Stability and Performance of Nafion-117 Membranes for the Concentration of HI/Water and HI/Water/Iodine Mixtures

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Abstract

Thermochemical water splitting processes for generating hydrogen have been researched for at least thirty years in which over 100 chemical cycles have been proposed, some of which are purely chemical processes and others that contain electrochemical steps. A common theme of all of the proposed cycles is the use of a heat source, potentially as high as 2000 °C. Proposed heat sources include nuclear reactors and solar reflectors. One of the most promising cycles is the Sulfur-Iodine (S-I) process, where aqueous HI is thermochemically decomposed into H_2 and I_2 at approximately 400 °C. Regeneration of HI is accomplished using SO_2 generated from a sulfuric acid decomposition cycle performed at 800-900 °C, thus the cycle actually consists of two concurrent oxidation-reduction loops. As HI is regenerated, co-produced H_2SO_4 must be separated prior to decomposition. Current flowsheets employ a large amount (~83 mol% of the entire mixture) of elemental I_2 to cause the HI and the H_2SO_4 to separate into two phases. Removal of water from this system has the direct result of lowering the required quantity of I_2, thus reducing the amount of material that must be physically moved within an S-I plant.

Efforts at the INL have focused on studying the application of pervaporation to the de-watering of an HI/water/I_2 feedstream. Nafion-117® [1]and Nafion-112® were characterized for their ability to pass water with a high degree of separation from both concentrated HI and HI_x feed streams. Both Nafion-117® and Nafion-112® were shown to be effective in the removal of water from these feeds and showed no degradation, even upon testing at temperature as high as 135 °C. Typical in the transport behavior of these membranes was the trade-off between flux and separation performance. With lower water concentrations in the feeds, flux rates tended to decrease while the separation performance increased. Nafion-117®, the thicker membrane (0.007"), was characterized by more modest water fluxes and high separation factors. Nafion-112® membranes, which are thinner at 0.002", were characterized with substantially higher fluxes, however the separation factors were considerably lower.

Introduction

Thermochemical water splitting cycles are methods that have been proposed to generate hydrogen on a commercial scale. In general, hydrogen today is formed from the steam reforming of natural gas. Hydrogen generated using this method is consumed in industrial processes, such as petroleum refining. Interest exists in using hydrogen as an energy carrier for the transportation energy sector and other applications where petroleum is used today.

Formation of hydrogen from thermochemical cycles has been proposed using nuclear reactor supplied thermal energy.[2] The only chemical input is water and the only effluent is oxygen and hydrogen. From an energy input standpoint, heat, in the range of 750 °C to 1000 °C, is provided to drive the reactions, which tend to be endothermic. Thermochemical cycles were principally investigated from the 1960's through the 1980's. However, interest waned with the drop in crude oil prices in the 1980's. Recent energy price increases and U.S. national security issues have renewed interest in hydrogen production. Advantages of nuclear driven hydrogen production include hydrogen's inherent renewable nature, a reliance of the process on U.S. domestic resources, and an absence of CO_2 emissions. Similar advantages can be obtained through the use of high temperature solar concentrators.

In the literature, more than 100 thermochemical cycles have been proposed and studied to some degree.[3] One of the more developed cycles, the sulfur-iodine process (S-I), [4], is comprised of three chemical reactions. Water enters the cycle as a reactant in the Bunsen reaction[5], as shown in Eq 1.

$SO_2 + I_2 + 2H_2O \bullet H_2SO_4 + 2HI$ eq 1

In Eq.1, hydriodic acid (HI) is formed from the reduction of I_2 at an approximate temperature of 120 °C. HI is then decomposed to generate H_2 at 400 °C to 500 °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 900 °C, Eq 3.

$2HI \bullet H_2 + I_2$ eq 2

$2H_2SO_4 \bullet 2H_2O + 2SO_2 + O_2$ eq 3

Key to the operation of this proposed cycle is the Bunsen reaction. Current flowsheets indicate that 7500 Kg of material must be physically moved within a plant for every Kg of hydrogen generated, and much of this mass is iodine associated with the Bunsen reaction. A large excess of I_2 is added to separate the HI from the H_2SO_4, which causes the product mixture to separate into two phases. Water and H_2SO_4 comprise the lighter phase, while the heavier 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 has been proposed to be added to the system to remove water from the HI/I_2 mixture. Direct removal of water using a membrane process would allow for a large reduction in the amount of iodine, thus increasing the efficiency of the cycle by lowering the recycle ratio per Kg of hydrogen generated. However, membrane concentration of HI/I_2 mixtures has not been demonstrated. For these studies, we have focused on Nafion-117® and Nafion-112® membranes in the pervaporation of water from a HI/water/I_2 feed.

Experimental Methods

Nafion-117® and Nafion-112® membranes were obtained from Aldrich Chemical Co. and used as received. Membrane thicknesses were measured using a Mitutoyo micrometer to be approximately 180 μm and 50 μm for Nafion-117® and Nafion-112®, respectively. The HI_x feed was prepared by addition of deionized water (40 g) and elemental iodine (100.9 g, Aldrich Chemical Co.) to a 55 % aqueous solution of HI (86.9 g, Aldrich Chemical Co.). The HI feed consisted of the 55 % HI as received without dilution. HI concentrations in both the feed and permeate samples were determined by titration against standardized sodium hydroxide

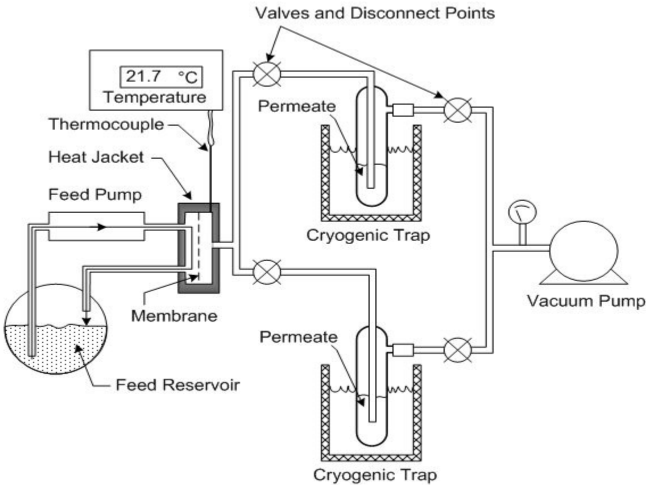

Figure 1. Pervaporation System

solutions to a phenolphthalein endpoint. A pervaporation apparatus, see Fig. 1, was constructed for this work using a Millipore 47 mm filtration cell modified with an extra port for feed side flow.

Membranes were secured using Viton O-rings and leak-checked against 50 psi nitrogen gas prior to use. All tubing and connectors were made of Teflon®. Pumping of the feed was accomplished using a Teflon® or Viton® rubber peristaltic pump obtained from Cole-Parmer Inc. Temperatures were measured at the cell using a calibrated thermocouple. The temperature of the cell was controlled with heat tape. Feed flow rates were sub-turbulent at approximately 10-30 ml per minute. Permeate side pressure was maintained at 100 mTorr using a mechanical vacuum pump. All permeates were trapped cryogenically and measured gravimetrically to determine the transmembrane flux.

Results and Discussion

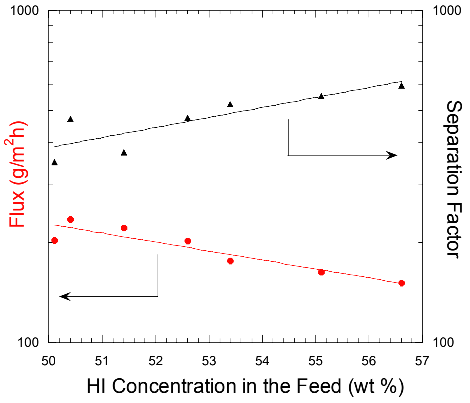

Figure 2. Nafion-117® membrane performance as a factor of feed HI concentration at 132 °C and a flow rate of 10 mL/min.

Nafion-117® Membranes. Nafion-117® is a commercially available perfluoroethylene sulfonate membrane with an ion exchange capacity of 1100 g/EW (grams per equivalent weight) and a thickness of 0.007" (180 μm). It is a durable plastic material that is easy to install into a pervaporation system. However, its structure is far more complex with a porous, phase-separated nature that results in both hydrophilic and hydrophobic regions. The hydrophobic portions of the polymer consist of Teflon-like perfluoroethylene units, while the hydrophilic sulfonates, which are attached to the polymer backbone through perfluorinated chains, tend to form inverse micelles giving tortuous pathway pore structures through which water can pass.

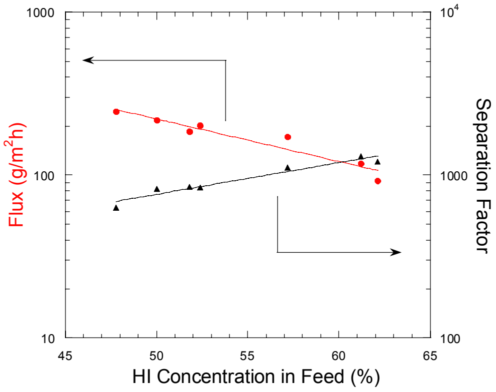

Figure 3. Nafion-117® performance at 134 °C and a flow rate of 28 mL/min using an HI/water feed as a factor of HI concentration.

Testing of Nafion-117® membranes was conducted at 132 °C as shown in Figure 2. Both fluxes and separation factors were determined using an HI/water feed. Flux of water ranged from 151 – 235 g/m^2h and decreased with increasing HI concentration, which also corresponds with decreasing water concentration. Separation factors ranged from 350 – 595, which are commercially competitive. With respect to increasing HI concentration, fluxes were observed to decrease and separations factors increased. This behavior is typical of membrane processes in which a trade-off is observed between flux and separation factor. Decreasing fluxes with decreasing water concentration also is typical of membrane processes.

An additional aspect that was addressed in this particular experiment was the feed flow rate. Flux changes with changes in flow rate across the surface of the membrane can be indicative of the presence of a boundary layer. A boundary layer is a permeant depleted zone at the surface of the membrane that inhibits further permeation. In Figure 2, the flow rate was 10 mL per minute. Increasing the flow rate as shown in Figure 3 to 28 mL/min revealed little significant difference in membrane flux performance suggesting that, at least at the flow rates examined, a boundary layer does not appear to inhibit water transport.

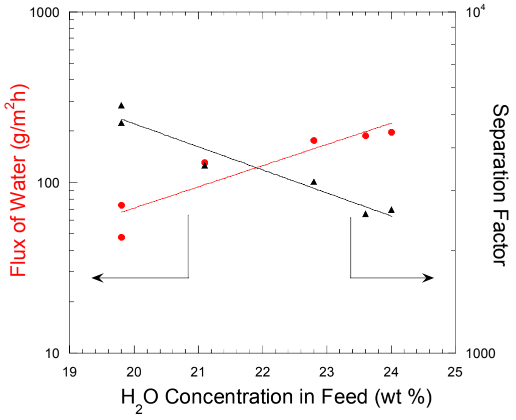

Figure 4. Performance of a Nafion-117® membrane using HI/water/I_2 feed at 85 °C in terms of the feed water concentration.

Experiments using a HI/water/I_2 feed were found to require a slight re-engineering of the test system. The most significant modification was the replacement of a half of the membrane cell with a Teflon® component. The membrane cells used in this work consist of two halves that are bolted together; a feed side and a permeate side with the membrane mounted as a separator. In this work, the feed side was duplicated by the INL machine shop using a Teflon block. The permeate side was retained because of the rigidity that it provided to the cell as a whole and due to the membrane's ability to perform the separation, the permeate side did not experience any significant corrosion.

Due to the use of the hybrid cell configuration, experiments were conducted first at 85 °C and then at 125 °C using a feed that consisted of a 1:6:1 molar ratio of HI, water and I_2, respectively. As shown in Figure 4, the data at 85 °C is plotted in terms of the water concentration, however the data is consistent with the above experiments in which higher fluxes of water are observed from feeds that have a higher water concentration. Fluxes of water range from 48-197 g/m^2h, depending on feed concentration. Separation factors, likewise, were observed to increase with decreasing feed water concentration, ranging from 2636 to 5330. These data are significantly higher than the previous experiments, which could be due to the extremely low concentration of HI_x in the permeate. However, the relative difference in separation factors from previous experiments shown above to this experiment should not be considered overly significant due to the mathematical implications of dividing large numbers by small numbers. Slight deviances in the

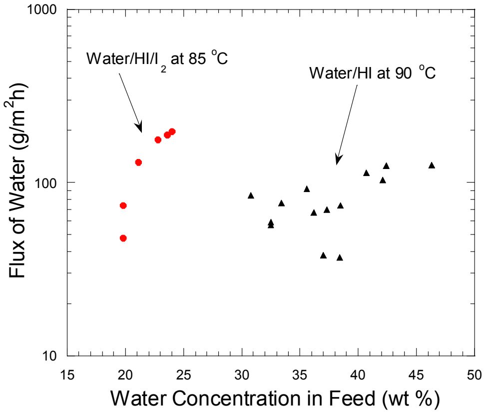

Figure 5. A comparison of the flux of water with the two feed types with respect to feed water concentration.

smaller terms, such as permeate HI_x concentrations in the $10^{-3} – 10^{-4}$ range, can cause inordinately large swings in the measured separation factor. The more meaningful conclusion that can be drawn from this experiment is that the permeate of both HI/water and HI/water/I_2 experiments are virtually the same in terms of their composition.

A comparison of flux data for the two differing feeds steams revealed an unexpected comparison. Typically, the flux is a function of the permeant content in the feed. In this instance this relationship was not observed, see Figure 5. Fluxes of water from iodine-enhanced feeds are roughly similar to that of the HI/water feeds although there is significantly lower water content in the iodine-added samples. This phenomenon has not been further studied in this work, however a potential explanation involves the fact that the molar ratios of HI/water and HI_x/water is nearly the same in these two experiments, thus yielding similar water fluxes.

Pervaporation experiments were also conducted at 125 °C on the HI/water/I_2 feed. In this experiment, a solution was prepared using additional water for an initial molar ratio of 1:12:1 for HI, water, and iodine, respectively. This was done due to a tendency for the I_2 to precipitate from more concentrated (water content < 20%) solutions of HI_x upon removal of water. Precipitated iodine clogs the pumping system and also fouls the membrane. This behavior could be alleviated by maintaining high system temperatures since the precipitation appears to occur during the cool down cycle between daylong experiments. The additional water in the feed allows for several days operating time on a single batch of feed without precipitation concerns.

Results for this experiment yielded high initial fluxes, up to 900 g/m^{2}h, which was expected due to the higher water content of the feed (~30%), see Figure 6. These flux rates rapidly fell to 282 g/m^2 as water was removed from the system. In comparison to the corresponding experiment at 85 °C, higher system operating temperatures yielded significantly higher flux rates. Also observed was the expected increasing trend in the separation factor from 106 to 885, consistent with the previous experiments. The actual magnitudes of the separation factors were considerably less than data measured at 85 °C, however these values, in general, are large for commercial membrane processes.

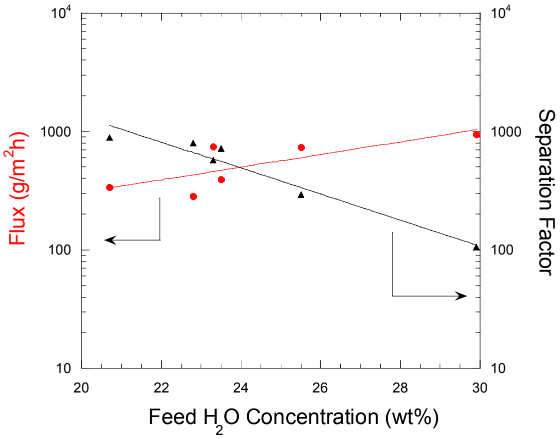

Figure 6. Nafion –117® performance using an HI/Water/I_2 feed at 125 °C.

Nafion-112® Membranes. Nafion-112® has the same equivalent weight of ion carrier as does the Nafion-117®. The only difference is the material thickness. Nafion-112® is substantially thinner at 0.002" (50 µm). Thinner membranes are expected to yield far higher permeant fluxes and lower separation factors. This was of interest because the Nafion-117® membranes yielded potentially greater separation than what should be required for the S-I process, so this provided an opportunity to take advantage of the “excess” separation capability to increase permeant fluxes. Permeant fluxes are directly reflected by the membrane area in that lower flux processes require larger membranes per unit volume of feedstream. Conversely, higher flux processes result in lower membrane area requirements, which, in turn, significantly lower the membrane process capital, operations, and maintenance costs.

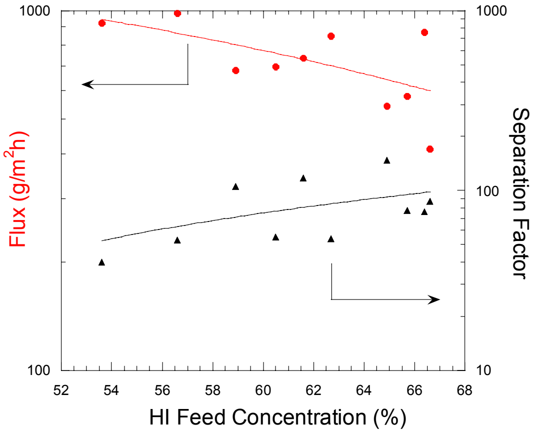

Figure 7. Performance of a Nafion-112® membrane at 133 °C using an HI/water feed.

At 133 °C, both fluxes and separation factors were measured as shown in Figure 7. With respect to feed HI concentration, the trade-off between flux rate and separation factor was again observed. However, the magnitude of each parameter was significantly different. For example, permeant fluxes ranged from 400 – 1000 g/m^2h, depending on feed concentration where lower water concentrations (higher HI concentrations) yielded lower fluxes. More significantly, it was noted that these flux rates were substantially higher than those derived from Nafion-117®, thus validating the expected relationship between flux rates and membrane thickness. Providing additional support were the separation factors, which ranged from 50 – 150. These values are much lower than the Nafion-117® data, as expected. An additional feature of this work that is worth noting is the concentration of the acid. During this experiment, the initial acid concentration was measured to be 53% HI. As the experiment was conducted, the acid was concentrated to approximately 67% HI. HI and water form a low boiling azeotrope at 57% HI. Thus, this is a clear demonstration of the use of pervaporation to “break” the HI/water azeotrope and yield a higher acid concentration than would be possible using distillation.

Conclusion

Two membrane materials were identified for their ability to pass water with a high degree of separation from both concentrated HI and HI_x feed streams. Both Nafion-117® and Nafion-112® were shown to be effective in the removal of water from these feeds and showed no degradation, even upon testing at temperature as high as 135 °C. Typical in the transport behavior of these membranes was the trade-off between flux and separation performance. With lower water concentrations in the feeds, flux rates tended to decrease while the separation performance increased. Nafion-117®, the thicker membrane (0.007"), was characterized by more modest water fluxes and high separation factors. Nafion-112® membranes, which are thinner at 0.002", were characterized with substantially higher fluxes, however the separation factors were considerably lower.

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References

[1] References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its

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