Evaluation and Characterization of Membranes for H_2SO_4/Water and I_2/HI/H_2O Water Separation and Hydrogen Permeation for the S-I Cycle

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ABSTRACT

In this report are the findings into three membrane separation studies for potential application to the Sulfur-Iodine (S-I) thermochemical cycle. The first is the removal of water from hydriodic acid/iodine mixtures. In the S-I cycle, iodine is added to the product of the Bunsen reaction to facilitate the separation of sulfuric acid (H_2SO_4) from hydriodic acid (HI). The amount of iodine can be as high as 83% of the overall mass load of the Bunsen product stream, which potentially introduces a large burden on the cycle's efficiency. Removal of water from the HI and iodine mixture would substantially reduce the amount of required additional iodine. In this work, performance data for Nafion® and sulfonated poly (ether ether ketone) (SPEEK) membranes is shown.

Second, experiments demonstrating the concentration of H_2SO_4 are detailed. In this work, the positive results of the HI experiments were applied to H_2SO_4 concentration for use after the decomposition step in which the reaction is equilibrium limited, suggesting that a large portion of the acid remains undecomposed and requiring recycle. Traditional methods including distillation are less desirable for H_2SO_4 concentration due to corrosion at the liquid-vapor interface. Thus, a concentration system that does not involve boiling the acid is highly desirable.

Third, a preliminary study into polymeric membranes that transport hydrogen was conducted. In the HI decomposer, the decomposition of HI yields hydrogen and iodine. To encourage greater conversion, hydrogen should be removed. Many new high performance polymers are capable of transporting hydrogen, one of the most diffusive gases, at temperatures as high as 300 ºC. This task focused on collecting hydrogen permeability data at 300ºC.

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In this report are the findings into three membrane separation studies for potential application to the S-I thermochemical cycle. The first is the removal of water from hydriodic acid/iodine mixtures. In the S-I cycle, iodine is added to the product of the Bunsen reaction to facilitate the separation of H_2SO_4 from HI. The amount of iodine can be as high as 83% of the overall mass load of the Bunsen product stream, which potentially introduces a large burden on the cycle's efficiency. Removal of water from the HI and iodine mixture would substantially reduce the amount of required additional iodine. In this work, performance data for Nafion® and SPEEK membranes is shown.

Second, experiments demonstrating the concentration of H_2SO_4 are detailed. In this work, the positive results of the HI experiments were applied to H_2SO_4 concentration for use after the decomposition step in which the reaction is equilibrium limited, suggesting that a large portion of the acid remains undecomposed and requiring recycle. Traditional methods including distillation are less desirable for H_2SO_4 concentration due to corrosion at the liquid-vapor interface. Thus, a concentration system that does not involve boiling the acid is highly desirable.

Third, a preliminary study into polymeric membranes that transport hydrogen was conducted. In the HI decomposer, the decomposition of HI yields hydrogen and iodine. To encourage greater conversion, hydrogen should be removed. Many new high performance polymers are capable of transporting hydrogen, one of the most diffusive gases, at temperatures as high as 300 ºC. This task focused on collecting hydrogen permeability data at 300ºC.

2.   INTRODUCTION

Thermochemical water splitting cycles are methods that have been proposed to generate hydrogen on a commercial scale. Most commonly, hydrogen today is formed from the steam reforming of natural gas. Hydrogen generated using this method is generally consumed in industrial processes. Considerable interest now exists in using hydrogen as an energy carrier for transportation and other applications where fossil fuels are used today. For the conversion from a fossil fuel based economy to a hydrogen-based economy, the amount of hydrogen produced must be significantly increased from alternative resources. Even if a fossil based economy is maintained for the longer term, lower grade sources of oil will have to be exploited through upgrading, which requires the use of hydrogen to increase the hydrogen to carbon ratio. Regardless of which way the nation turns, hydrogen will play a central role.

Formation of hydrogen from thermochemical cycles has been proposed using nuclear reactor supplied thermal energy.[1] Thermochemical cycles are processes in which hydrogen is produced through a series of chemical reactions where all other reactants are recycled. Thus, the only chemical input is water and the only by-product is oxygen. Heat, in the range of 750 °C – 1000 °C, is provided to drive endothermic reactions. Thermochemical cycles were principally investigated from the 1960's through the 1980's. Interest waned with the drop in crude oil prices in the 1980's; however recent energy price increases have renewed interest in hydrogen production from non-fossil based resources.

Advantages of nuclear driven hydrogen production include hydrogen's inherent renewable nature, a reliance of the process on domestic resources, and an absence of CO_2 emissions. Similar advantages can be obtained through the use of high temperature solar concentrators. More than 100 thermochemical cycles have been proposed in the literature.[2] The S-I process, which has been shown to be one of the more promising cycles using flowsheet development processes [3], is comprised of three chemical reactions. Water enters the cycle as a reactant in the Bunsen reaction [4], as shown in Eq 1.

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \qquad\qquad\qquad eq\ 1$$

In Eq 1, HI is formed from the reduction of I_2 at an approximate temperature of 400 °C. HI is then decomposed to generate H_2 at 350 °C to 400 °C, Eq 2, and the co-generated I_2 is recycled. To re-generate SO_2, H_2SO_4 is decomposed at temperatures as high as 1200 °C, see Eq 3.

$$2HI \rightarrow H_2 + I_2 \qquad\qquad\qquad eq\ 2$$

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2 \qquad\qquad\qquad eq\ 3$$

Key to the operation of this proposed cycle is the Bunsen reaction. Separation of the HI from the H_2SO_4 is accomplished by the addition of a large excess of I_2, which causes the product mixture to separate into two phases. Water and H_2SO_4 comprise the lighter phase, while the lower phase is a mixture of HI, water, and I_2 at an approximate ratio of 2:10:8, respectively. To facilitate this phase separation, a dehydration loop employing concentrated phosphoric acid is

added to the system to remove water from the HI/I_2 mixture. In the current flowsheets, additional water is removed and the HI would be decomposed using reactive distillation. [5] However, removal of water is limited by the HI/water azeotrope at 57% HI, distillation will not yield a more concentrated acid product. Direct removal of water using a membrane process would allow either the elimination or downsizing of the phosphoric acid system, and a large reduction in the amount of iodine that needs to be added to effect the phase separation of the Busen products. This increases the efficiency of the cycle by lowering the recycle ratio per Kg of hydrogen generated. However, prior to this investigation, membrane concentration of HI/I_2/water mixtures has not been demonstrated. Thus, this research was required to identify and study potential membrane candidates that could fill this role. Previously, we focused on Nafion-117® and Nafion-112® membranes in the pervaporation of water from a water/HI and water/HI/I_2 feeds. The first area of research described in this work is the study of SPEEK polymers as membranes for this application. SPEEK polymers have a similar physical structure as the Nafion materials with molecular channels that facilitate water transport, yet SPEEK polymers are cheaper and easily tailored to specific applications through control of the sulfonate content, as measured through their ion exchange capacities. Furthermore, SPEEKs are also far more processable resulting in easier membrane module construction. Also presented in this first section is the completion of the Nafion® study.

A second area of research described in this work was the application of the Nafion® membranes, successful in dewatering HI, to the concentration of H_2SO_4. Decomposition of H_2SO_4 has been planned to be performed at 850 ºC over a catalyst. This reaction is equilibrium limited and requires recycle to achieve high chemical efficiencies. H_2SO_4 decomposes into SO_2, O_2, and water. After the decomposition step, SO_2 and O_2 are easily removed yielding aqueous H_2SO_4 at a lower concentration than was originally fed into the reactor. Concentration of the acid can be accomplished through distillation; however the corrosion induced by boiling H_2SO_4 at the vapor-liquid interface is significant. Thus, this task is to study the applicability of pervaporation for H_2SO_4 concentration at sub-boiling temperatures, potentially obviating to corrosion issues noted above.

The third area of research described in this work is a study of potential candidate membranes for the separation of hydrogen from HI and iodine. Decomposition of HI is perhaps the most significant process in the S-I cycle since this step produces hydrogen. HI decomposes to hydrogen and iodine over a catalyst at approximately 350 ºC; however the reaction is equilibrium limited and current conversions are only around 20 %. To encourage higher conversions, either hydrogen or iodine must be removed. Hydrogen is the more obvious target species to remove due to its small size and highly diffusive nature. Upon consultation with General Atomics, it was learned that hydrogen selective palladium membranes failed due to the oxidative nature of HI and iodine. It was proposed that an oxidation resistant polymer membrane could perform the removal of hydrogen and maintain physical stability. During the latter part of FY 2006, studies were begun into the characterizing potential membrane candidates for hydrogen permeation at 300 ºC.

3.   METHODS AND MATERIALS

3.1   Pervaporation

A diagram of a typical pervaporation apparatus is shown in Figure 1. The heart of the system is the membrane cell. A 47 mm stainless steel filtration cell modified for feed side flow was used to secure the membrane with the following alteration. In place of the stainless steel cell half on the wetted upstream (feed) side of the membrane, a replacement was machined from solid Teflon® and fitted with Teflon® bayonet fittings for attachment of tubing. Pumping was provided by a peristaltic pump using ¼ inch Viton® pumping tubes to connect the cell to the pump and the feed reservoir. Initial experiments using the HI/water feeds indicated that this apparatus worked well, although the Viton® pumping tube showed limited pumping life, necessitating periodic replacement.
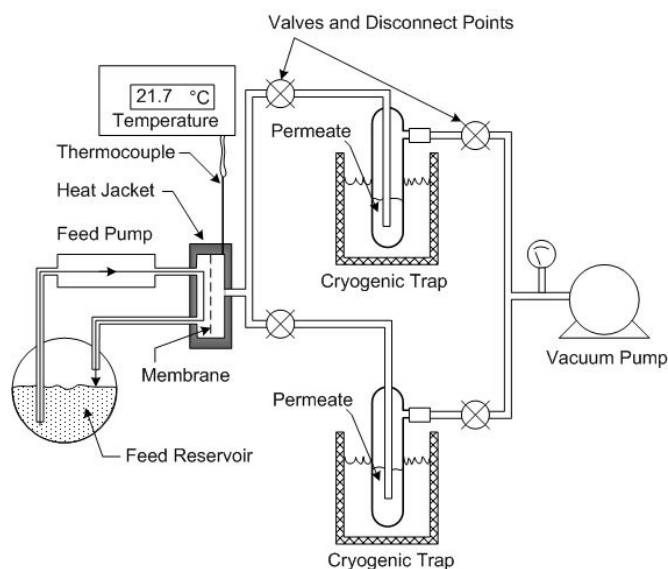

Figure 1. Pervaporation System.

Maintenance of cell temperatures was accomplished using electrically operated heat tape applied directly to the cell with external shielding of aluminum foil. Additionally, the membrane cell and feed supply reservoir were located in an oven. This "dual zone" heating method was required because cell temperatures in the 120-140 °C range were difficult to achieve using only the oven because of cell cooling due to feed flow and evaporation of permeate off the backside of the membrane. To achieve the desired cell temperatures, the oven often had to be heated to temperatures as high as 160-170 °C, which adversely affected some of the Teflon® components and also caused spattering of the feed solutions. For experiments at or above 120 °C, the oven was maintained at 100-110 °C, while the heat tape provided localized heat to the cell itself to boost it to the desired temperature.

To characterize any particular membrane's performance, two central factors must be determined. First, is the flux across the membrane, which is the amount of permeate that can be collected off the backside of the membrane per unit membrane area per unit time. Units for flux used in this work are g/m2h (grams of flux per square meter of membrane area per hour). Second, the separation factor must be measured. The separation factor is a relative measure of the membrane's ability to effect the desired separation and is calculated according to equation 4:

$$\text{Separation factor } (\alpha) = \frac{[H_2O]_p / [HI]_p}{[H_2O]_f / [HI]_f} \qquad \text{eq 4}$$

where $[H_2O]_p$ and $[H_2O]_f$ are concentrations of water in the permeate and feed, respectively, as weight percents. Likewise, $[HI]_p$ and $[HI]_f$ refer to the HI concentrations. Larger separation factors equate to a better separation. For the HI/water/I_2 feed experiments, the acid term encompasses both the HI and I_2 concentrations. Concentrations of HI were determined through titration of both feed and permeate samples using a standardized sodium hydroxide solution to a phenolphthalein endpoint. Feeds with added I_2 yielded homogenous solutions and the added I_2 was accounted for by consideration of the HI-I_2 complex concentration was the sum of the HI and I_2 concentrations in terms of weight percent. Likewise, the H_2SO_4 experiments were conducted similarly where direct titrations of the acid also were accomplished using a standardized sodium hydroxide solution.

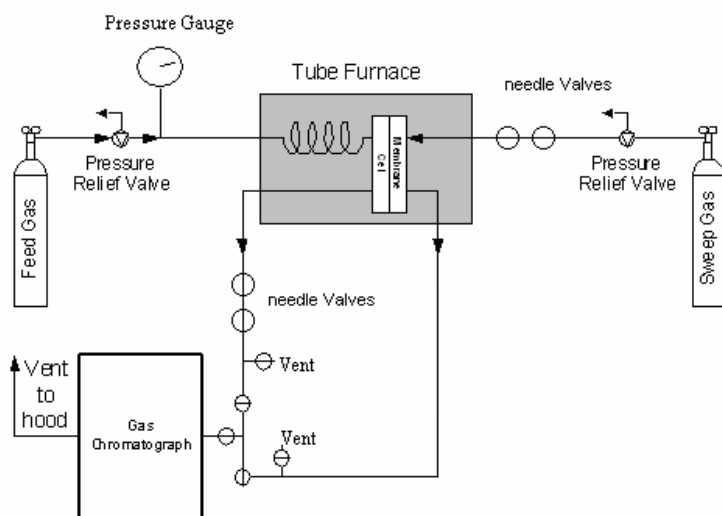## 3.2   High Temperature Gas Permeation Testing

Figure 2. High temperature gas permeation apparatus

Figure 2 shows the test apparatus used for the high temperature hydrogen permeation experiments. A Thermodyne tube furnace was used to maintain a test temperature of 300 ºC. The feed side of the membrane test cell was maintained at a pressure of 20 psi. A set of needle valves were used to control the feed gas flow and maintain a fresh feed gas supply. The feed gas flow was set to ~4 ml/min. Gases that permeated through the membrane were swept away in a helium gas stream controlled by another set of needle valves and the sweep flow rate was set at ~2 ml/ min. The gas mixture used in this testing was purchased from Scott Specialty Gas. The mixture contains 3% each of the following gases: H_2, Ar, CH_4, and CO_2 in a balance of N_2. The total permeate flow during testing was measured directly using an electronic soap bubble meter. The permeate flow was directed through a gas chromatograph (GC). The GC used in this testing is equipped with TCD detectors for the analysis of permanent gases and CO_2. Two different columns were used, a- Restek Q-Plot, and a Restek Mol-Sieve 5A. Injections were made through a set of automatic gas sampling valves. Permeabilities were calculated using eq. 5, where: $\Delta V/\Delta t$ is the total flow per unit time through the membrane, $T_{exp} P_{stp} / T_{stp} P_{exp}$ corrects to standard temperature and pressure, l is membrane thickness, A is membrane area, and Δp_1 is the pressure differential taken from the feed pressure and concentration determined from the GC analysis.

$$p = \frac{\Delta V}{\Delta t} \frac{T_{exp} P_{stp}}{P_{exp} T_{stp}} \frac{l}{A \Delta p_1}$$

eq 5.

4.   ACCOMPLISHMENTS

During FY 2006, all three technical tasks were studied and the findings and conclusion are detailed below.

4.1   HI Concentration

4.1.1   Nafion® membrane experiments.

During the initial stages of FY 2006, the study of Nafion-117® and Nafion-112® membranes at 134 ºC was completed. This work entailed testing of the Nafion® membranes against a feed of HI/iodine/water at 134ºC where the difference in the two membranes was the thickness. Nafion-117® is 180 μm thick while Nafion-112® is 50 μm thick. The data indicated the typical trade-off in membrane performance between membrane flux and separation factor, Fig. 3. For instance, Nafion-117® membranes yielded decreasing flux of water with decreasing concentration of water in the feed. Correspondingly, the separation factor increased over the same decrease in feed water concentration.

The separation factors between the two membranes were roughly consistent, as would be expected for membrane materials with identical chemical structure that differed only in their thickness. In terms of transmembrane flux, Nafion-117® membrane yielded a flux of 1353 g/m^{2}h at 31.2 % water. The flux decreased exponentially down to 242 g/m^{2}h at 22.7 % water. Over this span of concentrations, the separation factor increased from 3875 to 7241 with decreasing water concentration. Typically, use of a thinner membrane should provide enhanced flux rates without loss of separation factor. In this experiment, Nafion-112® yielded flux of 4353 g/m^{2}h at 32.5 % water, approximately a four-fold increase over the Nafion-117® at similar water concentration. As the water was removed from the feed, the flux decreased exponentially to 431 g/m^{2}h at 19.5 % water. Separation factors in this experiment were maintained, as expected, with data derived from Nafion-117® with values ranging from 2552 to 7948, with respect to concentration. The increase in flux with decreasing membrane thickness without loss of separation factor indicates that the thinner
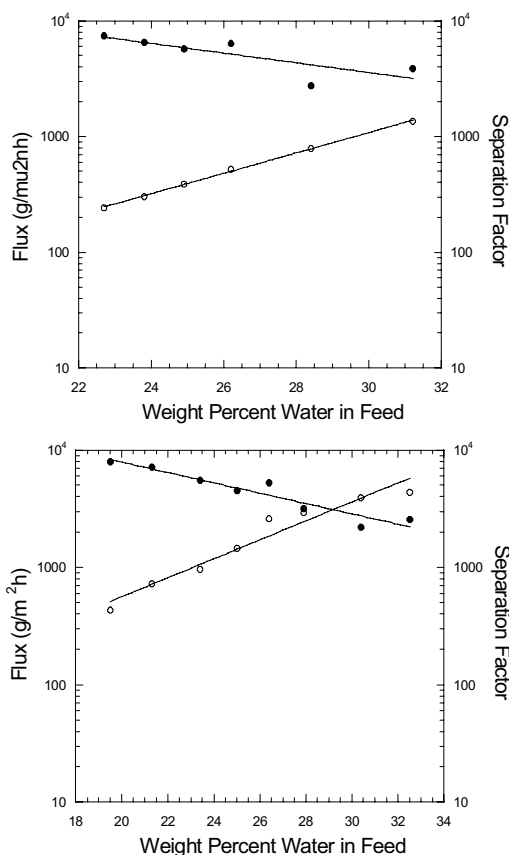

Figure 3. Flux (?) and separation factor (?) performance data for Nafion-117® (top) and Nafion-112® (bottom) at 134 ºC using an HI/iodine feed.

Nafion-112® is an effective membrane for this separation and would be more economical to purchase and operate than the thicker Nafion-117®. Moreover, no chemical degradation of either membrane was detected.

4.1.2   SPEEK membrane formulation and testing.

SPEEK membranes were also investigated for this separation. The principal advantages of SPEEK are that it is substantially cheaper and more processable than Nafion® polymers. Preparation of SPEEK membranes first required sulfonation of commercially obtained Poly (ether ether ketone) (PEEK). Sulfonation readily occurred by immersion of PEEK in concentrated H_2SO_4 (98 %) followed by heating to 68 ºC for controlled periods of time, following the method of Huang[6]. Longer heating times yield polymers with higher densities of sulfonate groups, which equates to correspondingly higher ion exchange capacity (IEC).

Membranes of SPEEK were prepared by solution casting of a 10 % (w/v) DMSO-polymer solution on to a glass plate preheated to 100 ºC on a hotplate. While drying, the membrane was covered to control the solvent evaporation rate. After 3 hours, the membrane was removed from the glass plate and further drying was accomplished using an argon-vacuum oven at 160 ºC for 3-4 days.
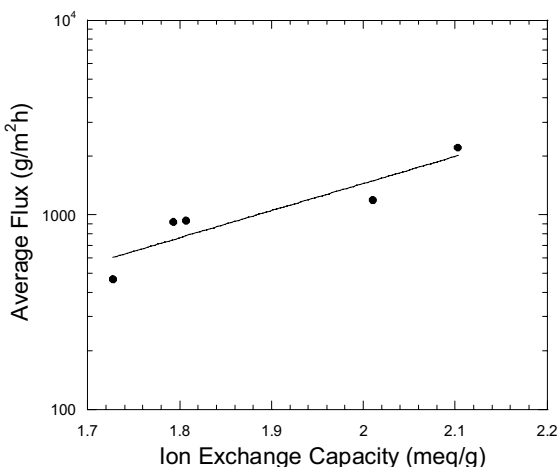

Figure 4.   Plot of average flux at 22 ºC vs. SPEEK ion exchange capacity.

Initial testing of the SPEEK membranes was performed using pure water pervaporation. A clear correlation between the IEC and the room temperature flux was observed, Fig 4. In this series, useful polymers were synthesized with IECs ranging from 1.7 to 2.1 meq/g. As expected, higher water permeabilities were noted for the higher IEC polymers. This result corresponds with the increased relative loading of hydrophilic sulfonate groups. Thus, more sulfonate groups equates to greater water permeability; however a simple application of this concept to membrane separations can be problematic. Increasing sulfonate content, for example, can result in polymers that are soluble in aqueous systems, including the HI feed.

Polymers with IECs of 2.3 meq/g were found to be soluble in water. At an IEC of ~1.8 meq/g, robust polymers that were soluble in DMSO (for membrane casting) but insoluble in water were formed. SPEEK 1.8 (SPEEK with and IEC of 1.8 meq/g) was measured to swell in water ~25%, comparable to Nafion®, and maintained dimensional stability when swollen. Membrane tests against HI feeds was performed on polymers with IECs of 1.7-1.8 meq/g. Control of membrane thicknesses was accomplished by polymer concentration in the casting solution. For this work, 10% (by weight) solutions in DMSO yielded membranes varying from 50 – 100 μm in thickness. Each membrane was measured with a micrometer prior to use.
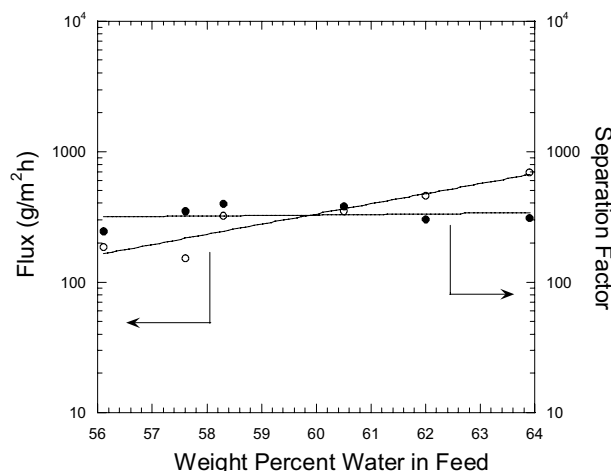
Figure 5. SPEEK 1.8 membrane performance in the concentration of HI at 22 ºC. Membrane thickness = 100 μm.

fluxes ranged from nearly 1200 to 600 g/m²h. Separation factors for this range were measured from 75 to 330. A further comparison of this data to the lower temperature 22 ºC experiment indicated increased flux with increasing temperature; however the separation factors decreased slightly.

Experiments at 131 ºC were performed using SPEEK 1.7 with an average thickness of 70 μm. In general, lower fluxes were observed than was expected. At this time, this is not clearly understood in that it may be a function of the lower IEC. Moreover, this conclusion would be supported by the data in Fig 4, which indicates that SPEEK 1.7 pure water flux is
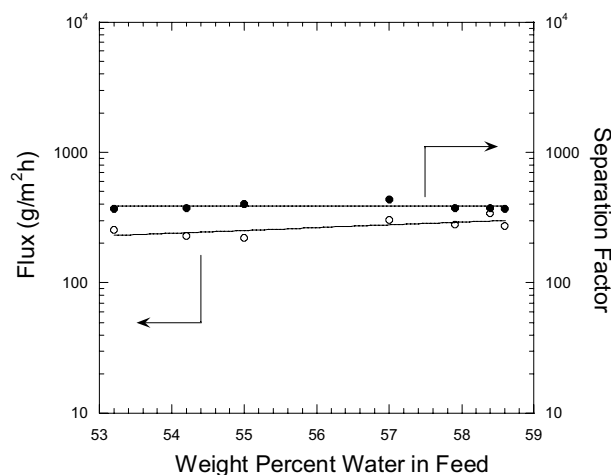

Figure 7 HI concentration performance of SPEEK 1.7 at 131 ºC. Membrane thickness = 70 μm.

Initial tests of SPEEK 1.8 membranes were performed using aqueous HI feeds at 22 ºC, Fig 5. In this ex periment, the water concentration was reduced from 64 % to 56 %. Over this span of concentrations, the flux was initially 693 g /m2h and decreased to 187 g/m²h, while the separation factors were steady at an average of 330.

Data on the performance of the SPEEK 1.8 membranes at 57 ºC is shown in Fig. 6. In this experiment, the water concentration was reduced from 68 % to 58%. As seen with the Nafion® membranes, flux decreases as the concentration of water decreases. A comparison to the 22 ºC data reveals higher fluxes for higher temperature experiment with respect to feed water concentration. Over the concentrations studied,
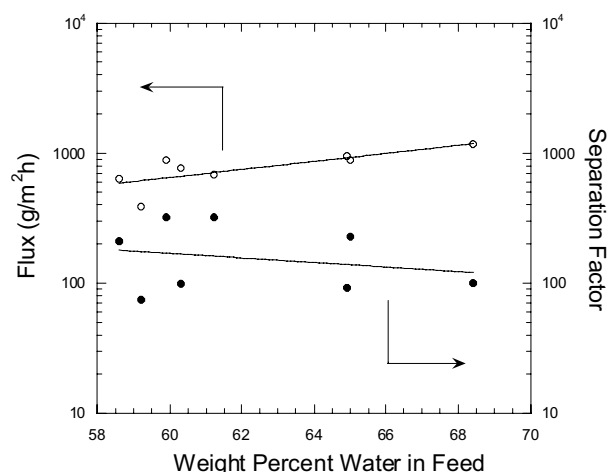
Figure 6. Performance of SPEEK 1.8 for the concentration of HI at 57 ºC using an 80 μm thick membrane.

approximately half of that measured for SPEEK 1.8. The separation factors for the SPEEK 1.7 are also somewhat higher than observed at 57 ºC, but roughly equal to those at 22 ºC. Loss of separation factor can be induced by higher operating temperatures and this data may suggest that the separation factor also can be due to the IEC. Most significantly, in this experiment, no deterioration of the membrane was observed suggesting that the SPEEK materials can withstand the desired conditions for this separation and perform the separation. However, it should be noted that these

materials have not been, as yet, exposed long term to HI/iodine mixtures in the pervaporation system. Immersion data indicates that the SPEEKs are resistant to degradation in HI/iodine feed. The scatter in the data is also much less for this data set due to a necessary redesign of the cell. It was extremely difficult to perform these separations using the cell that was originally designed for the Nafion® materials. Numerous instances of membrane leakage and failure occurred. The Teflon® portion of the membrane cell was redesigned to be thicker and was given a metal retaining ring on the top cover with the goal of reduced use-induced deformation. Teflon® does flow slightly at the high temperatures used in this study. The designed cell cover provides more stability to the membrane mount, and thus better data.

4.1.3   Task Summary.

A study of the concentration of HI/iodine/water was completed using the Nafion-117® and Nafion-112® membranes. In this work, a trade-off was observed between the permeability and the separation factor as a function of the water concentration in the feed. As the water content was reduced, fluxes of water were also reduced; however the separation factor was increased. Reducing the membrane thickness was clearly advantageous in that higher fluxes of water were measured for the thinner Nafion-112® without loss in the separation factor. Although Nafion® is an effective membrane, SPEEK membranes were studied because they are considerably cheaper and are more processable, which may be a benefit on implementation of this technology. A series of water permeable polymers were synthesized, characterized, and tested for HI concentration. Synthesis of SPEEK was accomplished through dissolution and heating of PEEK in concentrated H_2SO_4. Materials with a range of ion exchange capacities were made and characterized for variable temperature pure water flux. An exponential correlation was made between the water flux and the IEC. Membranes at the lower end of the IEC range, 1.7-1.8 meq/g, were selected for HI concentration experiments due to the relatively low amount of swelling (approximately 25 %) that these materials exhibited as excessive swelling can lead to mechanical failure of the membrane. It should be noted that the swelling amount is roughly consistent with that noted for Nafion®. SPEEK membranes were studied for HI concentration at 22, 57, and 131 ºC with result comparable to that of Nafion®. For example, using data for the various experiments, an extrapolation of performance can be made at a specific water concentration to provide a direct basis for comparison. In Table 1, the data from Nafion-112®, Nafion-117, and SPEEK 1.7 are compared for HI feed. HI/iodine data is also provided

For the HI feed, the Nafion® membranes appear to offer better performance. For instance, the fluxes of Nafion-117® and SPEEK 1.7 are roughly equal; however the separation factor for Nafion-117® is nearly six time larger suggesting that it performs the separation more effectively. Nafion-112®, as compared to SPEEK 1.7, offers superior fluxes with similar thickness membranes. Changing the feed to HI/iodine provided unexpectedly large increases in performance and whether this will be observed for the SPEEK 1.7 membrane will be determined.

Table 1   Calculated performance of Nafion® and SPEEK 1.7 membranes at 30 % feed water concentration.

Membrane	Feed	Flux (g/m2h)	Separation Factor	Temperature (°C)	Membrane Thickness (µm)
Nafion-112®	HI	433	-	134	50
Nafion-117®	HI	66	1870	134	180
SPEEK 1.7	HI	72	384	131	70
Nafion-112®	HI/iodine	3615	2857	134	50
Nafion-117	HI/iodine	1082	3571	134	180

4.2   Sulfuric acid concentration

During FY 2006, a brief "proof of principle" task was conducted to apply the concept of pervaporation to H_2SO_4 concentration. Large separation factors have been measured for the HI/water separation due to both the low solubility of HI within the membrane and the low vapor pressure of aqueous HI, as compared to water. Logically, this condition would also apply to H_2SO_4. Furthermore, H_2SO_4 has a lower vapor pressure than HI, suggesting that higher separation factors should be possible.
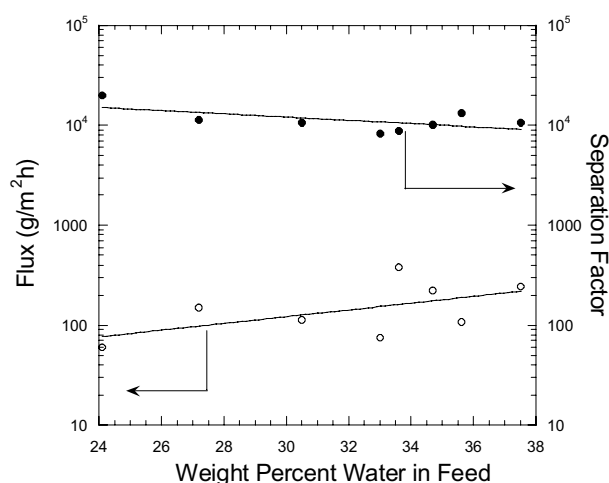

Figure 8. Concentration of Sulfuric Acid using Nafion-112® at 100 °C.

Both Nafion-117® and Nafion-112® membranes were studied against an aqueous H_2SO_4 feed. In an example collected using Nafion-112® at 100 °C, the water concentration in H_2SO_4 was reduced from 37 to 24 %, Fig 8. Fluxes varied from 381 to 60 g/m^2h and decreased with increasing acid concentration (decreasing water concentration). Separation factors for this separation were quite high, ranging from 8000 to 13000. Also, no degradation of the membranes was observed at these temperatures. Further experiments are planned for FY 2007 to determine the feasibility of long term use of Nafion® membranes for this separation.

4.2.1 Task Summary.

Nafion® materials are suitable for study as pervaporation membranes for H_2SO_4 concentration. A recommendation of the technology for concentration of H_2SO_4 decomposer effluent requires more work at appropriate concentrations and temperatures. Furthermore, the application of the cheaper SPEEK membranes for this separation is possible; however the dimensional stability of SPEEK membranes in concentrated H_2SO_4 is unknown. Considering the fact that SPEEK is formed by dissolution of PEEK in concentrated H_2SO_4, it is possible that the membrane may be soluble in the feed. However, processed SPEEK membranes (cast, dried, and heated in an argon oven) tend to be no longer soluble in their casting solvent (DMSO) suggesting that they also may no longer be soluble in concentrated H_2SO_4.

4.3 High temperature hydrogen transport membranes.

In the HI decomposition step, conversion of HI to iodine and hydrogen is equilibrium limited and has been measured at only 20 %. To encourage a greater degree of conversion, hydrogen removal has been proposed. In this task, membrane materials were sought that could selectively remove hydrogen from the reactor while retaining HI and iodine. The desired operating temperature is 300 ºC. In this initial work, high performance polymeric materials were screened for thermal stability and hydrogen permeability at 300 ºC. High performance polymers of interest for this work tend to be glassy, which suggests that their gas transport behavior would be dominated by diffusion, rather than solubility as observed in this project's pervaporation work. Thus, membrane selectivity is dictated by molecular size. Hydrogen is substantially smaller than HI or iodine and would be expected to be favored in an actual separation.

Polyimides, such as Kapton and Kevlar, are known for their thermal and physical durability; however their hydrogen permeability was unknown. As shown in Table 2, commercially available VTEC polyimide had a permeability of 47.9 Barrers, which equates to a flux of 17.8L/m²h (standard liters/square meter of membrane per hour). Modest increases in the permeabilities were achieved in this polymer by the inclusion of non-volatile inorganic species. For example, the permeability of the VTEC was increased to 81.64, 110.7, and 108.1 Barrers by the addition of 5 wt % Br_2, 1 wt % Br_2, and 1 wt % LiCl, respectively. Conversion of these permeability values into permeance yields 15.2, 15.4, and 20.1 L/m²h for the three materials. For the most permeable of these materials, VTEC with 1 % LiCl, this permeability equates to a membrane size of 54 m² to remove 1000 L/h. The CMS-3 film was somewhat problematic. Decomposition points for all membranes were determined using standard thermogravimetric analysis (TGA) techniques. From this data, it was determined that the CMS-3 sample should have been stable to almost 500 ºC. However, decomposition was observed at 300 ºC in the membrane test system. At 290 ºC, the material was stable and yielded the highest hydrogen flux (153.5 L/m²h) of all the membranes studied. At this flux rate, to remove 1000 liters of gas per hours, only 6.7 m² of membrane area would be required. Mylar is a durable polymer that was readily available in our laboratory. It is known to be relatively impermeable to most gases and hydrogen was not an exception with a permeability measured at only 2.5 Barrers, substantially lower than any of the other membranes in this study. The most surprising piece of data was collected from the SPEEK membrane. This particular SPEEK membrane had an IEC of 2.139 meq/g. This material had a permeability of 95.8 Barrers and a decomposition point of 485 ºC.

Table 2 Performance data for selected membranes at 300 ºC.

	Membrane Formation Method	Hydrogen Permeability (Barrers)	Hydrogen Permeance (L/m^{2}h)*	Decomposition Temperature (ºC)
VTEC (polyimide) Polymer Lot# 851	Solution Cast film	47.9	17.8	546
VTEC Polymer Lot# 80-851 With 5% by wt Br$_2$	Solution Cast film	81.64	15.2	553
VTEC Polymer Lot# 80-851 With 1% by wt Br$_2$	Solution Cast film	110.7	15.4	556
VTEC Polymer Lot# 80-851 With 1% LiCl by wt	Solution Cast film	108.1	20.1	524
Dupont Kapton (HN) 50 um thick Film	Purchased Film	39.2	4.4	574
Dupont Kapton (HN) 30 um thick Film	Purchased Film	45.6	8.5	574
CMS 3 Resin Film 50 um thick	Purchased Film	1100**	153.5	482
Mylar 15 um Film	Purchased Film	2.5	0.9	418
SPEEK (IEC = 2.139)	Solution Cast film	95.8	13.4	485

* Standard liters of gas per square meter of membrane per hour.
** Data collected at 290 ºC. At 300 ºC, this material unexpectedly degraded.

4.3.1   Task Summary.

Nine different high performance polymer membranes were screened for hydrogen permeation at 300 ºC and a range of permeabilities was obtained. As a measure of these membranes, the polymeric materials from this study can be compared to palladium membranes that have permeances as high as 26,000 L/m^{2}h.[7] This value is 2-3 orders of magnitude higher than any of the studied polymeric membranes. Palladium is an intriguing membrane material for hydrogen separation because it is transported by an activated process. Hydrogen uniquely transports across palladium membranes by oxidative addition of hydrogen to the palladium, followed by diffusion and recombination. Palladium membranes were tested by General Atomics for hydrogen separation from the HI decomposer. The membranes were found to rapidly fail due to oxidation of the palladium metal by HI and iodine. Thus, there is a trade-off between the transport behaviors and properties of polymers and palladium. Palladium has high permeability, but is oxidatively unstable. Polymers are stable, but exhibit far lower rates of hydrogen permeation.

5.   PROJECT SUMMARY AND IMPLICATIONS OF THE RESEARCH

Three separate membrane tasks have been investigated during FY 2006. First, membranes were investigated for the concentration of HI. SPEEK were prepared and characterized according to literature reports. The polymers, ranging in IECs of 1.7-2.3, were found to be soluble in dimethylsulfoxide for membrane casting. Procedures for membrane formation were developed as well as procedures for membrane testing. At this time and with the limited data available, the SPEEK polymers do not appear to have the effectiveness of the Nafion® polymers, although they do perform the separation and are resistant to deterioration. To fully investigate the behavior of the SPEEK polymers, additional experiments are required using higher IEC samples. It is expected that membranes with a higher concentration of sulfonate groups, which facilitate water transport, should result in increases in transmembrane flux. However the separation factor should be measured carefully. Significant losses in separation factor, in reference to the SPEEK 1.7 131 ºC result as compared to Nafion®, may not be acceptable.

Second, Nafion® membranes were investigated for use in the concentration of H_2SO_4 by pervaporation. This "proof of principle" study was used to assess the overall feasibility of this membrane material for this particular application. Data obtained at 100 ºC indicated significant fluxes of water at high separation factors with no observable deterioration of the membranes suggesting that this is a valid concept for pursuit. The next step in this research should be to perform the separations at conditions more closely aligned to the application of concentrating H_2SO_4 for recycle to the decomposer. This would most likely be concentration of the acid from 85 wt.% to 95 wt.%, or greater. This work has been proposed as a part of the FY 2007 work scope.

Third, membranes were characterized for hydrogen permeability at 300 ºC. Currently, the HI decomposition has an approximately 20 % conversion, which is far too low for practical deployment. The reaction equilibrium can be influenced by the removal of reaction products. Removal of hydrogen appears to be a facile route due to its small molecular size. In this task, high performance polymeric membranes were characterized for their stability and transport behavior. An application for these membranes would be in a catalytic membrane reactor in which the HI is decomposed over a catalyst and the product hydrogen is selectively removed in one homogenous unit. Although no studies have been performed to characterize transport of the other constituents, HI and iodine, found in the decomposer, it is reasonable to suggest that their permeability will be substantially lower than hydrogen. Thus, it may be possible to directly employ these membranes in lab scale HI decomposer tests to study separation effectiveness.

6. PUBLICATION AND PRESENTATIONS

1. Frederick F. Stewart and Christopher J. Orme, "Stability and Performance of Nafion-117® Membranes for the Concentration of HI/Water and HI/Water/Iodine Mixtures" AICHE Proceedings, Annual AICHE Meeting, Cincinnati, OH, Paper 257g, **2005**.

2. Frederick F. Stewart, Christopher J. Orme, and Michael G. Jones, "Membrane Processes for the Sulfur-Iodine Thermochemical Cycle", International Journal of Hydrogen Energy **2006**, In press.

3. Frederick F. Stewart and Christopher J. Orme, "Advances in Acid Concentration Membrane Technology for the Sulfur-Iodine Thermochemical Cycle" AICHE Proceedings, Annual AICHE Meeting, San Francisco, CA, **2006**.

4. Frederick F. Stewart and Christopher Orme, "Pervaporation of Water from Aqueous Hydriodic Acid and Iodine Mixtures Using Nafion Membranes", Manuscript in preparation for the Journal of Membrane Science.

5. Frederick F. Stewart and Christopher J. Orme, "Stability and Performance of Nafion-117 Membranes for the Concentration of HI/Water and HI/Water/Iodine Mixtures" Presented to the Annual AICHE Meeting, Nuclear Engineering Division, Cincinnati, OH, November 2005.

6. Frederick F. Stewart and Christopher J. Orme, "Advances in Acid Concentration Membrane Technology for the Sulfur-Iodine Thermochemical Cycle" To be presented to the Annual AICHE Meeting, Nuclear Engineering Division, San Francisco, CA, November 2006.

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