

Design and Development of New Glass-Ceramic Proton Conducting Membranes

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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 $\sim 500^\circ\text{C}$, 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-perfluorosulfonic acids such as NafionTM, 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 $1,000^\circ\text{C}$, 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 $\sim 200^{\circ}\text{C}$ and $\sim 700^{\circ}\text{C}$ 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 $\sim 500^{\circ}\text{C}$, 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 versus 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 versus 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 , $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2$, $0.29 \text{ Al}_2\text{S}_3 + 0.71 \text{ GeS}_2$, and $0.05 \text{ MoS}_2 + 0.95 \text{ GeS}_2$ 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 $\text{H}_2\text{Ge}_2\text{S}_5$ 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, $\text{H}_2\text{Ge}_2\text{S}_5 \cdot n\text{H}_2\text{S}$, 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 H₂O and O₂. Fundamental vibrations that may be assigned to specific oxide modes were noted before and after exposure to H₂O and O₂. 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 H₂S of a 0.14 Ga₂S₃ + 0.86 GeS₂ glass and 0.05 MoS₂ + 0.95 GeS₂ 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 ~ 2521cm⁻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 H₂S.

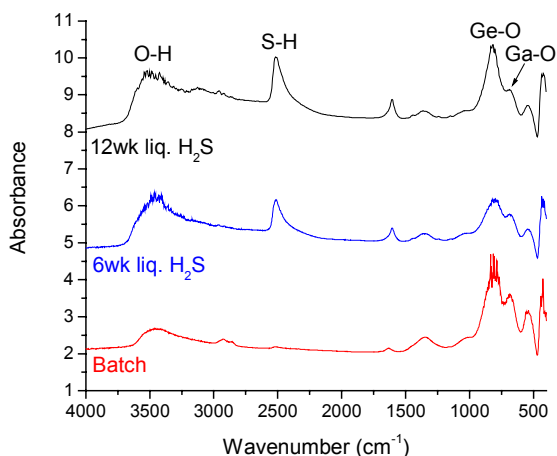


Figure 1. MIR spectra of 0.14 Ga_2S_3 + 0.86 GeS_2 glass as a function of reaction time with liquid H_2S at room temperature.

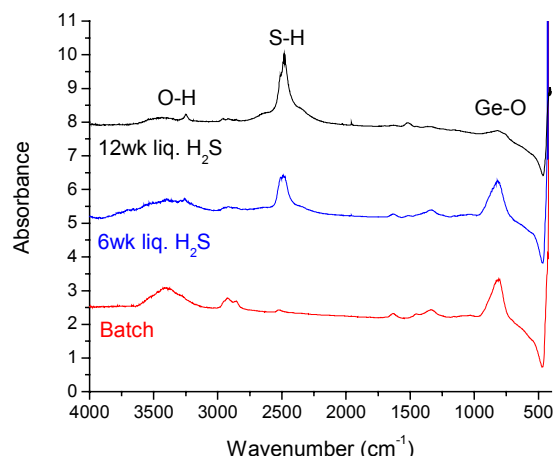


Figure 2. MIR spectra of 0.05 MoS_2 + 0.95 GeS_2 as a function of reaction time with liquid H_2S at room temperature.

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 .

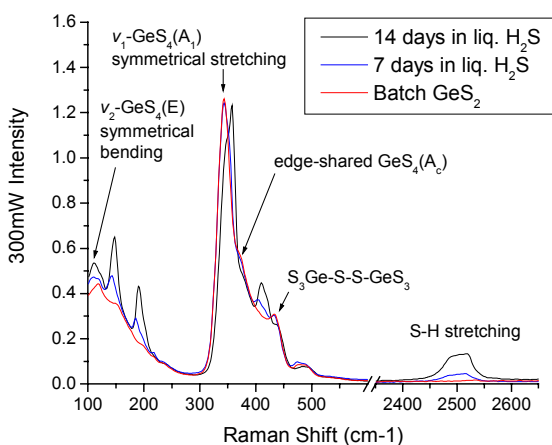


Figure 3. Raman spectra of GeS_2 as a function of reaction time with liquid H_2S at room temperature.

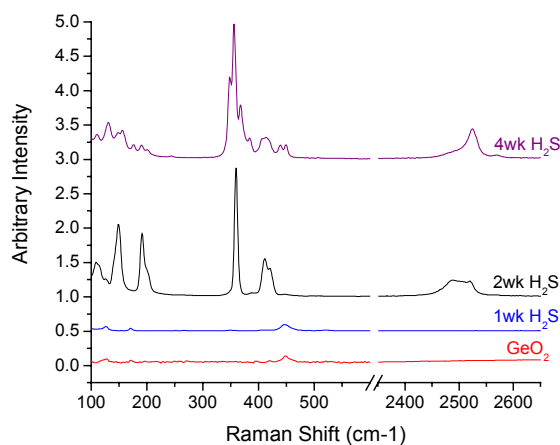


Figure 4. Raman spectra of GeO_2 as a function of reaction time with liquid H_2S at room temperature.

Conductivity

Figures 5 and 6 show the DC conductivity values for the $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2 + \text{H}_2\text{S}$ system and the $0.05 \text{ MoS}_2 + 0.95 \text{ GeS}_2 + \text{H}_2\text{S}$ 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.

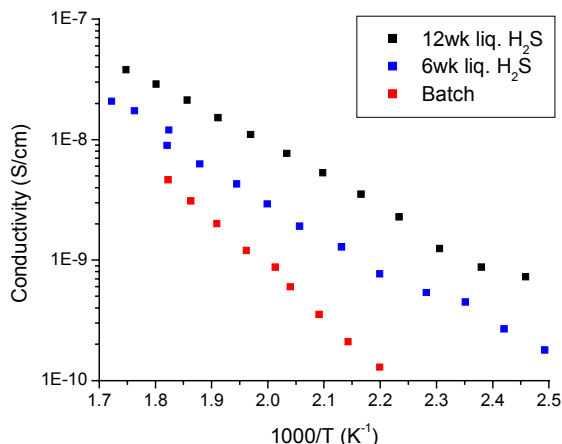


Figure 5. Proton conductivity values for the $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2 + \text{H}_2\text{S}$ system as a function of reaction time between 125°C and 300°C .

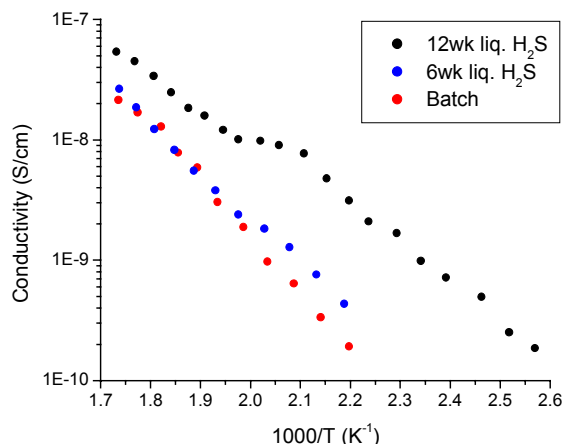


Figure 6. Proton conductivity values for the $0.05 \text{ MoS}_2 + 0.95 \text{ GeS}_2 + \text{H}_2\text{S}$ system as a function of reaction time between 115°C and 300°C .

Figure 7 shows the conductivity values for the $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2 + \text{H}_2\text{S}$ and $0.29 \text{ Al}_2\text{S}_3 + 0.71 \text{ GeS}_2 + \text{H}_2\text{S}$ 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 $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2 + \text{H}_2\text{S}$ 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 $\sim 8^\circ\text{C}$; this may be explained by thermal stability of the $\text{H}_2\text{Ge}_2\text{S}_5 \cdot n\text{H}_2\text{S}$ compounds. At higher temperatures these compounds appear to lose the intercalated H_2S to yield the crystalline thiogermanic acid.

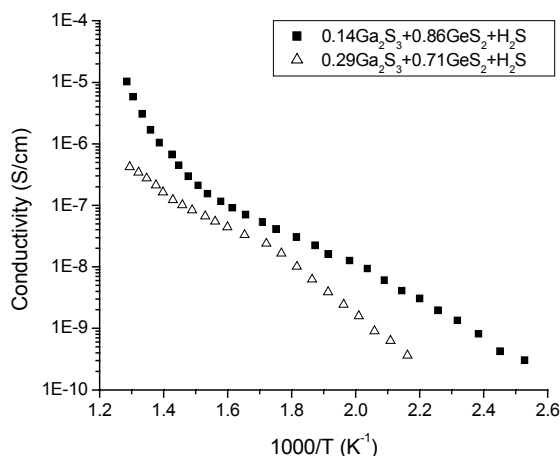


Figure 7. Proton conductivity values of the 0.14 Ga₂S₃ + 0.86 GeS₂ + H₂S and 0.29 Al₂S₃ + 0.71 GeS₂ + H₂S systems between 110°C and 500°C.

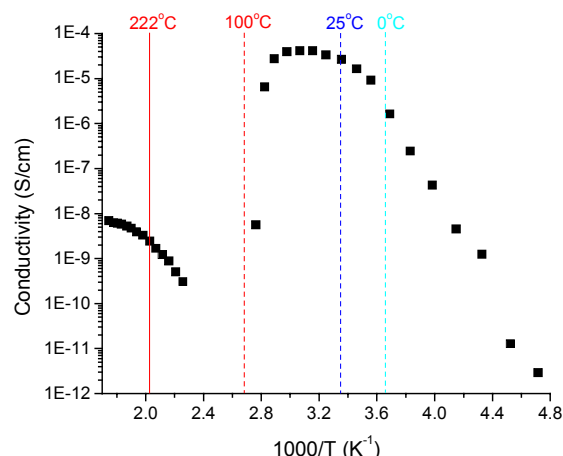


Figure 8. Proton conductivity values for the thiogermanic acid between -61°C and 300°C.

The thiomolybdc acid, H₂MoS₄, 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 thiomolybdc acid. Specifically, the crystalline thiogermanic acid corresponding to a two week reaction in liquid H₂S 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 H₂S appears to be more stable, starting to decompose around 200°C. The thiomolybdc acid starts decomposing above 95°C to H₂S + MoS₃. Among the more thermally stable compounds were glassy GeS₂, the 0.14 Ga₂S₃ + 0.86 GeS₂ + H₂S system, and the 0.29 Al₂S₃ + 0.71 GeS₂ + H₂S system. Specifically, GeS₂ does not decompose in an inert atmosphere up to 500°C. The 0.14 Ga₂S₃ + 0.86 GeS₂ + H₂S 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 Al₂S₃ + 0.71 GeS₂ + H₂S 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 Ga₂S₃, ZnS, SiS₂, Al₂S₃, BaS, SrS, etc.

Chemical Stability

Among the less inert compounds are the thiogermanic acid and the 0.29 Al₂S₃ + 0.71 GeS₂ system. Specifically, the thiogermanic acid produced after two weeks of reacting GeO₂ in liquid H₂S appears to be stable with short term exposure to air (e.g. one day), however, exposure to water converts this phase to GeO₂ 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 GeO₂.

The $0.29 \text{ Al}_2\text{S}_3 + 0.71 \text{ GeS}_2$ 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 thiomolybdc acid, and the $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2$ system. Specifically, glassy GeS_2 appears to be stable with exposure to air and short term exposure to water. The thiomolybdc acid appears to be stable with exposure to air or water. The $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2$ 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 $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2$ system submersed in water for one month; the structure is very similar to that of the starting structure.

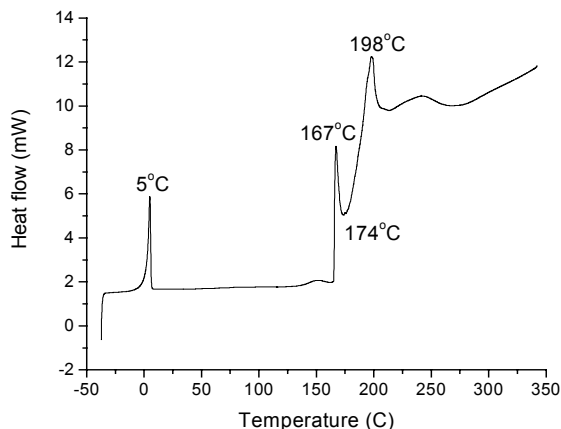


Figure 9. DSC scan at $10^\circ\text{C}/\text{min}$ of the thiogermanic acid, endothermic up.

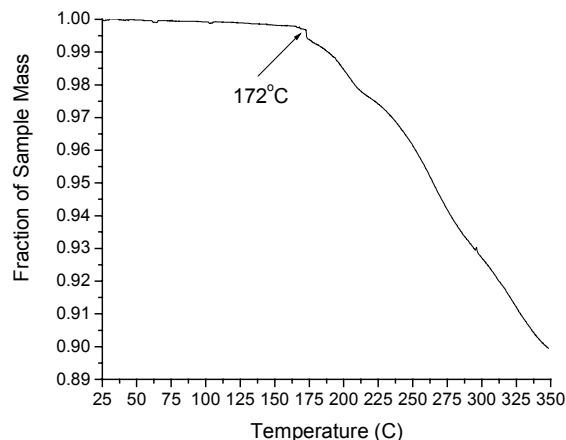


Figure 10. TGA scan at $10^\circ\text{C}/\text{min}$ of the thiogermanic acid.

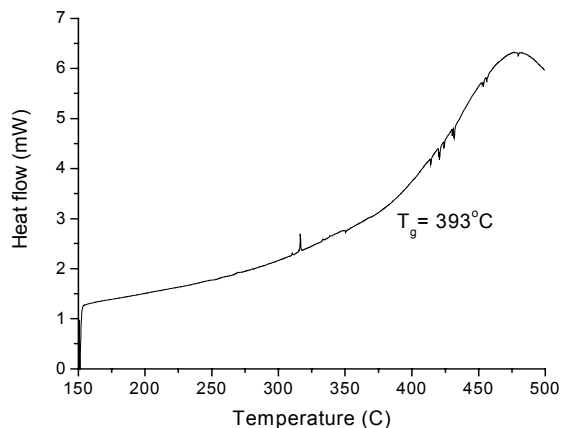


Figure 11. DSC scan at $10^\circ\text{C}/\text{min}$ of the $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2 + \text{H}_2\text{S}$ system, endothermic up.

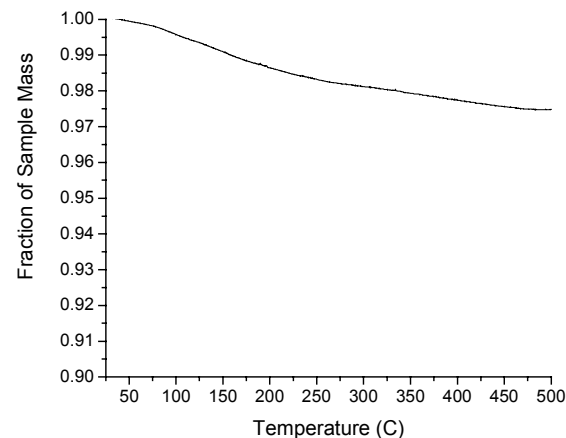


Figure 12. TGA scan at 10°C of the $0.14 \text{ Ga}_2\text{S}_3 + 0.86 \text{ GeS}_2 + \text{H}_2\text{S}$ system.

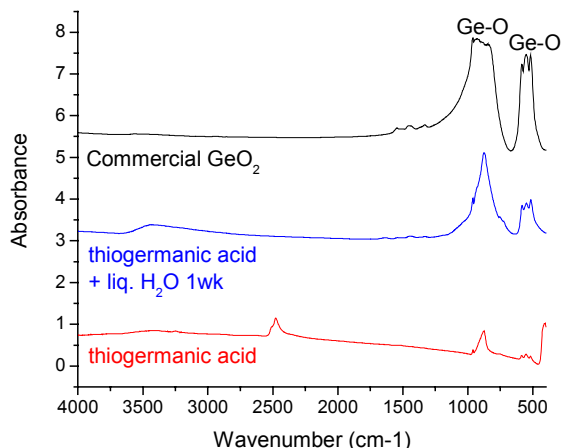


Figure 13. MIR spectra of the thiogermanic acid submersed in H₂O for one week.

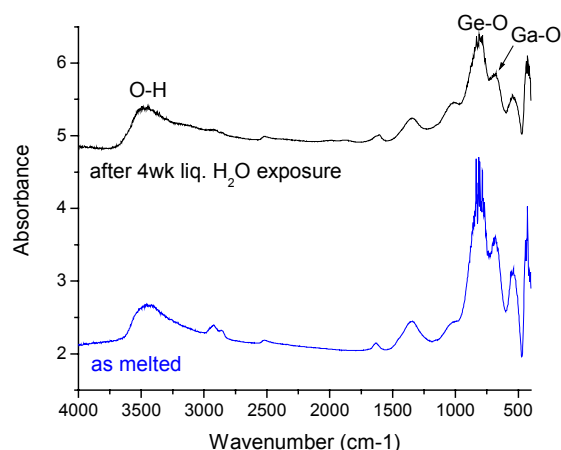


Figure 14. MIR spectra of the 0.14 Ga₂S₃ + 0.86 GeS₂ system submersed in H₂O for one month.

It is expected that mixing the thiogermanic acid with chemically stable compounds like Ga₂S₃, ZnS, BaS, and Sb₂S₃ can increase its chemical stability with respect to H₂O and O₂.

Summary

A new class of proton conducting membranes for hydrogen fuel cell applications is being developed. Conductivities values of 10⁻⁵S/cm at ~ 500°C were achieved with materials thermally stable to at least 500°C and chemically stable with H₂O 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 H₂S is being studied for the GeO₂ and GeS₂ 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, GeO₂ to H₂Ge₂S₅ and MoS₃ to H₂MoS₄ 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 H₂S 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. Ga₂S₃, Sb₂S₃, BaS, ZnS etc.) to obtain higher conducting GPCPMs. 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 H₂O and O₂, 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°C, and testing in a complete fuel cell setup using dry H₂ and O₂.

Acknowledgement

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