

## **New Proton Conducting Solid Sulfide Membranes for Intermediate Temperature Fuel Cells**

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### **Objectives**

- Investigate a new class of inorganic sulfide-based proton conducting membranes for hydrogen fuel cell applications.
- Produce anhydrous solid membranes having minimal fuel crossover capability and address many of the problems associated with current hydrogen fuel cell technologies.
- Optimize membrane materials to yield high proton conductivities ( $10^{-3}$  to  $10^{-1}$  S/cm) in the intermediate temperature range of 125°C to 300°C.
- Demonstrate performance, thermal stability, and chemical stability to H<sub>2</sub>O and O<sub>2</sub> in a typical fuel cell setup at operating temperatures.

### **Technical Barriers**

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- F. Heat Utilization
- O. Stack Material and Manufacturing Cost
- R. Thermal and Water Management

### **Approach**

- Synthesize new protonated sulfides (thio-acids).
- Synthesize membrane materials from thio-acids; final product may be a glass, glass/ceramic, or ceramic material with stable sulfur-hydrogen bonds.
- Measure the proton conductivity between -70°C and 500°C.
- Determine the thermal stability.
- Determine the chemical stability with respect to H<sub>2</sub>O and O<sub>2</sub>.
- Determine electrochemical properties, including reduction and oxidation potentials, and cyclic voltammetry.
- Cooperatively fabricate and test membrane electrode assemblies (MEAs) using the most promising membranes. This is to be done in partnership with an external company specializing in fuel cells.

### **Accomplishments**

- The hydrosulfides of potassium, rubidium, cesium, and barium have been synthesized. Proton conductivity of  $10^{-9}$  to  $10^{-6}$  S/cm has been achieved in the temperature range of 25°C to 200°C.

- Mixed hydrogen alkali thiogermanates have been synthesized with the adamantane-like  $\text{Ge}_4\text{S}_{10}^{4-}$  anion. Proton conductivity of  $10^{-10}$  to  $10^{-5}$  S/cm has been achieved in the temperature range of 50°C to 225°C.
- A new class of anhydrous proton conducting materials has been recently synthesized (patent protection pending). These materials achieve fast proton conductivity ( $10^{-3}$  to  $10^{-2}$  S/cm) from 65°C to 270°C.

### Future Directions

- Test the recently developed fast proton conducting anhydrous membrane materials (patent protection pending) under relative humidity (RH) conditions as subject by a fuel cell environment. Build MEAs using these membrane materials in cooperation with UTC Fuel Cells. Continue to synthesize and characterize structurally similar membrane materials.
- Synthesize perovskite and distorted perovskite type  $\text{AB}_2\text{S}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{etc.}; \text{B} = \text{Zr}, \text{Ce}, \text{etc.}$ ) precursor materials. These materials may then be doped with trivalent anions ( $\text{Y}, \text{La}, \text{etc.}$ ) and reacted with liquid  $\text{H}_2\text{S}$  to produce proton conducting membranes.
- Synthesize adamantane-like  $\text{A}_x\text{Ge}_4\text{S}_{10}$  ( $1.5 \leq x < 2$ ) and  $\text{M}_y\text{Ge}_4\text{S}_{10}$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}; 3 \leq y < 4$ ) precursor materials. These materials may then be reacted with liquid  $\text{H}_2\text{S}$  to produce proton conducting membranes.

### Introduction

Hydrogen-based fuel cells are becoming increasingly popular as an alternative energy source for automobiles. This is evident by the recent presidential Hydrogen Fuel Initiative to reverse America's growing dependence on foreign oil by developing the technology needed for commercially viable hydrogen-powered fuel cells. At the heart of the fuel cell is the proton exchange membrane (PEM), which transports protons from the anode to the cathode while providing electronic insulation between them. Currently, there are many types of electrolyte materials for application as PEMs. However, each material has specific limitations restricting its usefulness for application to fuel cells.

With these current fuel cell membrane materials, there remains a temperature region between 125°C and 300°C in which currently no one membrane can provide optimum performance. In this regime, we propose the use of sulfide-based proton conducting membranes. In general, these membranes are being developed to be anhydrous in nature, thermally stable up to 300°C, and chemically stable with respect to  $\text{H}_2\text{O}$  and  $\text{O}_2$ . Being solid in nature, these membranes are not expected to exhibit fuel cross-over problems. Additionally, proton conductivities of these

membranes are expected to be orders of magnitude higher than their oxide counterparts, assuming they follow the trend exhibited by monovalent cations such as Li and Ag in chalcogenide versus oxide host materials (Angell 1992). Well-ordered crystalline structures exhibiting fast proton conductivity may also be developed for sulfide materials analogous to those previously reported for various oxide materials (e.g. Huang 1995, Haile 2001).

### Approach

Various precursor materials, including oxides, hydroxides, sulfides, fluorides, chlorides, bromides, and iodides, that are capable of forming thio-acids in liquid  $\text{H}_2\text{S}$  solutions have been identified. As an example, the reaction of  $\text{GeO}_2$  or  $\text{GeS}_2$  with liquid  $\text{H}_2\text{S}$  at room temperature produces the thio-acid  $\text{H}_4\text{Ge}_4\text{S}_{10}$ . Membranes may be produced by tailoring precursor materials to obtain structural ordered reaction products with high proton conductivities. Taking various alkali or alkaline earth modified glassy or crystalline materials and reacting them in a liquid  $\text{H}_2\text{S}$  solution is one way to accomplish this.

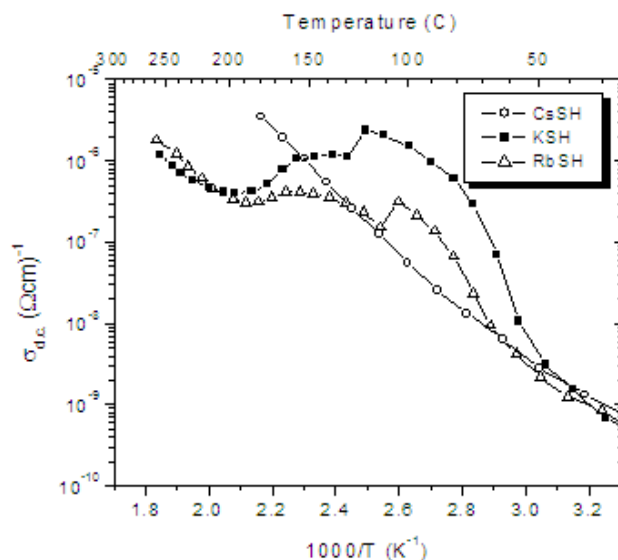
Proton conductivity in the protonated reaction products, i.e. membrane materials, is being

determined through impedance measurements as a function of temperature and frequency. Direct current polarization experiments have been used to determine the electronic versus ionic conductivity of these materials. Physical properties of the protonated materials have been determined, including decomposition, sublimation, and crystallization. Structural comparisons have been used to examine stability with exposure to  $\text{H}_2\text{O}$  and  $\text{O}_2$ .

Conductivity measurements under RH environments are underway. Additionally, a cooperative effort to fabricate and test MEAs using our most promising membranes is being carried out in partnership with UTC Fuel Cells.

## Results

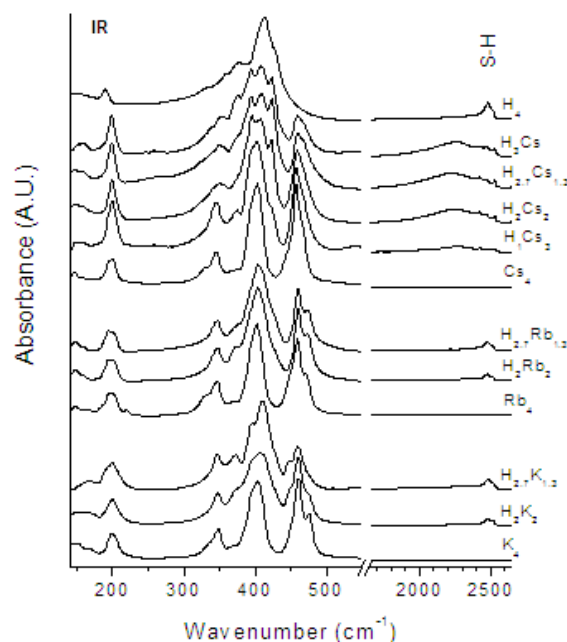
Many protonated sulfide materials have been produced from liquid  $\text{H}_2\text{S}$  reactions with various precursor materials. The conductivities of these protonated materials have been measured with reference to alkali and/or electronic base conductivity. Figure 1 illustrates proton conductivity for alkali hydrosulfides of K, Rb, and Cs. These materials have low conductivities ( $< 10^{-6}$  S/cm) and average thermal stability ( $< 200^\circ\text{C}$ ). Additionally, the alkali hydrosulfides readily react with  $\text{H}_2\text{O}$  and  $\text{CO}_2$  under atmospheric conditions, precluding them from being successful candidates for MEAs.



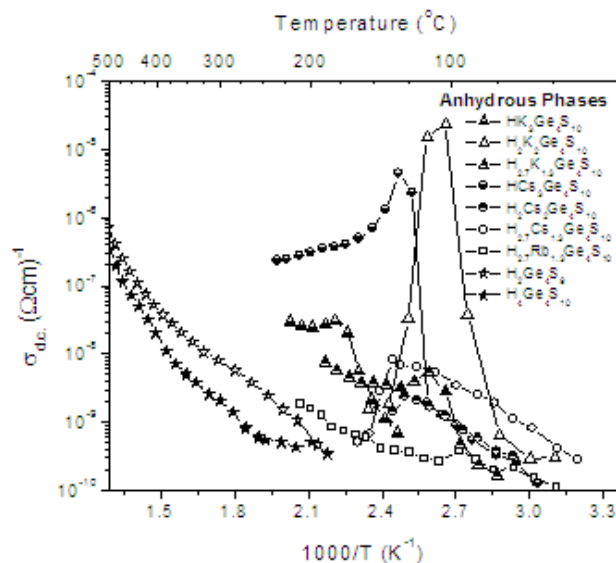
**Figure 1.** Proton Conductivity of Alkali Hydrosulfides of KSH, RbSH, and CsSH

Another class of protonated materials is based on the crystalline  $\text{Ge}_4\text{S}_{10}^{4-}$  anion. Figure 2 shows the infrared (IR) vibrational spectra illustrating mixed hydrogen and alkali terminal units. Peaks observed below  $550\text{ cm}^{-1}$  represent vibrational modes of the  $\text{Ge}_4\text{S}_{10}^{4-}$  structural unit cage, whereas the peaks around  $2500\text{ cm}^{-1}$  represent the S-H stretching mode. The broad mode  $\sim 2250\text{ cm}^{-1}$  for the hydrogen cesium systems indicates the presence of intercalated  $\text{H}_2\text{S}$ ; this is analogous to intercalated  $\text{H}_2\text{O}$  as required for many fast proton conducting materials (e.g. Nafion<sup>®</sup>). Figure 3 shows typical conductivity spectra of these hydrogen alkali thiogermanate phases. For the phases with higher alkali content ( $x \geq 2$ ), a discontinuity from Arrhenius behavior is typically observed with higher proton conductivity ( $\sim 10^{-5}$  S/cm), suggesting a well-ordered structure capable of effective proton transport. At higher temperatures ( $> 175^\circ\text{C}$ ), these phases start decomposing by losing mobile proton species, and as a result, the conductivity decreases. Further work is underway to optimize these materials for proton conductivity and thermal stability.

Figure 4 shows examples of proton conductivity for some of the recently designed anhydrous membrane materials (patent protection pending).



**Figure 2.** IR Spectra of Hydrogen Alkali Thiogermanates

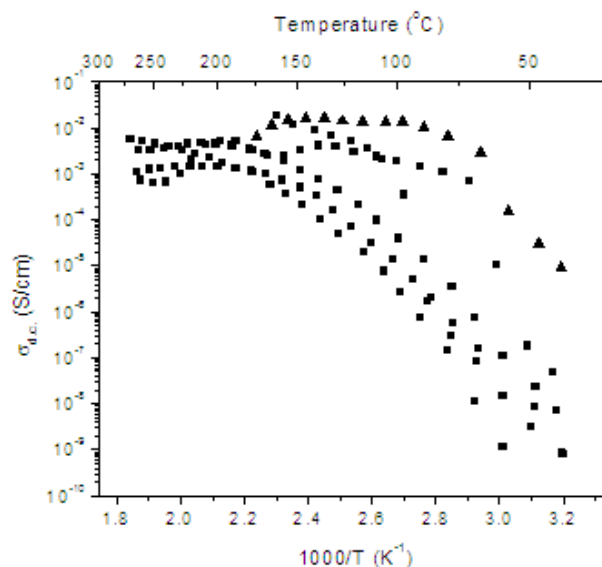


**Figure 3.** Typical Proton Conductivity for Hydrogen Alkali Thiogermanates

Fast proton conductivity is observed ( $10^{-3}$  to  $10^{-2}$  S/cm) from 65°C to 270°C. These new protonated materials illustrate the viability and promise of alternative proton conducting membrane materials for the intermediate temperature range of 125°C to 300°C. RH testing and MEA fabrication and testing are currently underway with these new anhydrous proton conductors.

### Conclusions

- A new synthesis route for producing thio-acids, hydrosulfides, and sulfides has been identified and patented.
- The structure, conductivity, thermal and chemical stability of many protonated materials have been investigated; many more are being pursued.
- Structurally ordered membrane materials have been identified as potential fast proton conductors, and effort is underway to produce these new protonated materials.
- Recently, one of these new classes of fast proton conducting materials have been identified and synthesised for the first time (patent protection pending).



**Figure 4.** Fast Proton Conductivity for Recently Developed Anhydrous Membrane Materials

- Preliminary ionic conductivity values as high as  $10^{-3}$  to  $10^{-2}$  S/cm have been realized from 65°C to 270°C; these materials are thus classified as fast proton conductors.

### References

1. Martin, S.W., Poling, S.A., Sutherland, J.T., Design and Development of New Glass-Ceramic Proton Conducting Membranes. *DOE Hydrogen Program Annual Review, Proceedings (2002)*: NREL/CP-610-32405.
2. Angell, C.A. 1992. Mobile Ions in Amorphous Solids. *Annual Review of Physical Chemistry*, 43:693-717.
3. Huang, P. and Petric, A. 1995. Electrical Conduction of Yttrium-doped Strontium Zirconate. *J. Mater. Chem.*, 5:53-56.
- 4. Haile, S.M., Boysen, D.A., Chisholm, C.R.I., and Merle, R.B. 2001. Solid acids as fuel cell electrolytes. *Nature*, 410:910-913.

### FY 2003 Publications/Presentations

1. S.A. Poling, C.R. Nelson, and S.W. Martin, "Anhydrous proton conductivity in hydrogen

- alkali thiogermanates,” submitted to Solid State Ionics (2003), talk presented at the 14<sup>th</sup> International Conference on Solid State Ionics (2003)
2. J.T. Sutherland, S.A. Poling, C.R. Nelson, and S.W. Martin, “Formation reaction routes for the thiogermanic acids with  $\text{GeO}_2$  and  $\text{GeS}_2$  precursors,” to be submitted to Solid State Ionics, poster presented at the 14<sup>th</sup> International Conference on Solid State Ionics (2003)
  3. C.R. Nelson, S.A. Poling, and S.W. Martin, “Synthesis and characterization of potassium, rubidium, and cesium thiogermanate glasses,” to be submitted to the Journal of Non-Crystalline Solids
  4. J.T. Sutherland, S.A. Poling, R.C. Belin, and S.W. Martin, “Exploration of the  $\text{H}_2\text{S}$ - $\text{GeS}_2$  system,” to be submitted
  5. J.T. Sutherland, S.A. Poling, C.R. Nelson, and S.W. Martin, “ $\text{H}_2\text{S}$  synthesis route for high purity L.T. 3-D  $\alpha$ - $\text{GeS}_2$ ,” in press, Material Science Letters (2003)
  6. S.A. Poling, C.R. Nelson, J.T. Sutherland, and S.W. Martin, “Crystal structure of thiogermanic acid  $\text{H}_4\text{Ge}_4\text{S}_{10}$ ,” in press, Inorganic Chemistry (2003)
  7. S.A. Poling, C.R. Nelson, J.T. Sutherland, and S.W. Martin, “Proton conductivity in anhydrous and hydrous thiogermanic acids,” submitted to Solid State Ionics (2003)
  8. S.A. Poling, C.R. Nelson, J.T. Sutherland, and S.W. Martin, “Synthesis and characterization of the thiogermanic acids  $\text{H}_4\text{Ge}_4\text{S}_{10}$  and  $\text{H}_2\text{Ge}_4\text{S}_9$ ,” Journal of Physical Chemistry B 107 (2003) 5413-5418
- Special Recognitions & Awards/Patents Issued**
1. Synthesis and uses of Thio Acids, Steve W. Martin, Steven A. Poling, Jacob T. Sutherland, Iowa State University, ROI ISURF 2894, February 8, 2002. Provisional filing date of July 26, 2002.
  2. Record of invention for fast proton conductors, Iowa State University, ROI ISURF, July, 2003.
  3. Invited talk, 14<sup>th</sup> University Conference on Glass, “Preparation and Characterization of New Proton Conducting Glasses and Ceramics,” Rensselaer Polytechnic Institute, Troy, NY, August 13-15, 2003.