

DESIGN AND DEVELOPMENT OF NEW NANO-ENGINEERED GLASS-CERAMIC PROTON CONDUCTING MEMBRANES

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Abstract

New high-temperature, anhydrous fast proton conducting (FPC) membranes for use in new high-performance fuel cells are being developed. These new nanoengineered glass-ceramic proton conducting membranes (GCPCMs) are expected to yield high proton conductivities between 100 and 300°C, excellent thermal stability, up to 300°C, superior electrochemical and chemical stability, and zero fuel cross-over diffusion. These high-performance GCPCMs are expected to solve many if not all of the critical problems currently seen in the proton conducting membrane-of-choice, NafionTM, used in polymer electrolyte membrane (PEM) fuel cells.

In this effort, sulfide-based materials have been studied. These materials doped with H₂S are stable in air and water, which is an obvious requirement of a H₂-O₂ fuel cell. Glassy and crystalline sulfide-based materials have been synthesized and high-pressure protonating experiments performed. Using such a method, these experiments resulted in protonated amorphous materials. Structural characterization of the obtained protonated materials has been carried out using IR and Raman spectroscopies and x-ray diffraction.

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Introduction

Fuel cells, based upon hydrogen as the fuel and air as the oxidizer, are known to hold great promise as portable energy sources to replace the internal combustion engine as well as some battery technologies (Colombian 1999). While there are many different configurations of such fuel cells (e.g., Blomen 1993), polymer electrolyte membrane (PEM) fuel cells are among the most promising for a number of different reasons (Colombian 1999, pp.63 and 493). They offer a lower operation temperature, simplified cell configuration, relatively quick and efficient start-up, inexpensive cell design, and relatively high power densities. Much research has been done to move the PEM fuel cell from design into the production stage (e.g., Gottesfeld 1997).

However, PEM fuel cells are not without many critical problems and unresolved design issues. Low-temperature operation is required to protect the fragile polymer membrane and to keep it hydrated so as to maintain its high proton conductivity. Because the polymer membrane is hydrated, many fuels such as methanol rapidly diffuse across the membrane to the cathode and dramatically degrade the performance of the fuel cell (e.g., ONR-DOE 1999). The relatively low operation temperature also limits the catalytic efficiency of non-platinum catalysts.

For these reasons, higher temperature, anhydrous, solid, high-proton conductivity membranes are critically needed. By operating above the steam point of water, the by-product water is produced as a more easily managed gas, less expensive catalysts with good performance at elevated temperatures can be used, and, due to their solid structure, would have zero cross-over of fuels such as methanol.

In this project, new anhydrous, glass-ceramic proton conducting membranes (GCPCMs) are being designed and developed. Such membranes are expected to have proton conductivities in excess of $10^{-1}(\Omega^{-1}\text{cm}^{-1})$ above 100°C (see Figure 1), and zero electronic conductivities combined with superior thermal, mechanical, chemical, and electrochemical stabilities. Their solid and anhydrous structure will obviously limit fuel crossover as well. By using carefully controlled glass-ceramic processing, the anisotropy and texture of the nanostructures of the GCPCMs can be tailored to the perpendicular direction of the thin film and thereby optimizing the conductivity. The mechanical properties will also be optimized through the generation of a two-phase glass-ceramic with a carefully controlled and fine-grained nanostructure. Finally, because of their inherent increased thermal-mechanical stability, the thermal and electrochemical stability of the GCPCMs will be far superior to that of NafionTM and Nafion-like polymer membranes. Thin film processing of glass-ceramic materials is a well-known area of materials processing and will be used to process thin films of the GCPCMs.

Chalcogenide fast ion conducting (FIC) glasses proved unsuitable for use in rechargeable lithium batteries because of the volume changes that occur in the cells during both discharge and recharge cycles of the cells (Julien 1994). However, such volume changes do not occur in hydrogen-oxygen fuel cells because both reactants and products are brought to and carried away from the electrodes as liquids and/or gases. Hence, mechanical strain in the fuel cell during operation is not an issue and as such, the mechanical strength of the GCPCMs combined with their high proton conductivity, and high chemical and electrochemical stabilities gives them tremendous advantages over polymer membranes. For these reasons, GCPCMs become an

exciting and new alternative technology for solving many if not all of the problems associated with PEM fuel cells.

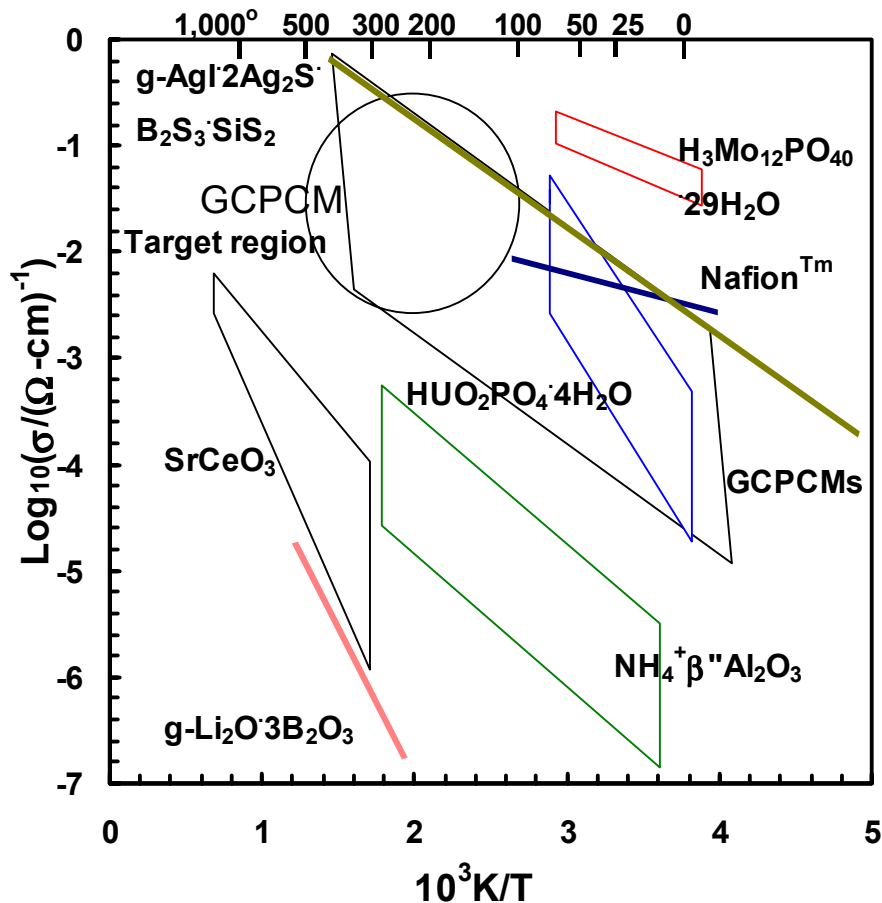


Figure 1: Arrhenius plots of the conductivity for different proton conducting solids (Colombian, P. 1999, Martin, S. W. 1991, Kincs, J. 1996). FIC glasses, $g\text{-Li}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ and $g\text{-AgI}\cdot 2\text{Ag}_2\text{S}\cdot 2\text{B}_2\text{S}_3\cdot \text{SiS}_2$, are included to show the level of conductivity increase that can be achieved when oxide chemistries are replaced by optimized sulfide chemistries.

Inorganic glassy FICs have been known for a long time and much success has been achieved at increasing their ionic conductivity through systematic manipulation of the glass chemistry (Martin 1991). Oxide glasses, like oxide ceramic proton conductors, exhibit ion conduction, but it is very limited due to the strong coulombic interaction between alkali and oxygen anions (Martin 1986). Proton conducting oxide glasses are likewise known and exhibit similar low conductivity values (Abe 1993). Higher values can be obtained by using heavily hydrated oxide glasses, but these glasses, like their hydrated salt and polymer analogs, suffer from low operating temperatures (Abe 1982) due to the boil-off of water.

Recently, chalcogenide-based glasses, those based on the elements S, Se, and Te, have been found to exhibit many orders of magnitude increase in the alkali ion conductivity over their oxide analogues (Angell 1992). For example, see the comparison of two such glasses on Figure

1, cf. $g\text{-Li}_2\text{O}+3\text{B}_2\text{O}_3$ and $g\text{-AgI}+2\text{Ag}_2\text{S}+\text{B}_2\text{S}_3+\text{SiS}_2$. Conductivities as high as $10^{-2}(\Omega\text{cm})^{-1}$ at room temperature have been observed for these chalcogenide glasses (Kincs 1996) and it naturally becomes a question of whether an attempt has been made to develop similar FPC chalcogenide glasses. After a very thorough search of both the open and patent literature, no record has been found of the attempt to synthesize a proton conducting chalcogenide glass that would determine whether the 1,000- to 1,000,000-fold increase in conductivity for alkali ion conducting sulfide glasses over that of the oxide glasses is also observed for proton conducting sulfide glasses. In fact, no record can be found of a proton-containing sulfide glass, independent of whether the glass was used a fast ion conductor or not.

Our research group has studied chalcogenide-based glass former systems extensively and has developed synthetic procedures to easily prepare these materials in large quantities (Cho 1995). The system that we have explored is based on strongly glass-forming sulfide compounds. Our base material is known to be relatively stable in air and water. H_2S has been added to this base material by gaseous reaction between H_2S and the base glass heated above their vaporization temperature.

Experimental Section

Preparation of the Base Materials

To prepare the sulfide-based material, the corresponding elements, mixed in stoichiometric amounts, were sealed under vacuum in a silica tube and heated at 900°C in a rotating furnace for eight hours. Slow cooling in the furnace leads to crystallization while water quenching leads to a glassy material. A glove box ($<4\text{ppm O}_2$ and H_2O) was used for all handling of starting and final materials.

Preparation of the Protonated Materials

H₂S Flow Protonation Experiment

A carbon crucible was loaded with the starting material and placed in a silica tube. This is accomplished in a glove box with an inert He atmosphere. The material was heated under a H_2S gas flow for 1 hour at temperatures higher than its sublimation temperature, which allows the reaction between gaseous starting material and H_2S . The product of the reaction is deposited in the cold part of the tube outside the furnace. It appears as a light brown powder and is the same whether the starting material crystalline or glassy.

High Pressure Protonation Experiments

In order to facilitate the reaction between H_2S and the base material, a high-pressure system, shown in Figure 2, was constructed. This system allows the reaction at pressures higher than atmospheric pressure, outside of the glove box. It is composed of a reaction vessel made of alumina surrounded by a stainless steel 310 sheath connected to two gas cylinders (H_2S and N_2). After the reactor is placed in a furnace, connected to the system and put under vacuum, it is filled with H_2S gas. A water-cooling collar is placed around the top part of the reactor.

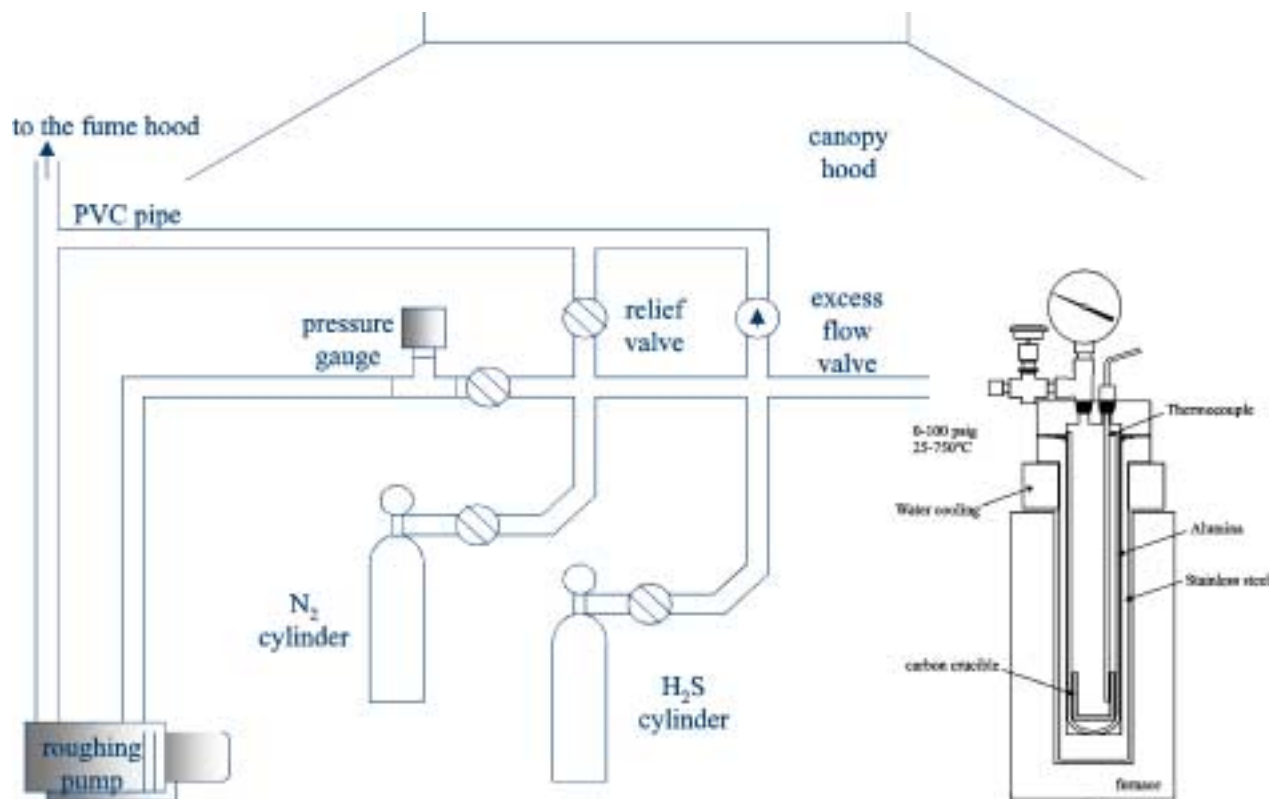


Figure 2: High-pressure synthesis system.

This device meets all the necessary safety requirements for handling and using H_2S gas: it is surrounded by polycarbonate protective sheets and is situated under the canopy hood. All the exhaust parts are linked to the main fume hood pipe through PVC pipes. A H_2S leak detector has been installed near the system and safety procedures have been developed for the use of H_2S in the laboratory.

High Pressure Protonation Experiments

Successful protonation experiments were conducted using the previously described system. The starting material was placed in a carbon crucible inside of the reactor then held for a few hours at high temperature under a high pressure of H_2S . After all the material was sublimated, a very thin brown powder was collected in the cold top part of the reactor.

Results and Discussion

Characterization of the Base Material

The Raman spectra of crystalline starting material are represented in Figure 3A ($100\text{-}500\text{ cm}^{-1}$) and Figure 3B ($100\text{-}4000\text{ cm}^{-1}$). These spectra are in good agreement with spectra reported earlier for tetrahedral sulfide-based materials (Kawamoto 1982, Boolchand 1986). It can be explained

in terms of vibrations of isolated tetrahedral units, even though the units are connected together. The four vibrational modes are Raman active. The more intense Raman peak at $\sim 360\text{ cm}^{-1}$ is assigned to the ν_1 (A_1) mode, while the ν_2 (E), ν_3 (F2), and ν_4 (F2) modes are observed at frequencies around 120, 424, and 157 cm^{-1} respectively (Kawamoto 1982). The X-ray diffractogram of the material shown in Figure 5 confirms its crystallinity.

The mid-IR spectrum, Figure 4, shows two bands around $3,400$ and $2,900\text{ cm}^{-1}$. They correspond to O-H and C-H impurities in the material. Such bands were observable in one the commercial starting elements. By examining the Raman spectra in a larger frequency range, shown in Figure 3B, it is clear that these bands have a very low intensity compared to the main vibrations bands, showing that the amount of impurities is quite small.

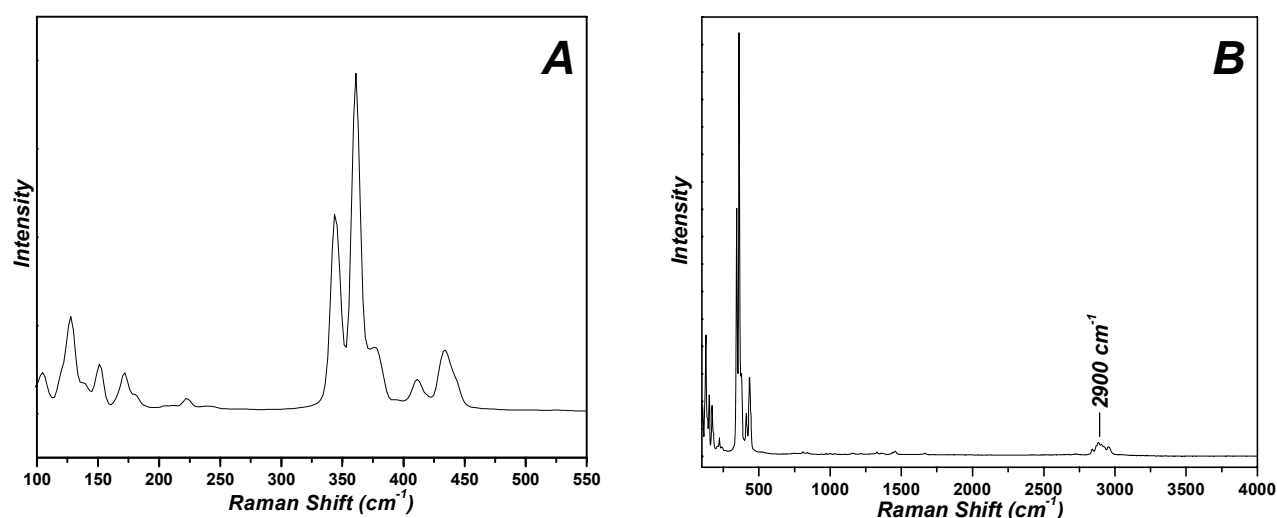


Figure 3: Raman spectra of the sulfide starting material, low frequency range (A) and full frequency range (B).

Characterization of the Protonated Materials

H₂S Flow Protonated Materials

Figure 4 shows the infrared spectra of the obtained material by using a flow of H_2S over the starting material compared to the starting material. If the material incorporated H_2S , an infrared band for the S-H vibration should be observable around 2500 cm^{-1} . Unfortunately, this is not the case, as the S-H band is as small as in the starting material itself.

High Pressure Protonated material

In order to characterize the nature of this material, x-ray diffraction, and IR and Raman spectroscopy have been carried out.

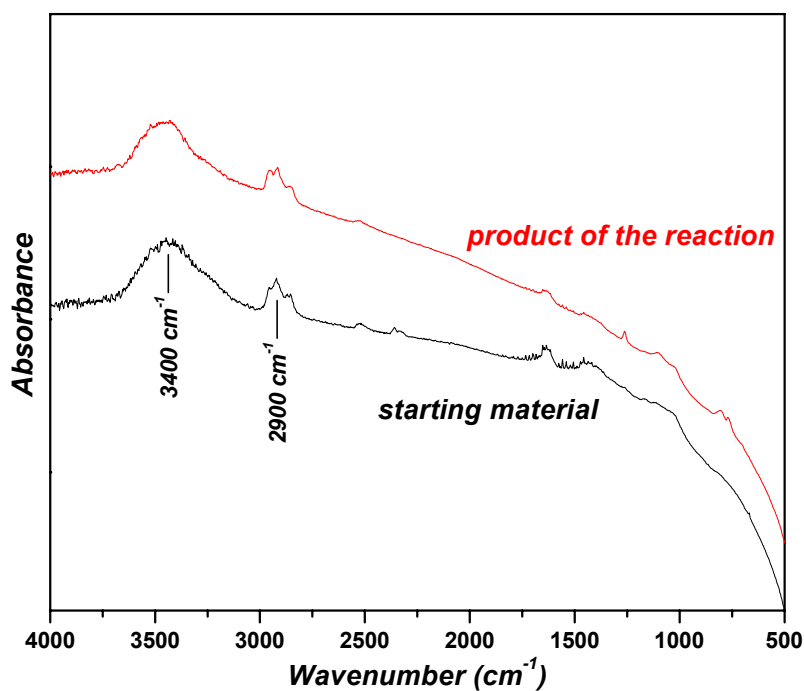


Figure 4: IR spectra of the starting material and of the obtained material.

The x-ray diffractogram on Figure 5 shows that this material is amorphous, as no diffraction peaks are observed. For comparison, the XRD pattern for the crystalline starting material is shown. The IR spectrum of Figure 6A shows a comparison between the glassy starting material and the protonated material. While the slight O-H and C-H contamination is still present, the S-H vibration band at 2500 cm^{-1} is now clearly observable, indicating the protonation of the material. The Raman spectra on Figure 6B shows that the structure of the protonated GeS₂-based material is very close to that of normal glassy material as the four tetrahedral bands ν_1 (A₁), ν_2 (E), ν_3 (F₂) and ν_4 (F₂) are still observable at 342, 115, 368 and 150 cm^{-1} . However, there is a main difference: the presence of a band at 415 cm^{-1} could account for a partial change of symmetry in the structure from T_d to C_{3v} and C_{2v} as the network is depolymerized and H₂S incorporated in the material. Kamitsos et al. have observed the same features in silver thiogermanates system (Kamitsos 1994).

The stability in air and water of the protonated material has been tested where samples have been kept in air and water for several days. Raman and infrared spectra were recorded after this. There were no noticeable differences between the original protonated material and the samples obtained after such a treatment, showing that this material is relatively stable to moisture, which is really promising for fuel cells applications.

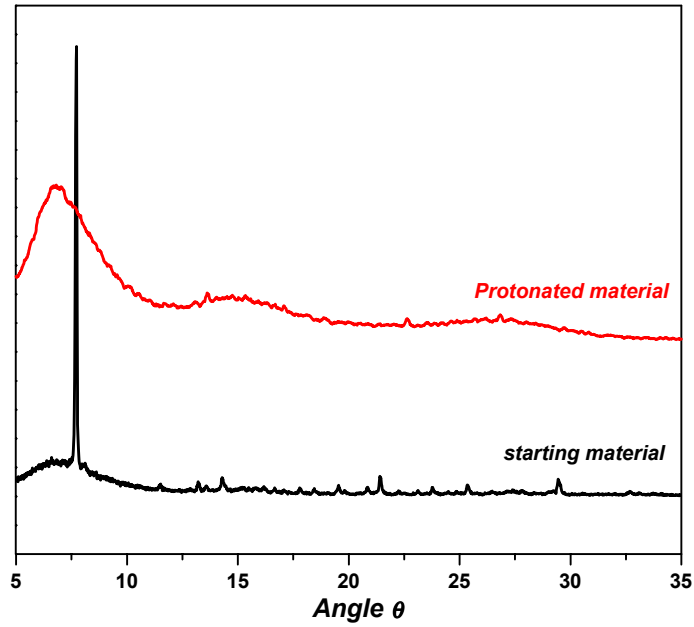


Figure 5: X-ray diffractogram of the starting material and of the protonated material.

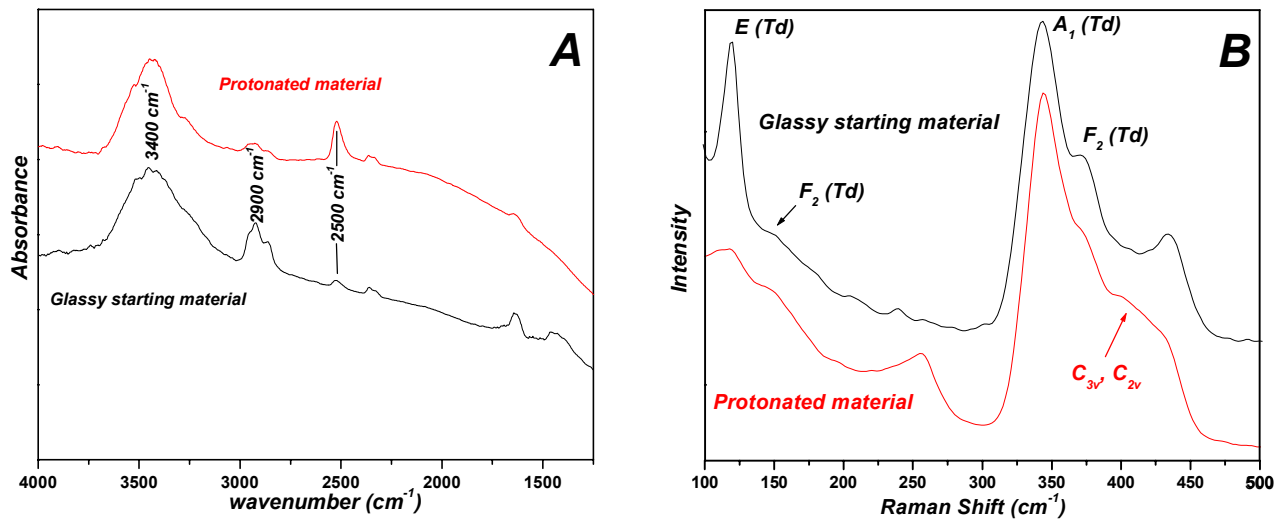


Figure 6: IR (A) and Raman (B) spectra of the protonated material and of the glassy starting material.

Future Work

Glass-ceraming these materials prior to use and optimizing the nanostructure and properties of the resulting glass-ceramic is expected to produce membranes with higher performance than the base-materials alone. The glass-ceramic will not only have a higher thermal stability since it is already crystallized it will be expected to have improved chemical and electrochemical stabilities as well. By controlling the nucleation and growth kinetics during the glass-ceramic processing, careful control will be achieved over the resulting physical properties of the GCPCMs. Multi-dimensional glass-ceramic processing “maps” will be developed by varying the processing conditions; nucleation temperature; nucleation time; growth temperature; growth time; and nucleating agent through predetermined ranges. Careful analysis of the resulting nanostructures will be determined using SEM, the physical properties of the GCPCMs will be carefully characterized. Proton conductivity will be determined using impedance spectroscopy. Electrochemical stability, chemical stability, thermal stability limit thermal expansion coefficient and mechanical strength will also be determined. ^1H NMR spectroscopy will be used to characterize proton conduction dynamics in GCPCMs.

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