# Design and Development of New Glass-Ceramic Proton Conducting Membranes

Steve W. Martin*, Steven A. Poling, and Jacob T. Sutherland
Department of Materials Science and Engineering
Iowa State University, Ames, IA 50011

*Author to whom correspondence should be directed
e-mail: swmartin@iastate.edu
phone: (515) 294-0745.

## Abstract

A new class of proton conducting membranes for hydrogen fuel cell applications are being developed using thio-acids. These membranes are being designed to yield high proton conductivities ($10^{-6}$ to $10^{-3}$ S/cm), to be anhydrous, thermally stable, chemically stable to $H_2O$ and $O_2$ in a typical fuel cell setup, and have minimal fuel cross-over capability. New thio-acids are being synthesized to fulfill these goals. Thus far, conductivity values of $10^{-5}$ S/cm are achievable at ~500°C, along with excellent thermal and chemical stability in contact with $H_2O$ and $O_2$. Conductivities of $10^{-5}$ S/cm are also achievable from thio-acids intercalated with $H_2S$ at room temperature; however, these compounds decompose above room temperature to form the crystalline thio-acid counterparts.

## Introduction

Hydrogen-based fuel cells are becoming increasingly popular as an alternative to crude oil-based internal combustion engines. Specifically, hydrogen can be converted to electricity through the use of a $H_2$-$O_2$ fuel cell. The by-product of this type of a fuel cell is water, making this a "green" or environmentally friendly technology. At the heart of the fuel cell is the proton exchange membrane (PEM), which transports the proton from the anode to the cathode while providing electronic insulation between them. There are many types of electrolyte materials, each with specific limitations. Some of the most popular ones are polymer exchange membranes, phosphoric acid membranes, and solid oxide membranes. Polymer exchange membranes, or more specifically solid organic polymer poly-perflourosulfonic acids such as Nafion™, require hydration and this limits their operation to temperatures below 100°C. These electrolytes also suffer from fuel cross-over due to their porous hydrated nature and require the use of expensive platinum electrodes. Phosphoric acid membranes are typically operated from 150°C to 200°C. Being a liquid electrolyte, they suffer from membrane leakage and fuel cross-over problems. They also require the use of expensive platinum electrodes. Solid oxide membranes are typically operated between 700°C to 1,000°C, where the use of platinum as an electrode material can be reduced. This temperature range is used to achieve the desired oxide anion conductivity. These membranes being solid in nature do not suffer from fuel cross-over problems.

With these current fuel cell membrane materials, there remains a temperature region between ~200°C and ~700°C that currently no one membrane can provide for optimum performance. We propose the use of glass-ceramic proton conducting membranes (GCPCMs) to help fill this temperature performance regime. These membranes are being developed to be anhydrous in nature, thermally stable up to ~500°C, and chemically stable with respect to $H_2O$ and $O_2$. Being solid in nature, these membranes are not expected to exhibit fuel cross-over problems. Proton conductivities of these membranes are expected to be orders of magnitudes higher than their oxide counterparts, assuming they follow the trend exhibited by alkali cations such as Li and Ag in chalcogenide verses oxide host materials (Angell 1992).

In last year's work on this project, we have demonstrated that protons can be incorporated into $GeS_2$ and $B_2S_3$ host materials through reactions with $H_2S$ (Martin 2001). In this year's work, we have investigated the optimum chalcogenide host materials in terms of thermal and chemical stability into which the greatest concentration of protons can be incorporated. Thus far, $GeS_2$-based materials have been the most successful. Proton conductivity in the glasses and glass-ceramics has been determined through impedance measurements as a function of temperature and frequency. DC polarization experiments have been used to determine the electronic verses ionic conductivity of the samples; all data reported here is predominately ionic in nature. Physical properties of the glass-ceramic proton conducting materials have been determined, including decomposition, sublimation, crystallization, and glass transition temperatures. Structural comparisons have been used to examine stability with exposure to $H_2O$ and $O_2$.

## Experimental Section

### *Synthesis of GCPCMs*

Two routes of production have been developed to produce proton conducting chalcogenide materials. The first route involves batch melting the required elements at elevated temperatures in evacuated silica tubes. The resulting glassy materials are then reacted with $H_2S$ at a temperature to incorporate S-H bonds into the structure. The optimum reaction temperature and pressure has been determined to be at room temperature with the liquid vapor pressure of $H_2S$ (~267 PSIA). Reaction times for this route are long, on the order weeks to months in some cases. The second route of producing proton conducting materials is by producing thio-acids directly from commercial oxide compounds. This method involves reacting oxide precursors with liquid $H_2S$ at room temperature on a time scale on the order of weeks. In some cases, the resulting product is a thio-acid with the addition of chemi-or physisorbed $H_2S$. This product may be heated at a predetermined elevated temperature to drive off the adsorbed $H_2S$ and to reduce the material back to a crystalline thio-acid with little incorporated $H_2S$.

Using the first route, glassy $GeS_2$, 0.14 $Ga_2S_3$ + 0.86 $GeS_2$, 0.29 $Al_2S_3$ + 0.71 $GeS_2$, and 0.05 $MoS_2$ + 0.95 $GeS_2$ materials have been synthesized in evacuated silica tubes. These materials were then reacted at room temperature for extended time periods with $H_2S$ at its vapor pressure which maintains liquid $H_2S$ in contact with the precursor. All reactions took place in stainless steel reaction vessels sealed with Teflon o-rings; in each, a sample is contained by an alumina tube. With the second processing route, new thio-acids were produced directly from the corresponding oxide, $GeO_2$, for example, and then used as proton source precursors for thermal and chemically stable GCPCMs. Optimized processing conditions to produce the crystalline thiogermanic acid $H_2Ge_2S_5$ involve starting with commercial $GeO_2$ and performing room temperature reactions with liquid $H_2S$. A reaction time of two weeks is typical. The resulting product, $H_2Ge_2S_5 \bullet nH_2S$, may be reduced thermally to the thio-acid analog.

***Conductivity Measurements***

Impedance values of the GCPCMs were determined by using a Gamry PC4/750 potentiostat on pressed powder samples. Hardened steel electrodes pressed into a Teflon sleeve sealed the powder samples for temperatures up to 300°C. For temperatures up to 550°C, an alumina tube was used to contain the powder samples. 60mg to 100mg of each sample was used for the ¼ inch inside diameter Teflon sleeves or alumina tubes. Samples were pressed using ~ 82 ksi of pressure, with thickness ranging from 0.5mm to 1.5mm. Constant pressure was maintained on the pellet/electrode assembly during the measurement by a metal frame. An aluminum frame insulated from the electrodes with Teflon was used for temperatures up to 300°C. For temperatures up to 550°C, constant pressure was applied by a stainless steel frame insulated from the electrodes with alumina. During the measurement, the sample was contained in a silica cell that maintained about one atmosphere pressure of Helium.

***Thermal Stability***

A Perkin Elmer Thermogravimetric Analyzer TGA 7 (TGA) and a Perkin Elmer Differential Scanning Calorimeter Pyris 1 (DSC) have been used to determine the thermal stability of the samples, including decomposition, sublimation, crystallization, and glass transition temperatures. For purposes of these experiments, the thermal stability limit is defined as the maximum temperature in an inert atmosphere with no decomposition or sublimation. Nitrogen was used as the sample purge gas to prevent any oxidation reactions for all experiments. For DSC experiments 5mg to 15mg of fine powder was sealed inside crimped aluminum sample pans. For TGA experiments about 25mg of each sample was placed inside an aluminum sample pan. A heating rate of 10°C per minute was used for all thermal stability experiments.

***Chemical Stability***

Structural investigations using a Bio-Rad FTS-40 mid-infrared (MIR) spectrometer and a Bruker RFS 100/S Raman spectrometer were used to examine the stability with exposure to $H_2O$ and $O_2$. Fundamental vibrations that may be assigned to specific oxide modes were noted before and after exposure to $H_2O$ and $O_2$. These vibrational modes may be IR, Raman, or active with both spectroscopy methods. Exposure time varied from a few hours to one month depending on reactivity of the select samples.

## Results and Discussion

***Characterization of GCPCMs***

Figures 1 and 2 show the MIR spectra illustrating the structural changes associated with reaction time in liquid $H_2S$ of a 0.14 $Ga_2S_3$ +0.86 $GeS_2$ glass and 0.05 $MoS_2$ + 0.95 $GeS_2$ glass, respectively. The most obvious change that appears with increased reaction time is the increase in the intensity of the S-H stretching band at ~ 2521$cm^{-1}$; this correlates with an increase in the concentration of protons bonded in the material. A gradual shifting of this band to lower wavenumbers is also observable with increased reaction time (as much as 25 $cm^{-1}$); this represents a decrease in the S-H bonding energy. Both of these trends are expected to result in an increased proton conductivity for the material. Also, observed is the decrease in the impurity mode attributed to the Ge-O-Ge asymmetric stretching located at roughly 812 $cm^{-1}$; this illustrates the stability of Ge-S bonds over Ge-O bonds in liquid $H_2S$.

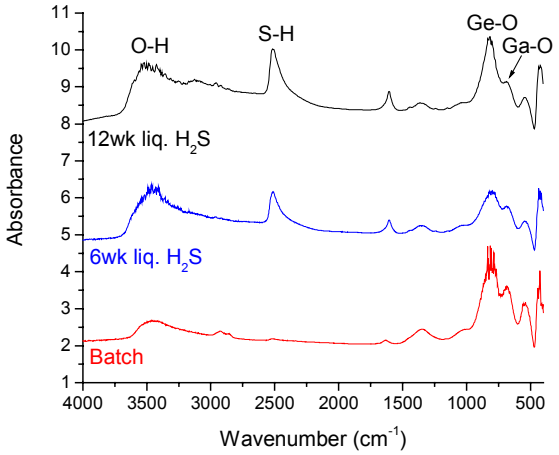


**Figure 1.** MIR spectra of 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ glass as a function of reaction time with liquid $H_2S$ at room temperature.

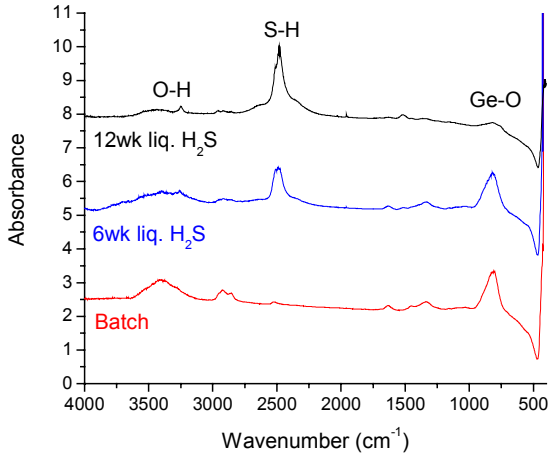


**Figure 2.** MIR spectra of 0.05 $MoS_2$ + 0.95 $GeS_2$ as a function of reaction time with liquid $H_2S$ at room temperature.

Figures 3 and 4 show the Raman spectra illustrating the time scale required to make the thiogermanic acid starting from $GeS_2$ and $GeO_2$ precursors, respectively. As can be seen, vibrational modes associated with the crystalline thiogermanic acid are noticeable starting around 2 weeks with both precursors. It can be noted that at longer reaction times the structure becomes more disordered. Significantly, the precursor $GeO_2$ can be commercially purchased for half the price of Germanium and Sulfur elements and does not require the specialized handling and processing required to synthesize $GeS_2$.

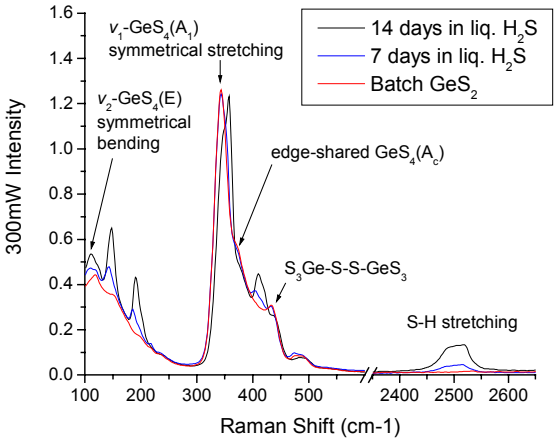


**Figure 3.** Raman spectra of $GeS_2$ as a function of reaction time with liquid $H_2S$ at room temperature.

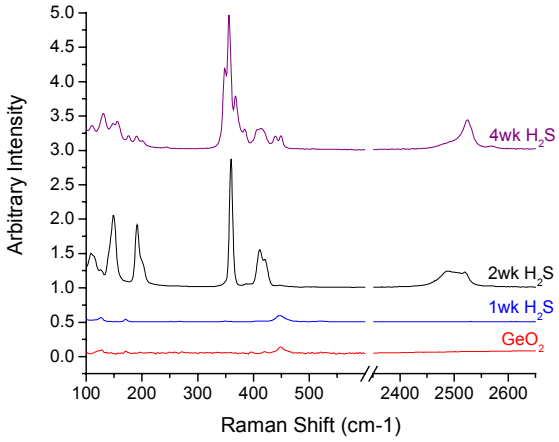


**Figure 4.** Raman spectra of $GeO_2$ as a function of reaction time with liquid $H_2S$ at room temperature.

***Conductivity***

Figures 5 and 6 show the DC conductivity values for the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ + $H_2S$ system and the 0.05 $MoS_2$ + 0.95 $GeS_2$ + $H_2S$ systems, respectively, as a function of inverse temperature for increasing reaction times in liquid $H_2S$. The temperature range of 115°C to 300°C is shown using hardened steel electrodes pressed into a Teflon sleeve to contain the sample pellet. As mentioned in the previous structural characterization section, the higher conductivity values associated with longer reaction times are a result of higher proton concentrations and decreased bonding energies. The trend of decreasing activation energy with increasing reaction time is also noticeable.

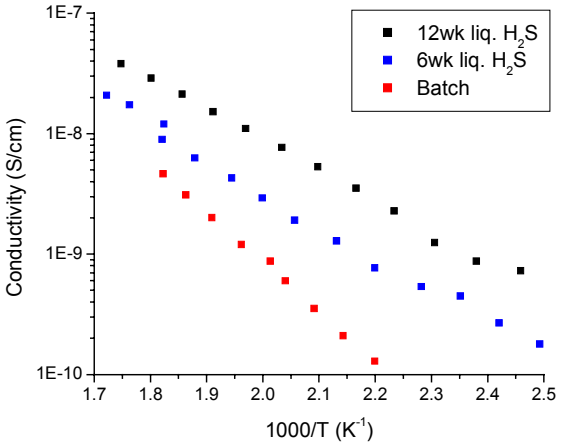


**Figure 5.** Proton conductivity values for the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ + $H_2S$ system as a function of reaction time between 125°C and 300°C.

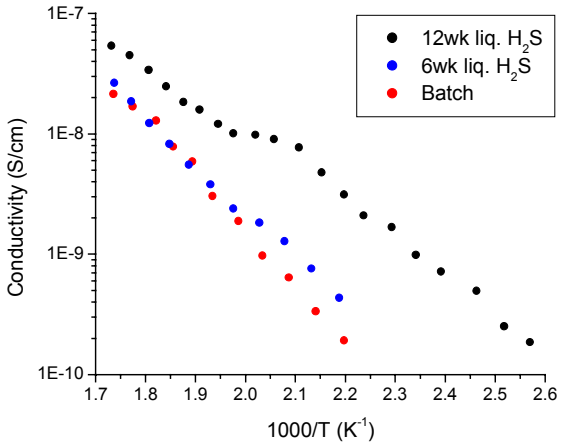


**Figure 6.** Proton conductivity values for the 0.05 $MoS_2$ + 0.95 $GeS_2$ + $H_2S$ system as a function of reaction time between 115°C and 300°C.

Figure 7 shows the conductivity values for the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ + $H_2S$ and 0.29 $Al_2S_3$ + 0.71 $GeS_2$ + $H_2S$ systems in the temperature range of 110°C to 500°C using an alumina tube to contain the sample pellet and electrodes. The resulting conductivity values are reported for the most protonated starting materials. The nonarrhenius behavior starting around 378°C in the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ + $H_2S$ system can be attributed to the glass transition, which was measured to be around 393°C. A higher activation energy is noted after the transition with increasing temperature, ultimately a conductivity value of $10^{-5}$ S/cm is reached at 500°C.

Figure 8 shows the resulting proton conductivity values for the thiogermanic acid after four weeks using $GeO_2$ reacting with liquid $H_2S$. The data is presented in the temperature range of -61°C to 300°C using hardened steel electrodes pressed into a Teflon sleeve to contain the sample pellet. One can observe a decrease in the conductivity starting at ~8°C; this may be explained by thermal stability of the $H_2Ge_2S_5 \bullet nH_2S$ compounds. At higher temperatures these compounds appear to lose the intercalated $H_2S$ to yield the crystalline thiogermanic acid.

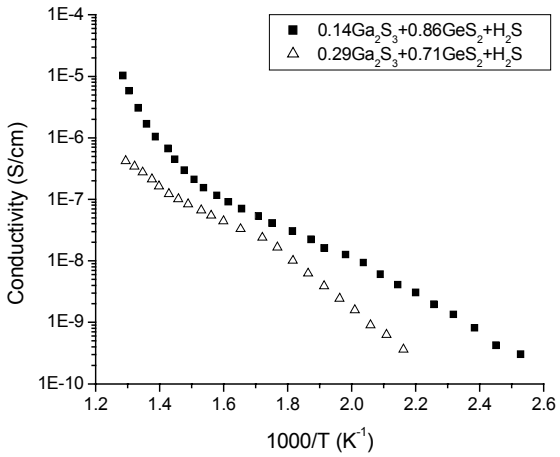


**Figure 7.** Proton conductivity values of the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ + $H_2S$ and 0.29 $Al_2S_3$ + 0.71 $GeS_2$ + $H_2S$ systems between 110°C and 500°C.

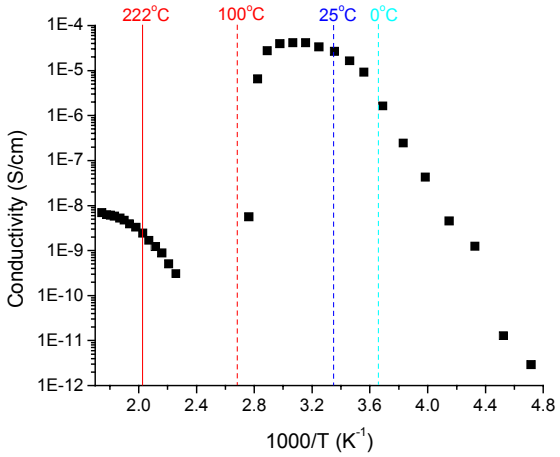


**Figure 8.** Proton conductivity values for the thiogermanic acid between –61°C and 300°C.

The thiomolybdic acid, $H_2MoS_4$, appears to conduct both protons and electrons (Fermi level within the d band gap). Possible catalytic behavior and electrode application of this acid are undetermined at this time.

***Thermal Stability***

Among the less thermally stable compounds were the thiogermanic acid and thiomolybdic acid. Specifically, the crystalline thiogermanic acid corresponding to a two week reaction in liquid $H_2S$ appears to start sublimating and decomposing above 170°C; Figures 9 and 10 shows the resulting DSC and TGA scans, respectively. The more disordered thiogermanic acid structure corresponding to a four week reaction in liquid $H_2S$ appears to be more stable, starting to decompose around 200°C. The thiomolybdic acid starts decomposing above 95°C to $H_2S$ + $MoS_3$. Among the more thermally stable compounds were glassy $GeS_2$, the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ + $H_2S$ system, and the 0.29 $Al_2S_3$ + 0.71 $GeS_2$ + $H_2S$ system. Specifically, $GeS_2$ does not decompose in an inert atmosphere up to 500°C. The 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ + $H_2S$ system does not decompose in an inert atmosphere to at least 500°C, well above its glass transition temperature of ~393°C; Figures 11 and 12 show the resulting DSC and TGA scans respectively. Similarly the 0.29 $Al_2S_3$ + 0.71 $GeS_2$ + $H_2S$ material does not decompose in an inert atmosphere until at least 500°C.

It is expected that the thermally stable temperature range of compounds like the thiogermanic acid can be increased by mixing them with thermally stable compounds like $Ga_2S_3$, ZnS, $SiS_2$, $Al_2S_3$, BaS, SrS, etc.

***Chemical Stability***

Among the less inert compounds are the thiogermanic acid and the 0.29 $Al_2S_3$ + 0.71 $GeS_2$ system. Specifically, the thiogermanic acid produced after two weeks of reacting $GeO_2$ in liquid $H_2S$ appears to be stable with short term exposure to air (e.g. one day), however, exposure to water converts this phase to $GeO_2$ after one week. Figure 13 shows the IR spectra of the thiogermanic acid submersed in water for one week; note the structure is similar to that of $GeO_2$.

The 0.29 $Al_2S_3$ + 0.71 $GeS_2$ system is stable with short term exposure to air, but completely decomposes with submersion in water after one day. Among the more inert compounds are glassy $GeS_2$, the thiomolybdic acid, and the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ system. Specifically, glassy $GeS_2$ appears to be stable with exposure to air and short term exposure to water. The thiomolybdic acid appears to be stable with exposure to air or water. The 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ system appears to be stable when exposed to air and stable with exposure to water for at least one month. Figure 14 shows the IR spectra of the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ system submersed in water for one month; the structure is very similar to that of the starting structure.

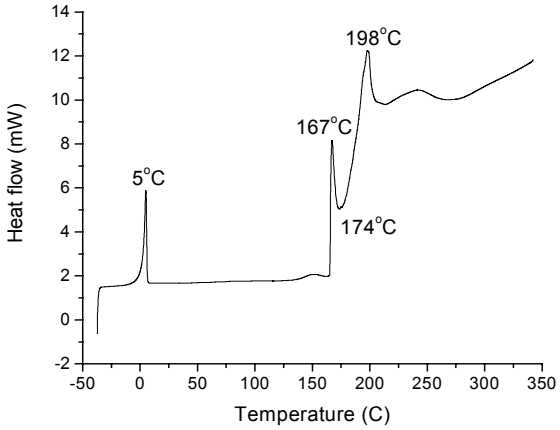


**Figure 9.** DSC scan at 10°C/min of the thiogermanic acid, endothermic up.

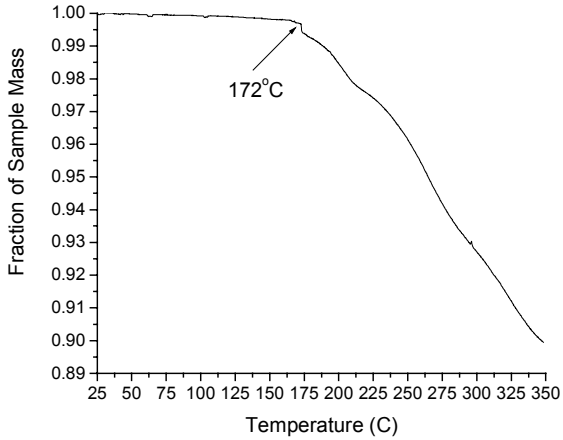


**Figure 10.** TGA scan at 10°C/min of the thiogermanic acid.

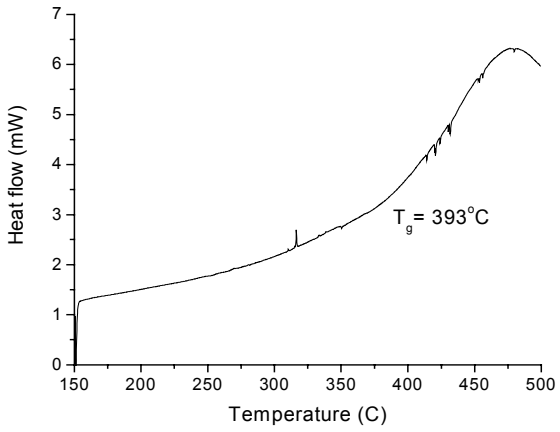


**Figure 11.** DSC scan at 10°C/min of the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$+ $H_2S$ system, endothermic up.

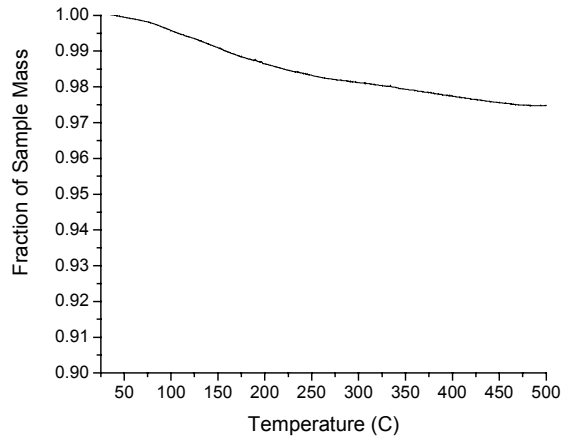


**Figure 12.** TGA scan at 10°C of the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$+ $H_2S$ system.

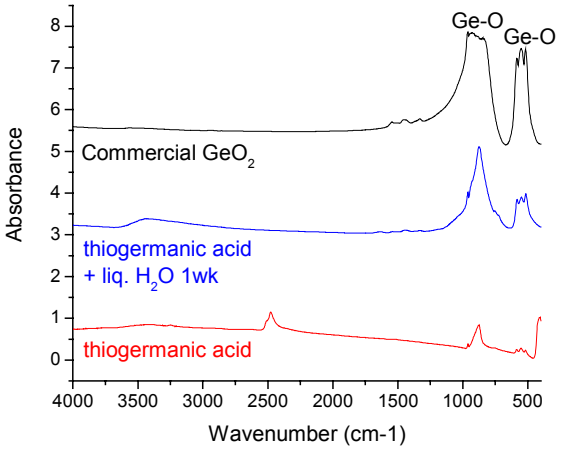


**Figure 13.** MIR spectra of the thiogermanic acid submersed in $H_2O$ for one week.

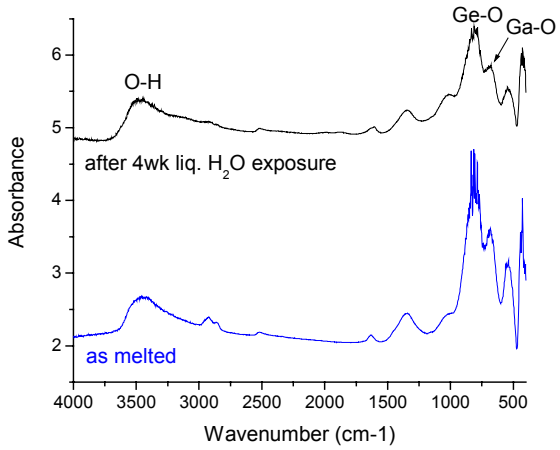


**Figure 14.** MIR spectra of the 0.14 $Ga_2S_3$ + 0.86 $GeS_2$ system submersed in $H_2O$ for one month.

It is expected that mixing the thiogermanic acid with chemically stable compounds like $Ga_2S_3$, ZnS, BaS, and $Sb_2S_3$ can increase its chemical stability with respect to $H_2O$ and $O_2$.

## Summary

A new class of proton conducting membranes for hydrogen fuel cell applications is being developed. Conductivities values of $10^{-5}$S/cm at ~ 500°C were achieved with materials thermally stable to at least 500°C and chemically stable with $H_2O$ for prolonged exposures. We have also synthesized new thio-acids, namely thiogermanic and thiomolybdic acid. The thiogermanic acid is now serving as a proton source material to synthesize other proton conductors. The net result is to create ceramic structures with stable S-H groups. IR and Raman spectroscopy have been used to determine the structure of these materials. Structural modifications are being carried out to maximize the proton concentration and decrease proton bonding energy; thus increasing proton conduction.

## Future Work

The kinetics of the reaction of oxide and thio precursors with liquid $H_2S$ is being studied for the $GeO_2$ and $GeS_2$ systems. This study is exploring the effect of temperature, time, and pressure on the kinetics of these types of reactions in order to maximize production efficiency. The investigation into new thio-acid compounds from oxide precursors is also being carried out. To date, $GeO_2$ to $H_2Ge_2S_5$ and $MoS_3$ to $H_2MoS_4$ have been successful. Along this line, we have obtained an invention disclosure concerning synthesis of thio-acids and thio-compounds from reactions of oxide precursors with liquid $H_2S$ solutions.

Work is now underway to mix the thiogermanic acid at elevated temperatures in evacuated silica tubes with thermally and chemically stable compounds (e.g. $Ga_2S_3$, $Sb_2S_3$, BaS, ZnS etc.) to obtain higher conducting GCPCMs. There are two reason to expect higher conductivity values by doing this: mixed glass former effect resulting in a more disorder structure, and the

prospect of protons bonding with other structural units that may be more mobile and thermally stable.

The electrochemical behavior of the GCPMs will be determined by using standard cyclic voltammetry methods; the GCPCMs will be configured with platinum electrodes and cycled in voltage between oxidizing and reduction potentials.

We are developing a partnership with Giner Electrochemical Systems, LLC to produce fuel cells using our GCPCMs. We have submitted an Army Research Office STTR proposal to conduct this development work. In this proposed work, we are responsible for preparing the GCPCMs and determining their ionic and electronic conductivities, thermal stability, chemical stability with respect to $H_2O$ and $O_2$, and proton concentration. Pressed powder samples will then be provided to Giner. Giner is responsible for designing and fabricating the MEA, evaluating the MEA from room temperature to 500$^oC$, and testing in a complete fuel cell setup using dry $H_2$ and $O_2$.

## Acknowledgement

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