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COMMISSION

ENERGY INNOVATIONS SMALL GRANT PROGRAM
Environmentally Preferred Advanced Generation

Novel Composite Membranes for
Fuel Cells

FEASIBILITY ANALYSIS

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PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

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- Environmentally-Preferred Advanced Generation
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The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
 - Appendix A: Final Report (under separate cover)
 - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:

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Executive Summary

Introduction

Fuel cells utilizing a polymer electrolyte membrane (PEM) have the desirable characteristics that they operate at near room temperature with high power density. A less desirable characteristic of the proton-conducting polymer is that it utilizes water, in the form of the hydronium ions, H_3O^+ , as the proton conductor. This leads to a requirement for water re-circulation and temperature control in the system. In addition, the need to maintain hydration limits the maximum allowable temperature and results in low efficiency in hydrogen-air fuel cells. PEM fuel cell operating at higher temperatures can demonstrate improved efficiency and reduced carbon monoxide poisoning of the catalyst.

If a substitute for the hydrous component in the fuel cell membrane were found, manufacturers could eliminate the need for water re-circulation, relieve thermal management issues and achieve the benefits of higher temperature operation's increase of catalyst efficiency in generating protons at the fuel cell anodes. This benefit is directly applicable to all PEM fuel cells including hydrogen/air fuel cells, and cells fueled by reformed hydrocarbons. These fuel cells are typical of those applied to power generation.

Many solid acids exhibit excellent proton transport properties, but less than ideal mechanical properties and chemical stability. For these reasons, the researcher selected and investigated composite materials utilizing an inert polymer matrix to support the embedded solid acid.

Objectives

The goal of this project was to determine the feasibility of using proton-conducting membranes that do not rely on hydrated polymer for proton transport in a PEM fuel cell. The proposed membranes are composites of inert polymers and "solid acids." The following project objectives were established:

1. Prepare, characterize and evaluate a broad range of polymer/solid acid composite membranes for subsequent development of membrane electrode assemblies.
2. Fabricate and Characterize electrodes and membrane-electrode assemblies. Understand and optimize electrode microstructure.
3. Demonstrate a single cell fuel cell utilizing a solid acid based membrane operating at temperatures between 100 and 180°C.

Outcomes

1. A large number of composite membrane systems (more than 12) were prepared, characterized and evaluated. The majority of these systems exhibited low conductivities and poor homogeneity, although some, notably composites formed using a ceramic matrix, had conductivities within an order of magnitude of the solid acid alone and excellent reproducibility. Because of the higher conductivity of the solid acid alone, such membranes (in which the inert matrix material was eliminated) were used for further fuel cell development.
2. Membrane electrode assemblies were fabricated using various techniques. The most successful technique discovered was the simultaneous cold-pressing of the electrode/electrolyte/catalyst layers and the electrolyte membrane material. A volatile organic

(naphthalene) was added to assure porosity. These assemblies were very thick because of the need to assure impermeability of the solid acid layer.

3. Fuel cells were demonstrated using several variations of electrode/electrolyte/catalyst layers. They can be generally characterized as exhibiting an open circuit voltage ranging from 1 to 1.12 volts, and producing power ranging up to 12 mW/cm².
4. An unanticipated outcome of this research was the discovery that in a reducing environment (flowing hydrogen) the sulfur content in the solid acid reduced to H₂S. The rate of conversion was higher in the presence of a metal catalyst. This chemical reaction limits the long-term stability of these fuel cells. Solid acids not containing sulfur were shown to be stable, but as of yet no solid acid combining high stability and high conductivity has been identified.

Conclusions

Knowledge was gained and conclusions were drawn from each step in the progress of this project as detailed in Appendix A. The researcher summarized the project in these words; "The problem of sulfur (or selenium) reduction has proved vexing indeed. The development of optimized membrane electrode assembly structures awaits the discovery of alternative solid acids with greater chemical stability (materials that exclude sulfur and selenium)." This project determined that the use of proton conducting membranes that do not rely on hydrated polymers for proton transport in PEM fuel cells is not feasible using *current* solid acid materials.

Benefits to California

In this project it was demonstrated that the path to a successful energy product that will benefit California electric ratepayers requires as its first step the development of alternative solid acid materials. It cannot be predicted at the outset whether such materials will be discovered.

Recommendations

The basic thesis for this project was sound and the research was carried out in a professional and competent manner. Unfortunately the chemistry involved did not result in a usable anhydrous membrane material. If one is to realize the potential advantages of anhydrous, thermally stable proton conductors, "alternate solid acids with greater chemical stability" must first be discovered.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

**ENERGY INNOVATIONS SMALL GRANT
(EISG) PROGRAM**

EISG FINAL REPORT

**NOVEL COMPOSITE MEMBRANES
FOR FUEL CELLS**

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Inquires related to this final report should be directed to the Awardee (see contact information on cover page) or the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

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Abstract

The key objectives of this research were to identify optimal solid acid / polymer composite materials and to demonstrate their utility in fuel cell applications. At the outset, higher risk was associated with the latter objective in that it was not clear whether water soluble solid acids could possibly be used in a fuel cell in which H₂O is generated as a by-product. In addition, the possibility of mechanical failure upon heating to the high conductivity phase of the solid acid, due to significant volume changes at the phase transition, were also of serious concern. This work clearly demonstrates that water solubility is not a detrimental property for fuel cell applications, and that there are no undesirable losses in mechanical integrity at the phase transformation. The conductivity of CsHSO₄, the model solid acid utilized for these studies, is stable over tens of hours at 160°C under H₂O saturated argon, and the open cell voltage of single cell fuel cells thermally cycling through the phase transition was independent of temperature. However, the catalysis of the reduction of sulfur and selenium in sulfate and selenate solid acids, respectively, by platinum has presented itself as a serious concern. Alternative catalysts, including tungsten carbide, iridium, palladium, gold and ruthenium, were shown to similarly induce reduction of sulfur in CsHSO₄. The development of optimized membrane electrode assembly structures awaits the discovery of alternative solid acids with greater chemical stability. Materials which exclude S and Se, and are comprised of phosphate, silicate or germanate groups show excellent stability, but as of yet none with high proton conductivity has been identified. Composite membranes, containing a mechanically stiff component in addition to the solid acid, may enable the development of free-standing, mechanically robust membranes. The most promising result along those lines has been the performance of YSZ-CsHSO₄ composites, where YSZ is yttria stabilized zirconia.

Introduction

Fuel cells are attractive alternatives to combustion engines for both mobile and stationary applications because they generate virtually no acid rain producing pollutants, and because of their high efficiency. Amongst the various types of demonstrated fuel cells, those utilizing a polymer electrolyte membrane (PEM) have received increasing attention in recent times because they permit fuel cell operation at temperatures close to ambient and are capable of generating high power densities. In a hydrogen/air fuel cell, hydrogen is either stored and then delivered to the (anode of the) fuel cell as needed, or hydrogen is generated on site from a hydrocarbon fuel, cleaned of CO, and subsequently provided. In contrast, in a direct methanol fuel cell (DMFC), a methanol/water solution is fed directly to the fuel cell, without any fuel processing. There are various advantages and disadvantages inherent within all three configurations, but all are, to a greater or lesser extent, limited by the performance of the proton conducting polymeric membrane.

Virtually all known proton conducting polymers, including the commercially important polymer, Nafion™, contain sulphonic acid side groups attached to a highly fluorinated backbone. The fluorinated backbone leads to high chemical stability, whereas the acid groups encourage the hydration of the polymer and subsequent proton conduction via the motion of hydronium ions, H_3O^+ . Because water is necessary to facilitate the proton transport process, loss of water immediately results in degradation in the conductivity. Moreover, this degradation is irreversible – a simple reintroduction of water to the system does not restore the conductivity. Thus, a key limitation of hydrated polymer based fuel cells is that the electrolyte membrane remain humidified during operation, which introduces a host of balance-of-plant needs for water recirculation and temperature control. A second limitation that derives directly from the need to maintain water in the membrane is that the temperature of operation cannot exceed 100°C. High temperature operation would be desirable, however, to increase catalyst efficiency in generating protons at the anode (in both H_2 and direct methanol fuel cells), and to improve catalyst tolerance to CO. Carbon monoxide poisoning of precious metal catalysts is particularly problematic in hydrogen/air fuel cells for which hydrogen is generated on-site and CO is inevitably present in the fuel. A third limitation of Nafion (and similar) electrolytes, which is unique to applications in direct methanol fuel cells, is the high permeability of these polymers to methanol. Direct transport of the fuel across the membrane to the air cathode results in unacceptable losses in efficiency. The high methanol permeability of Nafion, like its other limitations, is a consequence of the requirement that water be present in the membrane.

Accordingly, the key aims of the project was the development of alternative proton-conducting membranes which *do not* rely on a hydrated polymer for proton transport, and are instead based on “solid acids.” Many solid acids exhibit excellent proton transport properties, Figure 1, but less than ideal mechanical properties and chemical stability. Thus, we proposed to develop composite materials in which a solid acid is embedded in an inert polymer matrix. Such composites would ideally combine the excellent proton transport properties of the solid acid (CsHSO_4) with the excellent mechanical properties of the polymer. In addition, it was hoped that the matrix material might protect the water soluble solid acid from making direct contact with liquid water during fuel cell shut down. Overall through the use of these unconventional electrolytes, in which the hydrous component is eliminated, it was anticipated that water recirculation

hardware would not be necessary and thermal management issues would be relieved (greatly simplifying the overall fuel cell system), slightly elevated temperature operation would be possible (enhancing catalyst performance, improving efficiencies and further simplifying the overall fuel cell system by increasing CO tolerance), and methanol transport across the membrane would be negligible (enabling the development of high efficiency DMFCs.)

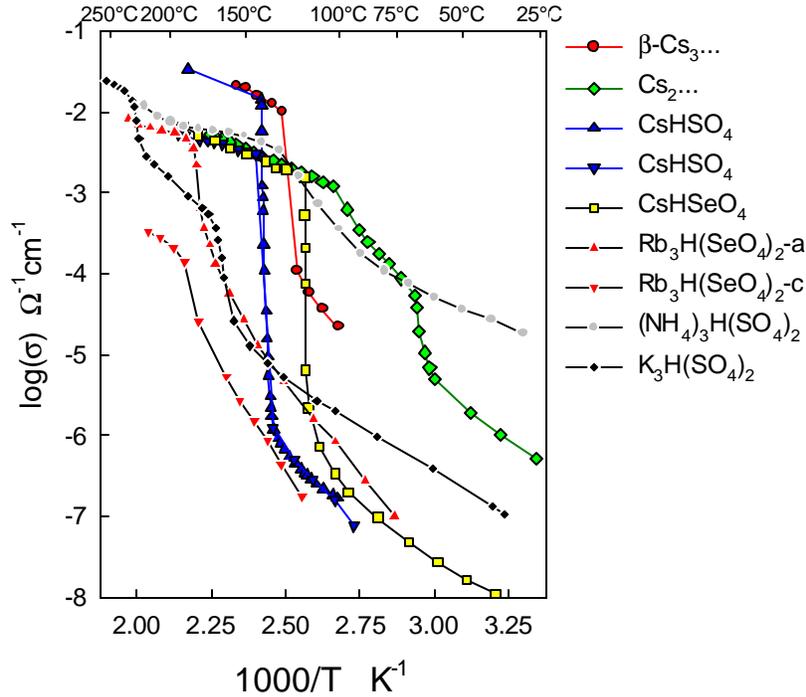


Fig. 1. Conductivity of selected solid acids [1]. $\beta\text{-Cs}_3\dots = \beta\text{-Cs}_3(\text{HSO}_4)_2[\text{H}_{2-x}(\text{S,P})\text{O}_4]$; $\text{Cs}_2\dots = \text{Cs}_2(\text{HSO}_4)(\text{H}_3\text{PO}_4)$. The compound $\text{Rb}_3\text{H}(\text{SeO}_4)_3$ is anisotropic and the appended letter in the legend indicates the crystallographic orientation of the measurement.

Project Approach

To meet the objective of the development of a mechanically robust, high proton conductivity composite fuel cell membrane, the project was organized into the following specific tasks.

Tasks

- 2.1. Synthesis of a first generation polymer/solid acid composite (PSAC) membranes for subsequent development of membrane electrode assemblies. Two specific formulations for these first generation membranes have already been identified.
- 2.2. Preparation, characterization and evaluation of a broad range of (PSAC) membranes. A wide variety of solid acid/polymer combinations are possible, and the optimal will depend on composite conductivity, chemical stability, and mechanical properties. Furthermore, several possible preparation methods are

available and the optimal will be selected based on projected large scale cost, ease of fabrication and composite properties. Characterization will include permeability and conductivity measurements, thermal analysis and microscopy.

- 2.3. Fabrication and characterization of electrodes and membrane-electrode assemblies utilizing first generation PSAC membranes. Various electrode formulation schemes will be pursued to optimize electrode microstructure and understand the roles of particle and phase distribution.
- 2.4. Fabrication and characterization of electrodes and membrane-electrode assemblies utilizing optimized PSAC membranes (as developed in Task 2.2) and optimized electrode formulations (as developed in Task 2.3).
- 2.5. Demonstration of a high performance single cell fuel cell utilizing a solid acid based membrane. Operation will be carried out at temperatures between 100 and 180°C.
- 2.6. Preparation of interim progress reports and final report.

Project Outcomes

Composite Membranes

Several different types of composite membranes were successfully fabricated as part of this project. These are listed in Table 1, along with the types of characterization experiments carried. The processing for each system was specific to the matrix material utilized, and is as described as part of the results below.

Table 1. Summary of composite systems examined.

Type	Solid Acid	Matrix	Fabrication	Characterization ¹
1	CsHSO ₄	poly(VDF)	hot press mixture	C, TA, X
2	(NH ₄) ₃ H(SO ₄) ₂	poly(DCPD)	<i>in situ</i> polymerization	C, FC
3	CsHSO ₄	poly(DCPD)	<i>in situ</i> polymerization	FC
4	CsHSO ₄	Castoglas (Buhler) 1-part resin	<i>in situ</i> cure	C
5	CsHSO ₄ ²	Evercoat 1-part resin	<i>in situ</i> cure	C
6	CsHSO ₄	Crystar (Dupont) 1-part resin	hot press mixture	C
7	CsHSO ₄	Devcon 2-part epoxy	<i>in situ</i> cure	failed
8	CsHSO ₄	3-part epoxy	<i>in situ</i> cure	C
9	CsHSO ₄	Silicone	<i>in situ</i> cure	FC
10	CsHSO ₄	Kevlar	melt solid acid	FC
11	CsHSO ₄	Silica filter paper	melt solid acid	FC
12	CsHSO ₄	(Zr,Y)O _{2-δ}	melt solid acid	C

¹ C = conductivity; FC = fuel cell (in most cases, only OCV measurements carried out to check for permeability); TA = thermal analysis; X = X-ray powder diffraction.

² solid acid Cs₅H₃(SO₄)₄•½ H₂O also utilized.

A first set of composites was fabricated from poly vinylidene fluoride (PVDF) and CsHSO₄ over the composition range 0-100% by volume in increments of 10%. Mixed powders were ground together in a mortar and pestle for 30 minutes, then uniaxially hot-pressed at 26 MPa (3.8 kpsi) and 170°C (356°F) for 20 minutes to a thickness of ~0.5 mm. Composites of greater than 30 vol% PVDF were flexible and relatively durable, whereas samples with less PVDF were brittle and easily broken. X-ray powder diffraction analysis of these samples showed that the composites contained crystalline CsHSO₄, whereas thermal analysis revealed that the superprotonic phase

transition of the acid salt at 141°C was unaffected by the presence of the polymer. The conductivities, Figure 2, of the composites were generally lower than that of the end-member solid acid, as would be expected. At low temperatures, however, additions of small amounts of polymer (up to 20 vol%) induced an increase in conductivity. While the conductivities of these composites were reasonable, it was generally observed that the membranes were highly inhomogeneous because of the tendency of the non-polar polymer to desegregate from the solid acid during melt processing. In addition, attempts to use these composite membranes in fuel cells were generally unsuccessful. It is believed this is because of the tendency of the polymer to flow when incorporated into a fuel cell test station, in which pressure must be applied to prevent gas leaks.

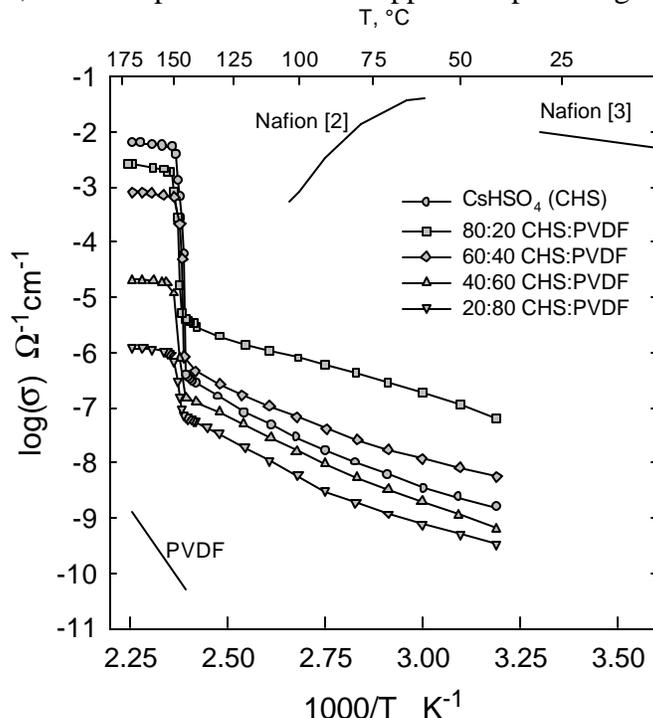


Fig. 2. Arrhenius plot of the conductivity of PVDF/CsHSO₄ composites of 0, 20, 40, 60, 80, 100 vol% CsHSO₄ upon heating. The conductivity of Nafion-117 [2,3] is plotted for comparison. The high temperature Nafion data were collected under 2×10^4 Pa H₂O partial pressure [2]. The low temperature data [3] were collected from a sample with a (fixed) water content of 21 moles H₂O per mole HSO₃.

In order to improve the homogeneity of the composite membranes several, more polar polymers were investigated, the first of these being poly(dicyclopentadiene). Poly(dicyclopentadiene) is a polymer for which excellent polymerization catalysts have been developed. Although the polar nature led to good mechanical contact between the solid acid particles and the polymer, the challenge of obtaining homogeneous composites remained. The polymerization process is extremely rapid, and results in the expulsion of the solid acid from any mixture containing it and the monomer. Attempts to perform the polymerization under pressure resulted in the expulsion of the fluid monomer. The most promising method developed was to blend mixtures of the solid acid, the catalyst (or initiator) and an inhibitor (to slow down the subsequent polymerization) and, from this

mixture of solids, press a high density pellet. The fluid monomer was then allowed to soak into the remaining pores of the pellet, yielding a sample with a solid acid loading [in this case $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$] as high as 90 vol % (not shown). The conductivity was within approximately one order of magnitude of that of the solid acid alone. As in the case of the composites comprised of polyvinylidene fluoride and CsHSO_4 , the superprotonic transition in $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ was generally unaffected by the presence of the polymer matrix material. Attempts to utilize these composites as electrolytes in fuel cells were hindered by the difficulty in attaching electrodes to these free-standing membranes. In one case, however, a stable, open circuit voltage of 1.01 V was obtained from a composite comprised of poly(DCPD) and CsHSO_4 .

Composites formed using CsHSO_4 and one of several commercial resins or silicone were also fabricated (Types 4 – 9). Fabrication in most cases involved mixing the solid acid and the resin components, then applying the appropriate heat treatment to induce polymerization / curing. It was hoped that by milling together all solid components, homogeneity would be enhanced. In most cases, mechanically robust composites could be obtained if polymer contents were 50 vol % or higher, but this led to a significant reduction in conductivity, Figure 3. In the case of the 2-part epoxy, Devcon, the solid acid inhibited the hardening of the resin. Despite the milling step, we again encountered difficulty in fabricating homogeneous materials with a uniform distribution of components and reproducible properties. In addition, application of electrodes to these free-standing membranes was again problematic. Our preferred method of cold-pressing the electrode materials onto the electrolyte could not be utilized because this typically caused the membrane to crack. The highest open circuit voltage measured for this class of composites was 0.90 V, obtained from the material fabricated from silicone and CsHSO_4 .

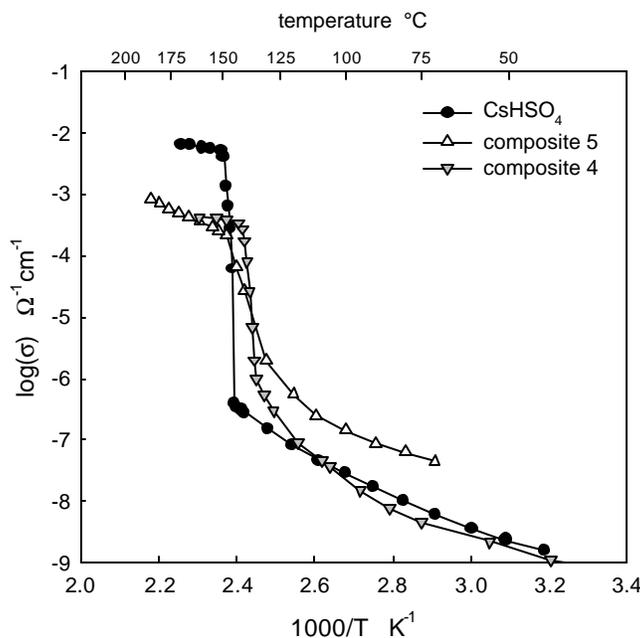


Fig. 3. An Arrhenius plot of the conductivity of CsHSO_4 alone and of two polymer/ CsHSO_4 composites; polymeric material and fabrication procedures as described in Table 1.

To order to surmount the difficulty we encountered in preparing homogeneous composites, an alternative approach, utilizing pre-formed, free-standing matrix materials, was pursued. In this case, composites were fabricated by melting the solid acid and allowing it to fill the pores of pre-formed porous structures. This process, employed with porous Kevlar, silica and zirconia, resulted in composites with excellent homogeneity, and where examined, good reproducibility in electrical properties, Figure 4. Because of the impossibility of cold-pressing electrodes onto these membranes without inducing fracture, an new electrode deposition method was utilized. Carbon supported platinum was suspended in acetone and painted onto either side of the membrane. The highest open circuit voltage measured for this class of composites was 1.12 V, obtained from the material fabrication from silica filter paper and CsHSO₄.

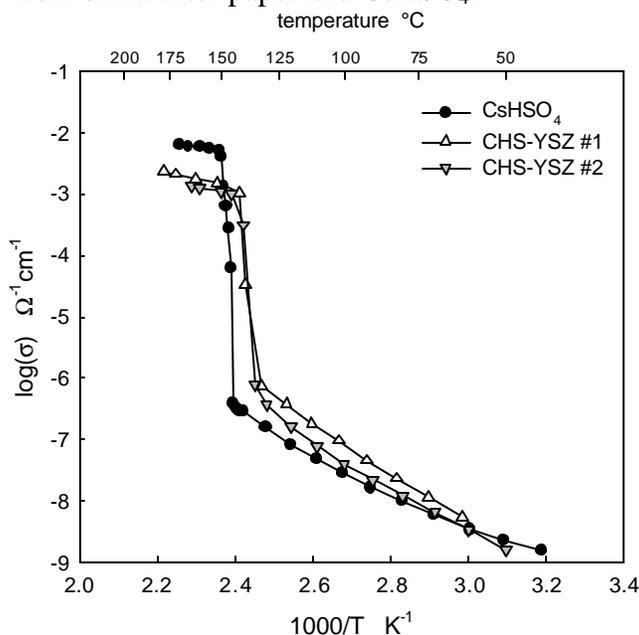


Fig. 4. An Arrhenius plot of the conductivity of CsHSO₄ alone and of ~30 vol % CsHSO₄ with yttria stabilized zirconia; two different samples characterized.

In sum, many, many avenues can be pursued for fabricating composite electrolytes with good mechanical properties, however, none emerged as a clear solution to the present challenge. Because single component membranes (i.e. those containing the solid acid alone) without a supporting matrix have higher conductivity than composites, and because solid acids could be fabricated in dense, impermeable form, first generation membranes for subsequent MEA development consisted simply of the solid acid CsHSO₄. Impermeability could only be achieved by utilizing rather thick membranes, 1 – 1.5 mm, and, ultimately, to process very thin membranes, which will be required for obtaining high power densities, composite membranes will likely be necessary. It is noteworthy that in no case examined did the matrix material interfere with the superprotonic transition of the solid acid.

Fuel Cell Performance

MEA Fabrication: General

Several routes have been pursued for developing electrocatalyst or electrode/electrolyte/catalyst layers (EECLs) and attaching such layers to the electrolyte membrane. These include:

- 1) melting a thin layer of solid acid onto a commercial electrode
- 2) painting a dispersion of EECL components onto a dense solid acid membrane
- 3) simultaneous cold-pressing the EECLs and membrane materials to high density

The most successful of these has proven to be the third. In order to obtain high porosity in the EECL a volatile organic (naphthalene) is incorporated into the EECL mixture and subsequently allowed to evaporate and leave behind open pores. The fuel cell polarization curves obtained from a single cell MEA in which CsHSO₄ alone served as the electrolyte are presented in Figure 5. The MEA was fabricated by sandwiching CsHSO₄ between two electrocatalysis layers comprised of CsHSO₄, Pt black, carbon black and a volatile organic in a mass ratio of 6:10:1:1 (approximate volume ratio of 4:1:3:2 and Pt loading of 18 mg/cm²). These layers were, in turn, placed between two sheets of porous, graphite current collectors. The entire assembly was uniaxially pressed at 490 MPa, to yield a dense electrolyte membrane 1.4 mm in thickness with good mechanical contact to the electrocatalyst layers. Upon heating to the measurement temperature, 160°C, the naphthalene in the electrode evaporated. Fuel cell polarization curves were collected at slightly elevated temperatures from MEAs placed in a standard graphite test station in which H₂O saturated O₂ and H₂O saturated H₂ were fed to the cathode and anode, respectively. After an initial measurement was made, the reactant gases were shut-off, the MEA flushed with argon, and then held at temperature under stagnant air. After 18 hours the reactant gases were re-introduced into the electrode compartments and a second fuel cell measurement made.

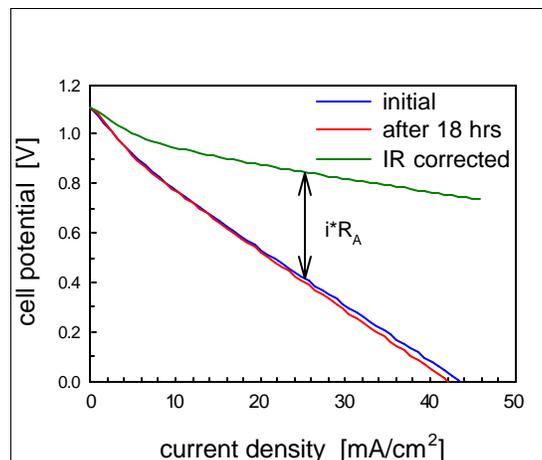


Fig. 5. Fuel cell polarization curve obtained from CsHSO₄ operated under an H₂/O₂ configuration at 163°C. Fuel and oxidant gases at 1 atm pressure, and containing 3% H₂O. Platinum loading of 18 mg/cm² and electrolyte thickness of 1.4 mm.

The data in Figure 5 show an open circuit voltage of 1.11 V (compared to an expected Nernst value of 1.22 V), and a maximum current at short circuit of 44 mA/cm² for the first measurement. The polarization curve is slightly reduced for the second measurement, and the reasons for this are discussed below. The type of performance shown in Figure 5, which corresponds to a maximum power density of ~ 11mW/cm², was obtained very reproducibly. The high open circuit potential (high as compared to typical polymer electrolyte fuel cell systems) was particularly reproducible. Attempts to improve the power densities, through either thinning the electrolyte or modifying the electrocatalyst layer, were not successful. Attempts to lower the Pt loading, however, while maintaining the observed performance, were moderately successful, as described below.

Platinum loading

Two approaches have been utilized to reduce the platinum content in our MEAs. In the first, the total amount of material in the electrocatalyst layer is reduced, without changing the processing methodology, or the relative ratios of the components in the layer. In Figure 6 the results from fuel cells in which the Pt loadings were 38, 9.5 and 3.8 mg/cm² respectively are shown. The measurements were made at 150°C and the cathode and anode gases air and hydrogen, respectively, utilizing membranes 1.9 mm in thickness. It is evident that the Pt loading as low as ~ 4 mg/cm² yield fuel cell performance that is comparable to that obtained using almost 10 times as much Pt. These results suggest further reductions in Pt content can be achieved.

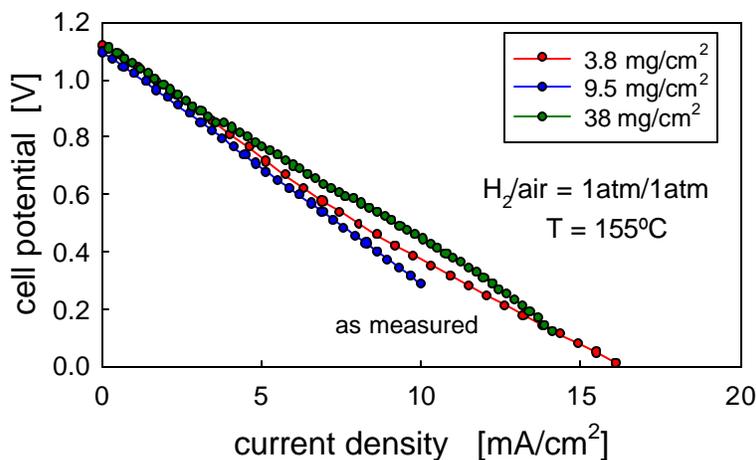


Fig. 6. Fuel cell polarization curves measured from pure CsHSO₄ membranes, 1.9 mm in thickness with Pt loadings as indicated. Data in Figs. 5 and 6 are not directly comparable because of differences in gases and membrane thicknesses.

Reductions in Pt loadings beyond 3.8 mg/cm² are not readily achievable by the simultaneous cold-pressing technique outlined above because it is difficult to obtain thin, uniform electrocatalyst layers. An alternative approach involves the use of similar electrocatalyst mixtures which are then dissolved/suspended into a solvent and then painted onto the carbon paper that serves as the current collector. Using the “standard mixture” with CsHSO₄ : Pt : carbon black : naphthalene = 6 : 10 : 1 : 1 by weight, MEAs

with three different platinum loadings were fabrication: 8.1, 3.6, and 2.3 mg/cm². In addition, one mixture containing excess naphthalene (6.4 : 10 : 0.8 : 4) and another deficient in the solid acid (2 : 10 : 0.8 : 0.8) were utilized

The fuel cell polarization curves obtained from MEAs prepared with these electrodes are presented in Figure 7 (the electrolyte in all cases was 1.42-1.46 mm in thickness, and the bulk of the differences in performance is attributable to differences in electrode behavior). The most important result to note is that we have been able to reduce the Pt loading from 18 mg/cm² to ~ 8 mg/cm² without a significant reduction in performance. Similar results were obtained for pressed pellets (results not shown), for which polarization curves were essentially independent of Pt loading over the range ~ 8 – 20 mg/cm², and were more sensitive to the details of the processing of the particular sample examined. Reduction of the Pt loading beyond ~ 8 mg/cm² will require optimization of the electrocatalyst layer composition. It is evident that for a given composition (“standard” results), the performance decreases with decreasing Pt content (for Pt content less than 8.1 mg/cm²). Introduction of excess volatile organic content appears to improve electrode performance, presumably by providing a more open electrode structure, whereas reduction of the solid acid content appears to slightly degrade the performance. Further experimentation will surely result in platinum contents which are competitive with conventional fuel cells. It should also be noted that high open circuit voltages are reproducibly obtained in these experiments.

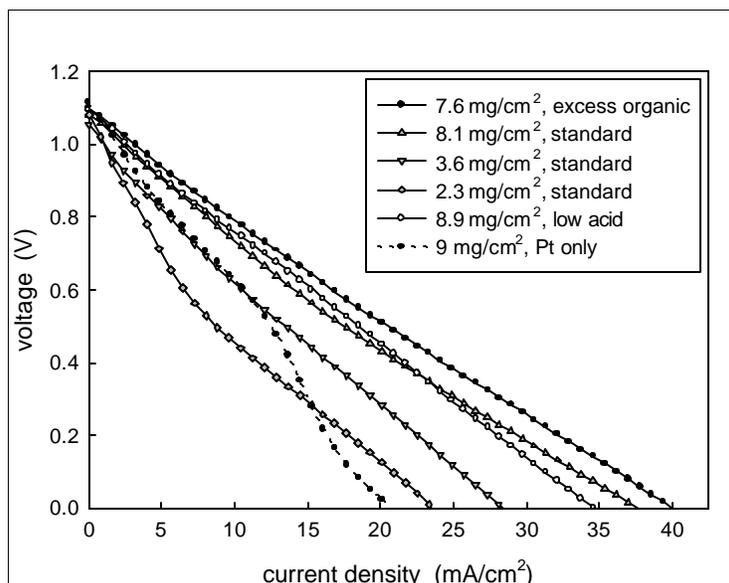


Fig. 7. Fuel cell polarization curves obtained from CsHSO₄ based MEAs with painted electrodes, and with Pt loadings as indicated. Electrolyte thickness of 1.42-1.46 mm, temperature of 150-160°C, with humidified O₂ and humidified H₂ fed to the cathode and anode respectively.

Direct Methanol Fuel Cells

Single cell fuel cells for direct methanol experiments were fabricated using CsHSO₄ alone as the electrolyte. The electrocatalyst was platinum black (not Pt-Ru as is standard for DMFCs), which was pressed onto the membrane in a single step procedure.

As reported earlier, a volatile organic was incorporated into the electrocatalyst layer so as to ensure a high degree of porosity and thus vapor access to the electrolyte. The MEA was placed in a standard fuel cell test station, and the temperature set to 163°C. Methanol and water were fed to the anode compartment by passing argon over heated flasks of the two liquids. The methanol to water molar ratio was not monitored, but is estimated at 1:1. Water saturated oxygen was fed to the cathode compartment. The membrane was 1 mm in thickness and the platinum catalyst loading 18 mg/cm². Results of the fuel cell test are presented Figure 8. While the power density of the solid acid fuel cell does not yet compare with that of polymer based fuel cells, it has clearly been shown that these new membrane materials hold significant promise in the DMFC arena.

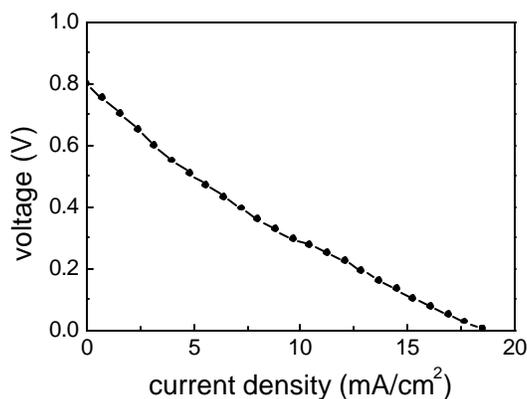


Fig. 8. Fuel cell polarization curve obtained from CsHSO₄ operated under vaporized methanol at 163°C. See text for further experimental details.

Alternative Catalysts

There are several reasons to consider alternatives to Pt for fuel cell catalysts, including cost and susceptibility to CO poisoning. In the case of sulfate and selenate based solid acids, it is demonstrated below that Pt is particularly undesirable in the anode because of its detrimental interaction with the membrane. Accordingly, WC and Ni-Al were examined as potential anode catalysts (while retaining Pt at the cathode). In all cases, single cell membrane-electrode-assemblies were fabricated by uniaxially pressing the electrolyte and two electrocatalyst layers between carbon paper electrodes at 71 kpsi and at room temperature. Polarization curves were measured while flowing humidified H₂ to the anodes and humidified O₂ to the cathodes, at temperatures between 148 and 158 °C, implying a theoretical open circuit voltage of ~1.22 V. Details of the fabrication procedures, catalysts properties and MEA performance are summarized in Table 2.

The results of Table 2 show that we have been able to obtain high open circuit potentials from alternative catalysts, however, overall fuel cell performance is not as good as that obtained using Pt. It may well be possible to improve the performance of WC based electrocatalyst layers by utilizing high surface area material, comparable to that used in the Pt based electrodes.

Table 2. Fabrication and performance characteristics of selected fuel cells.

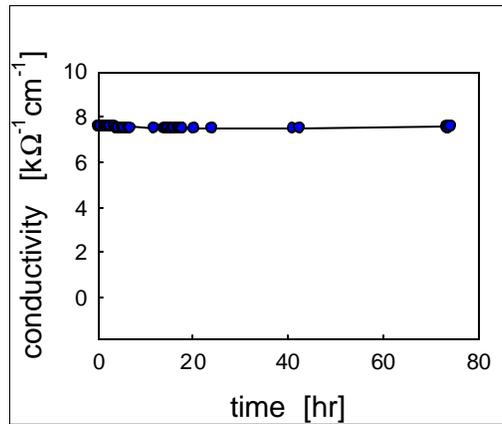
Cell	t, mm	cathode (catalyst surf. area / part size)	Pt, mg/cm ²	anode (catalyst surf. area / size)	catalyst, mg/cm ²	Power, mW/cm ²	OCV, V
1	1.33	standard mix	15	standard mix	15	12	1.12
2	1.39	Pt black, ~ 30 m ² /g	31	WC, ~ 1.3 m ² /g	126	2.4	1.06
3	1.42	Pt black, ~ 30 m ² /g	31	WC, ~ 1.3 m ² /g	135	4.3	1.00
4	1.42	Pt black, ~ 30 m ² /g	31	Ni-Al, < 7 μm	36	0.9	1.00
5	1.40	modified mix	21	modified mix	21	5.8	1.02
6	0.70	Pt black, ~ 30 m ² /g	31	Pt black	31	3.7	1.08

For cells 1-5, the electrolyte was CsHSO₄, whereas for Cell-6 it was the mixed sulfate phosphate Cs₂(HSO₄)(H₂PO₄). The standard electrocatalyst mix (at either cathode or anode) is as reported previously: Pt, CsHSO₄, carbon black and naphthalene in a 10 : 6 : 1 : 1 weight ratio. The modified mix contains the silicate solid acid, NaCaHSiO₄ rather than CsHSO₄, but all other components are unchanged.

Chemical Stability and Mechanical Suitability of Solid Acids

To address the question of long term stability of solid acid compounds as fuel cell electrolytes, the behavior of these materials under several types of conditions must be understood: under water saturated atmospheres at elevated temperatures (> 100°C); under oxidizing conditions; under reducing conditions; and under conditions of thermal cycling through the phase transition.

In Figure 9 the conductivity of CsHSO₄ as measured under H₂O saturated argon is shown. It is evident that even after tens of hours of exposure, the electrolyte conductivity is unchanged, and thus that vapor phase water does no damage to the solid acid.

**Fig. 9.** Conductivity of CsHSO₄ under humidified argon at 160°C.

The isothermal weight change of CsHSO₄ at 160°C under oxidizing conditions (flowing O₂, 20 cc/min) is shown in Figure 10(a). As would be expected, the solid acid is completely stable under these conditions. In contrast, the weight change under reducing conditions (flowing H₂, 20 cc/min), also at 160°C, is measurable after 10 hrs, ~ 0.03

wt%, and is highly exacerbated in the presence of Pt catalyst material (35 wt%), Figure 10(b), with a weight loss of almost 5% after a similar period of exposure.

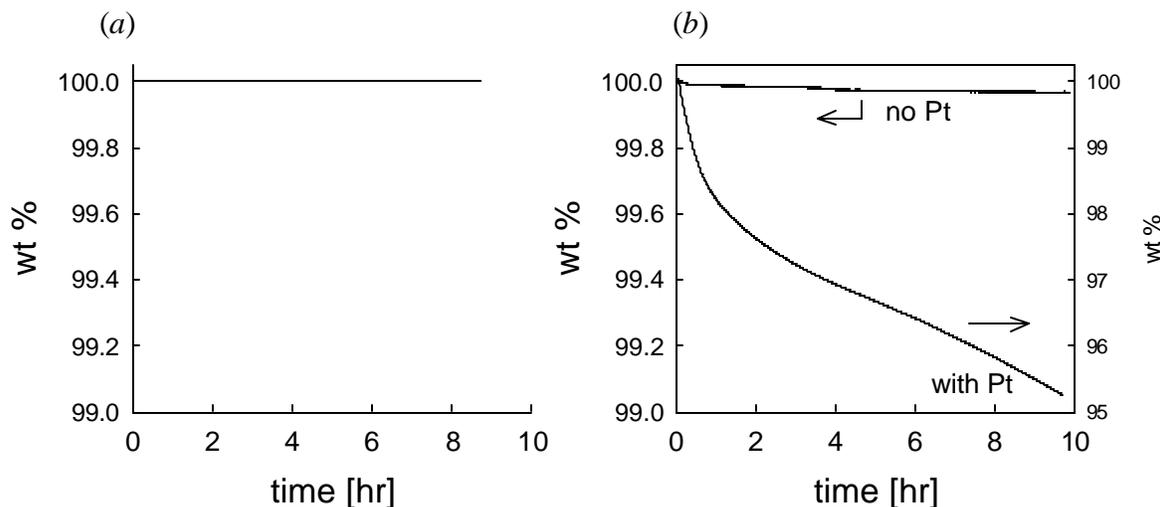


Fig. 10. Weight change of CsHSO₄ at 160C under (a) flowing oxygen (20 cc/min) and (b) flowing hydrogen (20 cc/min) both with and without Pt catalyst. Note the difference in weight % scale for the two measurements in (b).

The weight changes observed in Figure 10(b) can be attributed to the reduction of the sulfur in cesium hydrogen sulfate according to reaction (1)



From the differences in behavior of CsHSO₄ with and without Pt catalyst, it is apparent that reaction (1) is catalyzed by the metal. The hydrogen sulfide produced by this reaction can then poison the Pt, causing a very severe, but reversible loss in fuel cell performance. This poisoning is responsible for the slight difference in the two (uncorrected) polarization curves shown in Figure 5. During continuous fuel cell operation and continuous exposure to H₂, degradation was more rapid than reflected in Figure 5 (for which the MEA was exposed to stagnant air).

An attempt was made to discover alternative catalyst materials that would retain performance in fuel cell anodes, but be inactive towards reaction (1). Figure 11 shows the isothermal weight loss curves for CsHSO₄ mixed with several such alternative materials. It is evident that potential anode catalysts, Ni-Al, Pd, Ir, Ru and Au, in addition to Pt, induce significant weight loss in reducing atmospheres, and it appears unlikely this approach will succeed. Accordingly, we then examined a broad range of solid acids, Figure 12, with the aim of discovering a compound that was not susceptible to reduction. Here, we find that all solid acids containing either S or Se, both of the form MHXO₄ and of the M₃H(XO₄)₂, where M = alkali metal or NH₄, and X = S or Se, undergo reduction and weight loss. The reduction reactions can be written in the most general sense as



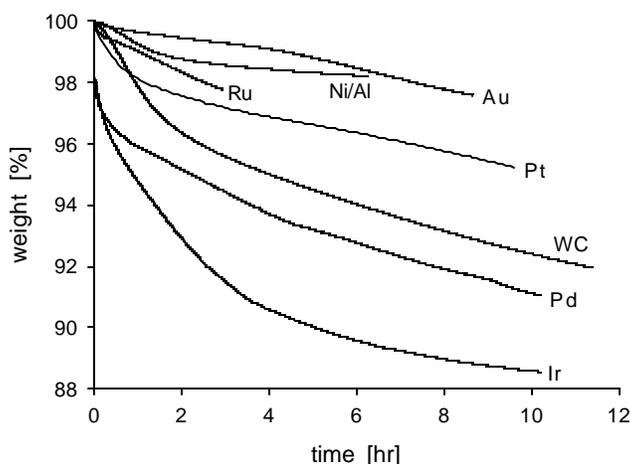


Fig. 11. Weight change of CsHSO_4 at 160°C under flowing hydrogen (20 cc/min) with several candidate fuel cell catalysts. Catalyst content 35 % by weight.

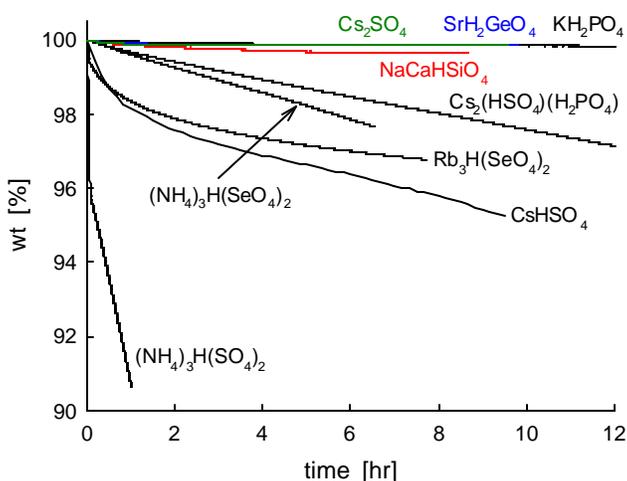


Fig. 12. Weight change of several solid acids at 160°C under flowing hydrogen (20 cc/min) in the presence of Pt catalyst (35 wt%). Data for Cs_2SO_4 , SrH_2GeO_4 and KH_2PO_4 coincide.

For those solid acids of silicates, phosphates and germanates, it is evident that reduction does not occur under these simulated fuel cell conditions. This reflects the much lesser tendency of the compounds H_3P , SiH_4 and GeH_4 , to form, as compared to H_2S and H_2Se . While these results are a promising first step towards developing stable solid acids for fuel cell applications, it must be noted that none of these stable alternatives exhibits superprotonic conductivity. To date, no solid acids combining the features of high conductivity and excellent stability have been identified.

To address the question of the impact of the monoclinic to tetragonal phase transition in CsHSO_4 on its mechanical suitability as a fuel cell electrolyte, a thermal cycling experiment was carried out. Specifically, an MEA was fabricated [31 mg/cm² Pt, standard electrode mix, 1.44mm membrane] and the open circuit voltage continuously

monitored as the temperature was cycled between 107 and 150°C. For comparison, the open circuit voltage for a similar MEA, held isothermally at 153°C was also monitored as a function of time. The results of these experiments, Figure 13, reveal that the voltage obtained from CsHSO₄ oscillates noticeably with time, but that these oscillations are not connected with the phase transition. We believe the oscillations are due to the reaction of H₂ with sulfur at the surface of the platinum catalyst particles.

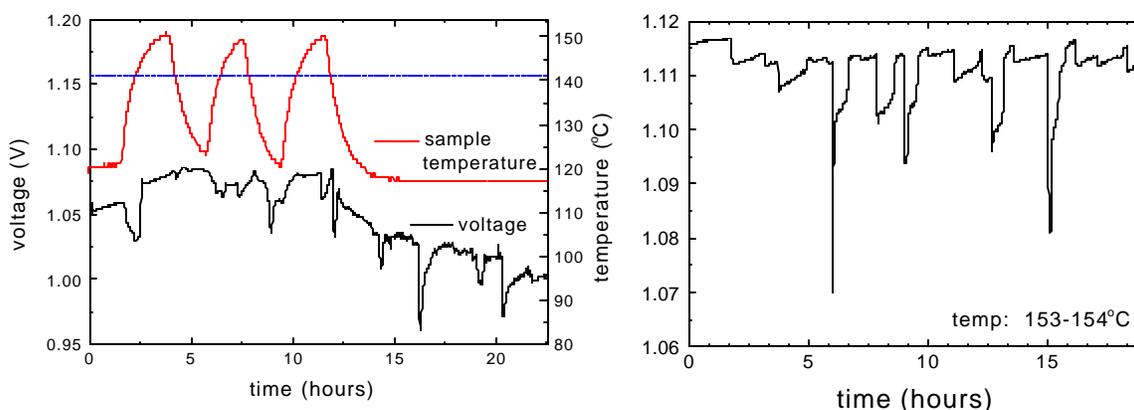


Fig. 13. Open circuit potential measured from CsHSO₄ based fuel cells in H₂(H₂O) / O₂(H₂O) configurations as a function of time; (a) with thermal cycling through the phase transition ($T_c = 141^\circ\text{C}$ indicated by horizontal blue line) and (b) isothermally at $\sim 153^\circ\text{C}$.

Conclusions

The key objectives of this research were to identify optimal solid acid / polymer composite materials and to demonstrate their utility in fuel cell applications. At the outset, higher risk was associated with the latter objective in that it was not clear whether a water soluble material could possibly be used in a fuel cell in which H₂O is generated as a by-product. At this stage it has been clearly demonstrated that water solubility is not a detrimental property for fuel cell applications nor are there undesirable losses in mechanical integrity at the phase transition. However, the catalysis of the reduction of sulfur and selenium in sulfate and selenate solid acids, respectively, by platinum has presented itself as a serious concern. Alternative catalysts, such as tungsten carbide, were shown to similarly induce reduction of sulfur in CsHSO₄. The problem of sulfur (or selenium) reduction has proved vexing indeed. The development of optimized membrane electrode assembly structures awaits the discovery of alternative solid acids with greater chemical stability (materials that exclude S and Se). Composite membranes, containing a mechanically stiff component in addition to the solid acid, may enable the development of free-standing, robust membranes. The most promising result along those lines has been the performance of the YSZ-CsHSO₄ composites (YSZ = yttria stabilized zirconia).

References

1. S. M. Haile, D. A. Boysen, C. R. I. Chisholm and R. B. Merle, "Solid Acids as Fuel Cell Electrolytes," *Nature* **410** 910-913 (2001).
2. J.J. Sumner, S.E. Creager, J.J. Ma, D.D. DeMarteau, *J. Electrochem. Soc.* **145**, 107 (1998).
3. R. T. C. Slade, A. Hardwick, and P. G. Dickens, *Solid State Ionics* **9 & 10**, 1093-1098 (1983).