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Qualitative Determination of H_2S Crossover Rates in Nafion™ Membranes using Ion-probe Techniques

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ABSTRACT

Polymer electrolyte membrane fuel cells are sensitive to impurities that may be present in either the oxidizer or fuel. H_2S, even at the ppb level, will have a dramatic and adverse affect on fuel cell performance. The H_2S permeability through dry and humidified Nafion™ PEMFC membranes was studied using ion probe techniques. A sulfide anti-oxidant buffer solution was used to trap and concentrate trace quantities of H_2S that permeated through 50 cm^2 samples of Nafion™ 117 and 212 membranes using a partial pressure difference up to 1030ppm at room temperature. Experiments were conducted for up to 24 hours in order to achieve sulfide ion concentrations high enough to be precisely determined by subsequent titration with $Pb(NO_3)_2$. The rate of H_2S crossover for dry 117 and 212 were identical at $1.2e^{-7}$ g/min. Humidification increased the crossover rate to $5.9e^{-7}$ g/min and $1.8e^{-6}$ g/min for 117 and 212 respectively. Although the data collected in this work show that the rate of H_2S crossover increases with water content and reduced membrane thickness, an accurate determination of permeation constants from this work was not possible because the H_2S partial pressure was not constant throughout the experiment.

Introduction

Commercially viable PEFCs for automotive applications will most likely operate, at least initially, on hydrogen derived from reformed fossil fuels [1]. Although reforming produces hydrogen-rich fuel streams there will be invariably several other unwanted accompanying constituents. Determination of the upper limits and permissible concentrations of impurities must be made since the wholesale hydrogen costs will be intimately tied to the extent of post-production cleanup. DOE's 2010 and 2015 technical targets for Pt decrease loadings from 0.2 to 0.05 mg Pt/cm^2 at the anode. At these levels, even trace amounts of contaminants may be detrimental to fuel cell operation. Therefore, efficient fuel cell operation relies on the availability of both high purity fuel and air.

In the hydrogen fuel, the impurities can be present in the primary source of fuel or can be generated during the reforming process. For example, steam reformation of fossil fuels such as methane or coal, besides H_2, may produce various impurities at levels that can easily be detrimental to FC operation [2]. Typical fuel impurities are carbon monoxide (CO), ammonia (NH_3) and hydrogen sulfide (H_2S). On the cathode side, ambient air contains pollutants (e.g. NO_x, SO_2, and particulates), mostly coming from fossil fuel combustion, which also degrade FC performance. Our work focuses on assessing the severity of the impurity effects and developing methods of mitigating their negative effects on performance.

To date, most effort (including our own) has focused individually on the effects of single impurities. CO studies, in particular, have been well documented at higher concentration (>5 ppm). It is well known that CO adsorbs onto Pt, blocking surface active sites and inhibiting hydrogen oxidation. Mitigating strategies for CO such as air bleeding, increased temperature, and using Pt-alloys have been well documented [see ref. 3 and references therein, for example]. Past H_2S studies indicate S-species as much stronger site blockers than CO because of a greater affinity for metals, with higher concentrations and longer exposure times capable of leading to irreversible poisoning [4,5,6]. Most recently, we have reported that H_2S concentrations as low as 10 ppb, produced negative effects on fuel cell performance [4]. We have also recently shown that open circuit voltage helps to recover some of the performance losses due to S-species adsorption. The extent of sulfur poisoning of anodes was also shown to be a strong function of fuel cell operating voltage during H_2S exposure. Furthermore, previous studies have shown that the catalytic activity of the Pt surface and proton conductivity of the ionomeric component is very sensitive to the presence of certain impurities [8-14].

This work focuses on determining the extent to which potential contaminants may crossover through the electrolyte membrane and potentially poison both catalyst layers. If impurities and contaminants on the fuel side can migrate across the electrolyte membrane and poison the cathode catalyst layer, then this potentially complicates electrochemical clean up techniques and may even complicate physical solutions to fuel cell poisoning such as filters and traps.

Experimental

Standards Preparation and Ion Probe Calibration

A Fisher Scientific, Accumet, ion selective silver/sulfide combination electrode was selected for this work. The reference fill solution used at all times was 1M KNO_3. A Keithley 236 source measurement unit was used to measure the open circuit electric potential generated by the ion probe. Before experiments, the performance of the ion probe was ascertained by the generation of a calibration curve; a plot of electrode EMF versus base ten logarithm of sulfide ion concentration of three solutions prepared from a single stock solution via serial dilution.

To make the stock solution, approximately 0.1 g of anhydrous Na_2S (Alfa Aesar) was placed into a 250 ml Nalgene™ volumetric flask and 18.5Mohm distilled/de-ionized water was added to the fill mark. This produced a solution concentration in the neighborhood of 0.5 mM. The flask was agitated until all the Na_2S was dissolved. An aliquot of 25ml was measured using a Nalgene™ graduate cylinder and this volume was transferred to another 250 ml Nalgene™ volumetric flask. The total volume was brought to 250 ml mark. This process was repeated one more time producing a third flask and three concentrations of sulfide ion in the range of 10^{-3}, 10^{-4}, and 10^{-5} M. Three 100 ml

Nalgene™ containers were cleaned and rinsed with distilled/de-ionized water. A 50 ml aliquot was taken from each of the flasks and transferred to the 100 ml sample containers. 50 ml of sulfide anti-oxidant buffer (SAOB, Orion – 2M NaOH with ascorbic acid and disodium EDTA) was then added to each of the three standards; the final NaOH concentration for all experiments was 1M and a pH = 12. Typical lifetime of sulfide standards prepared in this fashion is roughly 1 week to possibly 2 weeks depending on rate of buffer oxidation.

The three standards were placed in an isothermal bath and allowed to reach thermal equilibrium with the bath water at 26°C. The ion probe was then immersed in these standards (in order of low concentration to high concentration), equilibrated until the voltage output stabilized. A difference of around 30 mV between each of the standards is normal. While the slope of the calibration curve could be calculated at this point, the intercept was undefined because the exact starting sulfide ion concentration was unknown and a titration had to be performed.

The sodium sulfide solutions were titrated with lead nitrate. $Pb(NO_3)_2$ (Mallinkrodct) was first analyzed using TGA to determine if there were any waters of hydration. In this work, the reagent was found to be dry and a titrant solution was prepared using 10.23 g of salt to 1L of distilled/de-ionized water. A 10 ml aliquot of the 0.03M $Pb(NO_3)_2$ solution was transferred to a burette. A 50 ml aliquot of the 10^{-3} M standard was transferred to a Nalgene™ graduate cylinder cut down in size so that the tip of the ion probe could be immersed at least 1 cm below the surface of the liquid. A Teflon coated stirring bar was added. The assembly was placed into the isothermal bath and the temperature of the sample, probe, etc. equilibrated to 26°C. After achieving a steady-state EMF reading from the ion probe, the titrant was slowly added while the EMF change was recorded. When the probe EMF increased to slightly above -0.7V, the additions were made drop-wise (approximately 0.05 ml additions) until the endpoint was achieved signified by a rapid increase in voltage to between -0.64 and -0.62 V. The volume of titrant added divided by the initial sample size (50 ml) multiplied by the concentration of the titrant produced the sulfide ion concentration. A titration was only performed on the 10^{-3}M standard as the remaining two standards are defined by serial dilution.

Nalgene™ glassware was used in all of these aqueous experiments whenever sodium hydroxide and/or sulfide ions were involved.

Membrane Preparation

We employed protonated Nafion™ membranes with different thickness into fuel cell hardware (50 cm^2) without the presence of platinum electrodes. The Nafion™ membranes used in this particular work were 117 (174 μm thick) and 212 (50.8μm thick). Each of the membranes was subjected to identical pre-treatment steps. The membranes were boiled for 1 hour in a 3% H_20_2 solution to clean them. Next, the membranes were ion-exchanged from the 'as-received' H^+ form into a process friendly Na^+ form. The Na^+ form increases the glass transition temperature, which inherently allows us to employ an in-house MEA manufacturing process. This process is described in detail, elsewhere [15]. This is also the form in which we typically store our membranes. However, because we did not adhere electrodes to the membranes, we simply reverted back to the H^+ of the membrane by boiling in 0.5 M H_2SO_4 and then de-ionized H_2O, each for 1 hr.

In this manner, with the exception of that Pt electrodes were not employed, these membranes were subjected to the same processing conditions as a LANL-prepared fuelcell MEA.

The test cells were assembled and leak checked in an identical manner, again similar to a LANL-prepared single cell PEMFC. In the assembly step, we used commercially available GDLs from ETEK Corp. The fuel side contained a low temperature, ELAT® GDL microporous layer on woven web with a thin microporous layer on the backside. This was centered over the flow field channels by using a 10-mil silicon rubber gasket. Next, we placed a 1-mil Teflon sheet with a $50cm^2$ cutout over both the gasket and GDL to mark the fuel cell active area. The "oxidant side" mirrored the "fuel side", except we used single-sided GDL material instead of the above mentioned. These sides were enclosed about the Nafion™ membrane using 125 in-lbs of torque. The cells were then leak checked using 25 psi of N_2 on both sides of dead-ended hardware. They qualified for use if the leak rates were < 1 psig per 10 minutes. The details of this procedure are publicly available at the indicated web site in the reference. [Ref: www.usfcc.org]

In each crossover experiment, one side of the membrane was connected to a source of H_2S (Scott Specialty Gases, certified analysis); for this work, a cylinder of 1030ppm ± 2% H_2S with an Ar balance was used. The side exposed to the H_2S source will always be referred to as Side A. The humidification of the H_2S source was carried out by adding a water bubbler in line at room temperature (21-25°C). The opposite side of the membrane and its GDL was flushed either with UHP N_2 or with forming gas (6%H_2/Ar) with the latter sweep gas used for extended duration experiments. Forming gas was used in order to slow the rate of oxidation of the SAOB during experiments in excess of 10 hrs. As before, humidification was carried out using a water bubbler at room temperature (21-25°C). This side of the membrane assembly was only exposed to the sweep gas and will always be referred to as Side B.

Sulfide Ion Trap Preparation

A Nalgene™ graduate cylinder (250 ml) was cut-down to a length that would accommodate the length of the ion probe. A Teflon stir bar was added in addition to 30 ml of SAOB was diluted with 30 ml of D.I. water. A three-hole stopper was prepared to accommodate the diameter of the ion probe, a ¼" tube inlet, and a ¼" exhaust outlet. The gas inlet tube was connected to a Nalgene™ gas diffuser frit. The stopper was inserted into the graduate cylinder such that the bottom of the ion probe was approximately a centimeter below the liquid surface and the bottom of the diffuser frit was less that 0.5 cm from top of the stir bar. The whole assembly was placed in the isothermal water bath (26°C). The bath level was approximately the same level as the trap solution and the trap was constantly stirred. The exhaust tube was connected to a bubbler to prevent air from diffusing back into the trap and oxidizing the SAOB solution.

H_2S Crossover Experiments

Gas flow was controlled using analog MKS mass flow controllers. Dry (or humidified) 1030ppm H_2S source was always passed through the fuel cell hardware on

Side A. Dry (or humidified) UHP N_2 and/or forming gas were flowed at 50sccm through Side B. In previous experiments, it was confirmed that a 50sccm flow rate into the sulfide ion trap insured sufficient residency time such that all of the H_2S would be dissolved into trap solution before the Ar bubble left the solution. No un-reacted H_2S could be detected passing through the 1M NaOH. Faster flow rates may be possible but the trapping efficiency of any flow rate higher than 50sccm was not measured. A Kiethley 236 sourcemeter was used to measure the EMF output from the ion probe. Automated Labview™ control software was used to record the data throughout the experiment.

The gas outlet emanating from Side B of the fuel cell hardware – e.g. the side of the apparatus where any H_2S crossing over through the Nafion™ membrane would be caught by the sweep gas and be sent to the sulfide ion trap – was plumbed using Restek Sulfinert™ coated 316 stainless steel tubing. This special coating prevents loss of H_2S due to adsorption. H_2S has a high affinity for most surfaces. Without the Sulfinert™ tubing, some of the H_2S crossover would not immediately be trapped. The length of tubing was kept as short as possible; e.g. less than 12 inches.

The first experiments performed used UHP N_2 as the sweep gas, however, as experiment times grew longer, the probability of oxidizing the antioxidant buffer solution grew as well. The unwanted oxidation of the buffer solution was very evident because the ascorbic acid in the buffer turned from a clear or pale yellow to a dark brown; once the ascorbic acid was consumed, the oxidation of the sulfide ion was then possible. Subsequent experiments used hydrogen mixtures as the reducing conditions of the hydrogen slowed the oxidation of the ascorbic acid.

The data acquisition was started and once the ion probe reached a steady state reading, and typically the H_2S/Ar and forming gas were both started simultaneously. The data acquisition continued until termination of the experiment. So that a cross over rate could be calculated, the start and end times were precisely recorded.

Results and Discussion

In early experiments, we found that titration was necessary in order to achieve the highest possible accuracy from the ion probe. Thermogravimetric analysis performed on the sodium sulfide sources using both oxidizing and inert atmospheres showed that the sodium sulfide used for ion probe standardization contained variable numbers of water of hydration and even significant amounts of sodium sulfate. The anhydrous Na_2S contained sodium sulfate as well and began to absorb water from the atmosphere once the stock bottle was opened and the Ar atmosphere was compromised. The easiest method to determine the true sulfide ion concentration of the stock solutions was to perform a titration on the 10^{-3} M solution (the concentration of the other two standards was then known 10:1 and 100:1 dilutions) and calibrate the ion probe immediately before the crossover experiment. Once the weight of Na_2S was corrected for water and sulfate content, calculated $S^{=}$ concentrations agreed very well with values calculated using titration data.

The first sample prepared was of the configuration (metal flowfield)/GDL/Nafion™ 117/GDL/(metal flowfield). Before the crossover experiments, H_2S was used as a surface probe for adsorption on the GDL and flowfield surfaces. The purpose of this experiment was to gauge an upper limit as to how much H_2S might not be trapped by the buffer solution due to absorption onto all surfaces downstream of the membrane including the GDL, flowfield channels, tubing walls, etc. The 1030ppm H_2S gas mixture was flowed at 50 sccm for a predetermined amount of time. The experiment was stopped, the sulfide concentration in the ion trap was then determined through titration. A second experiment, called a blank, was conducted using identical parameters except no membrane, GDL, and hardware was present. The difference in trapped sulfide ion concentration between the two experiments is the amount of H_2S adsorbed onto all surfaces associated with the membrane, GDL, and flowfield structures. For a 50 cm^2 membrane and GDL, H_2S break-through took approximately 15 minutes using the 1030ppm concentration of H_2S/Ar at flow rate of 50sccm resulting in 1.96mg of H_2S adsorbed onto exposed surfaces. Depending on the crossover rate, this amount of H_2S might delay seeing any H_2S crossover (via change in EMF of the ion probe) for a significant amount of time.

After finishing these "surface area" characterization, the apparatus was configured for the crossover experiment. A new sulfide ion trap was prepared, and Sulfintert™ tubing was used to connect the flowfield outlet of Side B to the trap while Side A remained connected to the H_2S source. Figure 1 is the EMF versus time plot of this GDL/Nafion™ 117/GDL dry experiment. Both the 1030ppm H_2S and UHP N_2 gases were not humidified. The data up to 100 min show the ion probe settling to about -0.65V; the UHP N_2 sweep gas was started which cause a small deviation in the EMF measurement. The 1030ppm H_2S gas flow was started at 182.4 minutes. Surprisingly, the ion probe voltage began to show signs of significant deviation only 8 minutes after starting the flow of the H_2S was applied to Side A. Based on the adsorbed value calculated above, one would expect a delay of much more than 15 minutes assuming that any crossover rate would be less than simply flowing 1030ppm H_2S directly into the sulfide ion trap. Most likely enough H_2S permeated through during the characterization of the surface area on the H_2S side (Side A) of the cell to passivate the GDL and flowfield surfaces on Side B otherwise, the H_2S would not be detected in such a short time.

Figure 2 is a plot of sulfide ion concentration versus time since start of H_2S flow. The calibration data used to transform the data from Figure 1 into a concentration was made prior to the experiment as described in the experimental section. These concentrations are small; and below the operational window of the Accument probe (generally between 10^{-5} and 10^{-3} M concentrations). The amount of $S^{=}$ in solution was very small as the probe measurement indicated. Performing titration on such dilute solution using the ion probe as an endpoint indicator proved to be difficult and imprecise (less than several drops of 10^{-2} M lead titrant). An upper limit of sulfide ion concentration of 10^{-5} M was estimated; there was an almost imperceptible darkening of the buffer solution color however it was not clear if the darken was caused by oxidation of the SAOB solution. In order to confirm the presence of PbS following the titration, the titrated solution from the trap was filtered, the filter paper dried, and then the paper was qualitatively analyzed using a SPECTRAC X-ray fluorescence (XRF) spectrometer. The presence of Pb on the filter paper, and absence of Pb in the remaining filtrate proved that sulfide ion was present in the trap; the sulfide ion could only be present if H_2S permeated though the membrane or through pinholes in the membrane if present.

An approximate rate of H_2S crossover may be estimated from these data. Taking the measured concentration and converting to a mass and dividing by the total time that the H_2S flowed across Side A of the membrane gave an averaged value of $3.2e^{-8}$ g/min.

This rate is only an approximation. The rate of H_2S crossover decreased towards the end of the experiment as can be seen from the change in slope of either the EMF data or the concentration versus time data shown in Figure 2. We will address the possible cause of this observation later. Based on these initial results, the procedure for next series of experiments was modified accordingly: 1) the length of the experiment was increased so that a higher concentration of sulfide ion could accumulate in the trap making titration more precise and accurate. 2) The rate of oxidation of the SAOB solution in the first experiment was fast enough that significantly extending the experiment time would consume the ascorbic acid antioxidant. UHP N_2 was replaced with forming gas (6%H_2/Ar) to slow the rate of oxidation. 3) In order to insure that all surfaces leading up to the ion trap are pre-passivated with H_2S, in the subsequent experiments, both the 1030ppm H_2S source gas and 6%H_2 sweep gas were flowed across Sides A and B respectively for 48 to 72 hours prior to commencement of the trapping experiment. When crossover/trapping experiment was performed, the sweep gas and H_2S source gas flows were momentarily halted, the isothermal ion trap put in place, and then the gas flows were restarted after precisely recording the start time.

Since the observed H_2S crossover may be caused by the presence of pinholes, a new GDL/Nafion™ 117/GDL sample was prepared, mounted with flowfield hardware, and leaked checked as before. In this next experiment, both sweep gas and H_2S source were humidified by bubbling the gases into a water bubbler at room temperature. As stated above, the humidified gases flowed across both sides of the GDL and membrane for 72 hours. Hydrogen sulfide is water-soluble and this amount of time also allowed the amount of H_2S in the bubbler to saturate (approx. pH = 4). The total experiment time was extended to almost 24 hours.

As before, a Na_2S standards were prepared, titrated, and a calibration curve created prior to conducting the crossover experiment so that EMF data could be converted to a sulfide ion concentration. After the experiment was completed, the solution was titrated with a more dilute titrant, $3.09e^{-3}$M $Pb(NO_3)_2$, and the sulfide ion concentration was found to be $4.07e^{-4}$M [$S^=$]. This is significantly larger than that measured in the first experiment. In fact, there was no need to perform XRF analysis on the solution post titration because the solution turned black because of the formation of the PbS precipitate. An average crossover rate may again be calculated. The humidification of the membrane increased the crossover rate by a factor of 18 to $5.9e^{-7}$ g/min.

The bubblers were removed and the dry sweep gas and dry H_2S source gas were flowed across the membrane assembly, drying the membrane in the process. Another 72 hours elapsed. A new standardization of the ion probe was performed and a new trap solution was placed to capture crossover H_2S and left for a similar duration (1282 min compared to 1380 min above, humidified experiment). A titration was again performed and the sulfide ion concentration was found to be $8.27e^{-5}$M, roughly an order of magnitude smaller value for approximately the same amount of trap time. The estimated crossover rate decreased to $1.2e^{-7}$ g/min. Figure 3 summarizes all three experiments.

There is a significantly higher rate of H_2S permeation through the wet Nafion™ membrane compared to the same membrane dry. Moreover, once the wet Nafion™

membranes was desiccated the permeation rate decreased showing that the change in permeation rate between wet and dry states is reversible although the exact water content of the membrane upon drying was not known. Finally, the use of two different membrane assemblies tested would indicate that the measured H_2S crossover is not caused by pinholes given the strong, reversible dependence on humidity and because of the similar rates between the two membranes in the dry state.

As in Figure 2, the concentration versus time plots show non-linear behavior. In fact, close inspection of the data for the 2nd membrane, wet experiment shows at least three distinct slopes. Figure 4 is a plot of the 1st derivative of sulfide ion concentration versus time for the three experiments shown in Figure 3. These data are essentially a plot of H_2S crossover rate (in units of mole/L•min) for the 117 membrane. Again, the effect of water is to greatly enhance H_2S crossover in Nafion™ 117 and showing that the humidified membrane state during fuel cell operation may be more susceptible to H_2S crossover.

In the last two experiments, a third Nafion™ membrane and GDL assembly was prepared using 50.8μm thick 212 membrane. The thinner membrane should have a higher rate of H_2S permeation if a conventional first order diffusion mechanism is responsible. In the same experimental manner already discussed above, back-to-back experiments were performed first with the 212 membrane dry followed by the same experiment only with the 212 membrane humidified (bubblers at room temperature ca. 20-25°C). Figure 5 shows the concentration of sulfide ion trapped in the SAOB solution versus time H_2S was flowing across the membrane assembly overlaid with the 117 membrane data shown in Figure 3. In the wet membrane state, there was a substantial increase in the amount of H_2S trapped during the course of the experiment; the average crossover rate over the 1449 minute long experiment was $1.8e^{-6}$ g/min. In terms of the real-time concentration measured by the ion probe, after a similar overnight run, the sulfide ion concentration accumulated in the trap was over twice as much as that found for the 117 membrane when using the thinner Nafion™ 212 membrane. In contrast, the dry state of the 212 membrane showed the same averaged H_2S crossover rate compared to that value calculated after desiccating the 117 membrane; $1.2e^{-7}$ g/min. Figure 6 shows the same data set as Figure 5 with the axes blown up to show more detail. There is little distinction between the three dry-state experiments with the exception that at the trapped sulfide ion concentration was lower during the first half of the experiment only to surpass the concentration measured in the 117 experiment at end.

The slope of the sulfide ion concentration curve for the 212 membrane in the humidified state also shows non-linearity and there is a dramatic decrease in rate around 1200 minutes into the experiment. Similar behavior was shown in Figure 2. As noted earlier, inspection of Figure 3 will also show that the slope of the calculated concentration versus time curve for the 2nd membrane, humidified, is also not constant. In fact, at least three distinct slopes can be seen.

The slope of the concentration curve is a plot of the rate of H_2S crossover and why this rate may change was investigated next. A slight change in the slope of the concentration curve is to be expected since the volume of the ion trap is not constant. Even when humidified at room temperature, there is loss of volume in the ion trap due to evaporation. Naturally, the evaporation rate would be higher when dry gasses are bubbled through the SAOB solution. Loss of volume would cause a positive second derivative since the $S^{=}$ concentration would be increasing over time. This behavior was seen in

Figure 4 for the humidified membrane. However, the abrupt decrease in crossover rate in Figures 2 and 5 must be caused by something else.

Further investigation into the cause of this behavior suggests that the most likely reason for changes in crossover rate may be a non-constant partial pressure of H_2S. The source H_2S concentration may be verified by performing a blank experiment where the flow rate is set and the H_2S source is bubbled directly into the stirred SAOB trap for a predetermined amount of time. Once the sulfide ion concentration is determined via titration, the source H_2S concentration may be calculated provided the flow rate is precisely known. The flow rate delivered by the MFC unit was calibrated using an Agilent electronic soap-bubble flow meter. Several blank runs showed that the H_2S concentration would change overtime anywhere between 650 to more then 900ppm. Both values are less than the certified concentration measured by the gas supplier. Moreover, the H_2S concentration continuously changed presumably because the adsorption characteristics change strongly with temperature. While the trap, ion probe, and calibration standards, are maintained at 26°C with the aid of an isothermal bath, the stainless steel tubing, and the membrane assembly and flow field hardware temperature may float during the experiment. Furthermore, due to safety requirements, the H_2S gas bottle, regulator and about 20% of the stainless steel delivery tube are located out side of the building easily experienced temperature swings between -15°C to 10°C (winter months in New Mexico) while the experiments were being performed. Blank experiments run over 24 hours showed a falling H_2S source concentration correlated to the coldest outside temperatures and rising H_2S concentration as the outside temperature would rise. The atmospheric pressure was not constant throughout these experiments however the flow rate changes caused by the natural fluctuations in atmospheric pressure were less than the error in flow rate measurement using the electronic soap-bubble flow meter.

Moreover, we found that 1000ppm H_2S/Ar gas cylinders that remain unused for extended periods of time (more than 6 months), the delivery concentration would be higher than the certified value. Because of these findings, the values calculated for H_2S rate constants may not be directly compared and cannot be correct since the partial pressure of H_2S was not fixed. Future crossover measurements and calculations of constants, specifically actual permeation constants, must have a constant delivery H_2S partial pressure in order to be accurate and precise. A new H_2S mixing and delivery system is being constructed and calculation of firm rates of H_2S crossover and permeation constants will be the focus of future work.

Conclusions

We have found that H_2S will permeate through Nafion™ 117 and Nafion™ 212 membranes at room temperature. The rate of crossover was more than doubled upon humidification of the membrane. Several average crossover rates were calculated for the wet and dry states of the 117 and 212 membranes using the final trapped sulfide ion concentration and total H_2S application time; however, these values are only an approximation since there was obvious evidence the rate that the sulfide ion trapped was not constant. After pursuing the cause of several anomalies in this work, it was found that the delivery partial pressure of H_2S was not constant during the course of the experiments. This behavior was attributed to stratification of the H_2S and Ar contents of the source cylinder and temperature-related swings in H_2S partial pressure due to changes in adsorption onto the walls of gas cylinder, regulator, and stainless steel delivery tubing. Although the absolute crossover rates are naturally compromised, the relative differences in the sulfide ion concentration curves reflects the trends in crossover rate as a function state of humidification and membrane thickness. Future work will focus on designing and building a new H_2S delivery system that will deliver a constant partial pressure of H_2S to the Nafion™ membrane.

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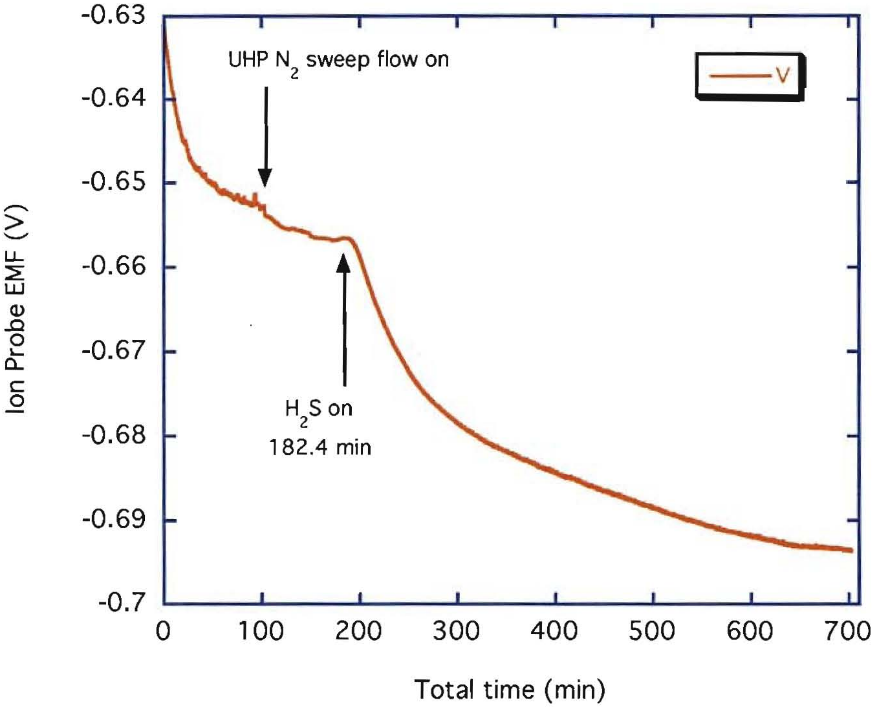

Figure 1. Plot of ion probe EMF versus time. The time when UHP N_2 gas sweeping Side B and H_2S/Ar mixture sweeping Side A are indicated.

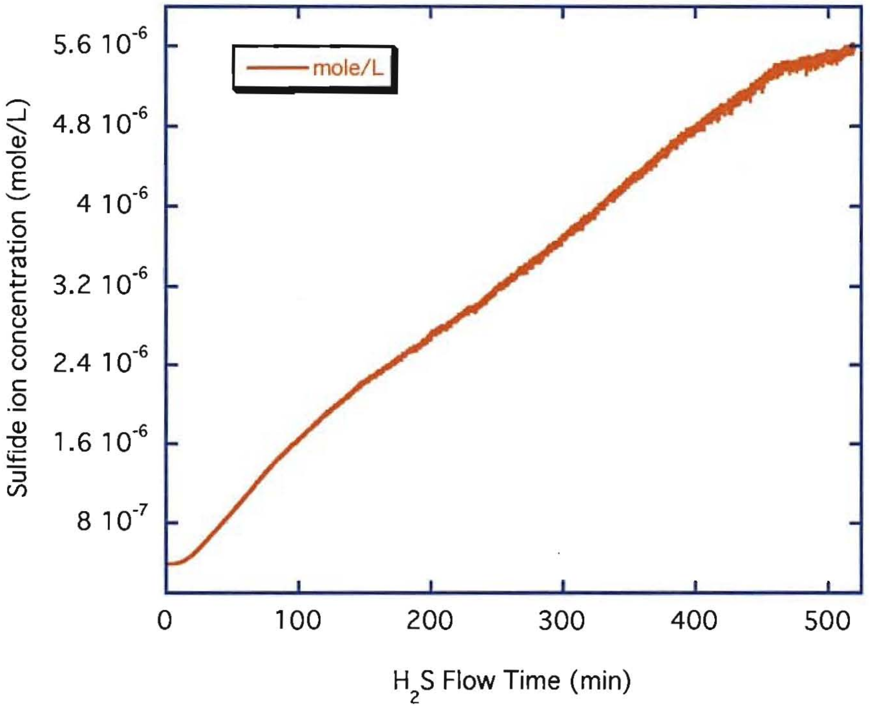

Figure 2. EMF data from Figure 1 converted to sulfide ion concentration versus elapsed time of H_2S/Ar flow across Side A.

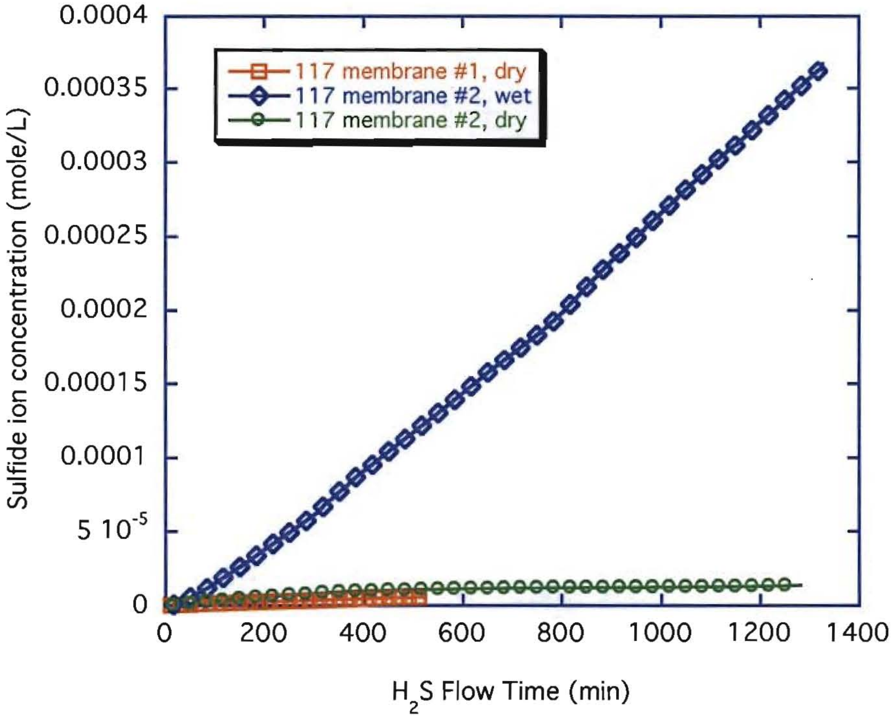

Figure 3. Plot of calculated sulfide ion concentration versus elapsed H_2S/Ar flow time across Side A for dry and humidified Nafion™ 117 membranes.

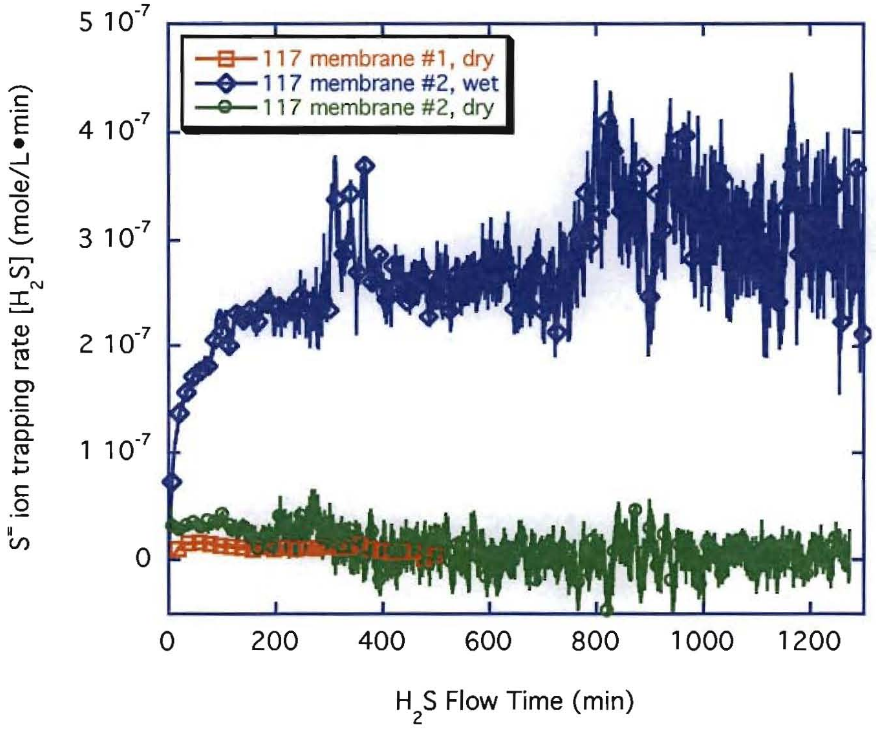

Figure 4. 1st derivative of the sulfide ion concentration versus time curves for the 117 membranes in Figure 3.

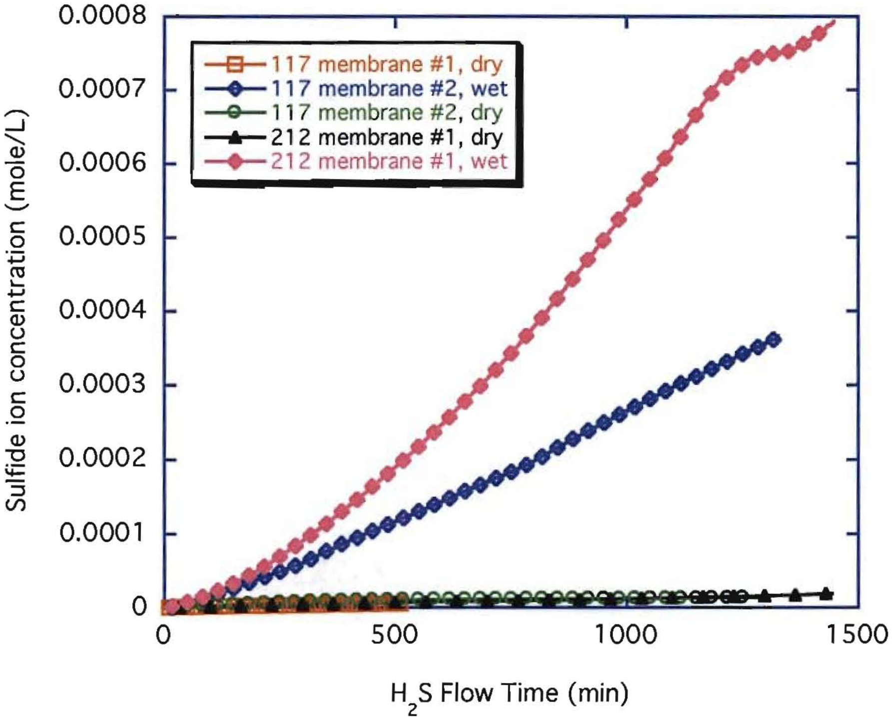

Figure 5. Plot of calculated sulfide ion concentration versus elapsed H_2S/Ar flow time across Side A for dry and humidified Nafion™ 117 and 212 membranes.

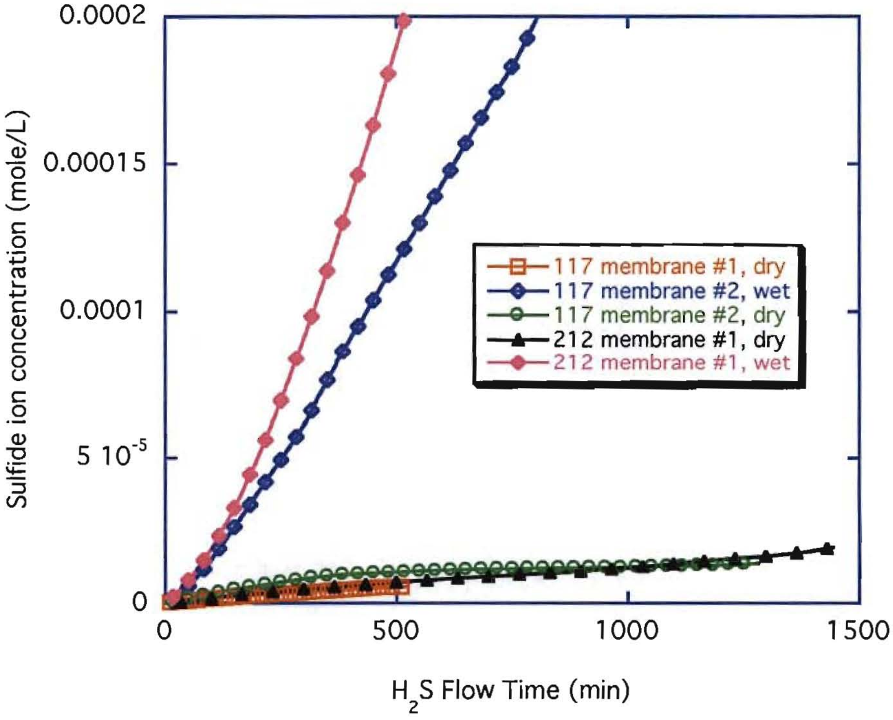

Figure 6. Expanded sulfide ion concentration axis showing similar H_2S crossover rates for dry 117 and 212 membranes.