal Salts of Bis Sulfonyl Methanes", *European Journal of Solid State and Inorganic Chemistry*, **28**, 905 (1991).
11. D. DesMarteau, S.S. Zuber, W.T. Pennington and B. B. Randolph, "Structural Studies of Silver (I) Salts of Cyclic Sulfonimide", "Synthesis of Perfluorobis Sulfur Imides", *European Journal of Solid State and Inorganic Chemistry*, In press.
12. M.A. Enayetullah, T.D. DeVilbiss and J.O'M. Bockris, "Activation Parameters for Oxygen Reduction Kinetics in Trifluoromethane Sulfonic Acid Systems", *J. Electrochem. Soc.*, **136**, 3369 (1989).
13. A. Parthasarathy, C.R. Martin and S. Srinivasan, "Investigations of the O₂ Reduction Reaction at the Platinum/Nafion Interface Using a Solid-State Electrochemical Cell", *J. Electrochem. Soc.*, **138**, 916 (1991).