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Development of Analytical Techniques to Study H₂S Poisoning of PEMFCs and Components

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ABSTRACT

Polymer electrolyte membrane fuel cells are sensitive to impurities that may be present in either the oxidizer or fuel. H₂S, even at the ppb level, will have a dramatic and adverse affect on fuel cell performance. Not only is it important to know a particular material's affinity to adsorb H₂S, when considering materials for PEMFC applications, issues such as permeation and crossover rates also become extremely important. Several experimental methods have been developed to quantify H₂S adsorption onto surfaces and to quantify H₂S permeation through Nafion® membranes using readily available and inexpensive Ag/AgS ion probes. In addition to calculating the H₂S uptake on commonly used XC-72 carbon supports and Pt/XC-72 catalysts, the H₂S permeability through dry and humidified Nafion® PEMFC membranes was also studied using these specialized techniques. In each ion probe experiment performed, a sulfide anti-oxidant buffer solution was used to trap and concentrate trace quantities of H₂S during the course of the measurement. Crossover 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(NO₃)₂. By using these techniques, we have confirmed H₂S crossover in Nafion® membranes and have calculated preliminary rates of H₂S crossover.

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/cm² 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 H₂, may produce various impurities at levels that can easily be detrimental to FC operation [2]. Typical fuel impurities are carbon monoxide (CO), ammonia (NH₃) and hydrogen sulfide (H₂S). On the cathode side, ambient air contains pollutants (e.g. NO_x, SO₂, 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 H₂S 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 H₂S 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 H₂S 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 developing analytical techniques that are compatible with existing PEMFC research and development methods and commonly used fuel cell testing protocols. Ag/AgS ion probes are readily available and are quite inexpensive devices. Moreover, their intrinsic specificity towards detecting sulfide ions makes their transduction mechanism very attractive around which to develop analytical techniques. In this work, we demonstrate two techniques that we developed to measure H₂S uptake in PEMFC catalyst materials and to determine the extent to which H₂S may crossover through the electrolyte membrane and potentially poison both catalyst layers.

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 KNO₃. 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 logarithm of sulfide ion concentration of three solutions prepared from a single stock solution via serial dilution.

To make a typical stock solution, approximately 0.1 g of anhydrous Na₂S (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 Na₂S 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 was considered 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. $\text{Pb}(\text{NO}_3)_2$ (Mallinkrodt) 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 $\text{Pb}(\text{NO}_3)_2$ 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 whilst 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™ containers were used in all of these aqueous experiments whenever sodium hydroxide and/or sulfide ions were involved.

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 1/4" tube inlet, and a 1/4" 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 than 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.

H₂S Adsorption Experiments

Figure 1 illustrates how the sulfide ion trap (see above) was utilized for H₂S adsorption studies. In the initial experiment (called a "blank"), a carrier gas containing a known amount of H₂S (e.g. certified H₂S/Ar mixture, typically 1000-1030 ppm) was bubbled into the ion trap at a known flow rate. The ion probe EMF was recorded and subsequently converted to a sulfide ion concentration using a previously determined calibration curve. The process was repeated with the exception that a powder sample (one that either H₂S affinity is desired to be quantified, or a sample for surface area determination assuming a monolayer coverage of H₂S) was placed in the gas flow prior to the sulfide ion trap. Any H₂S adsorbed onto the surface of the sample would not be captured by the sulfide ion trap and, consequently, would not be measured as cumulative S⁼ concentration at the ion probe. By performing both "blank" and sample experiments in this manner, at any given time, the difference in calculated [S⁼] concentration determined by the ion probe EMF, would be due to the amount of H₂S adsorbed onto the surfaces of the sample.

The preparation and situation of the sample in the experiment was important. A low-volume quartz tube with a ground glass joint centered in the middle of the length of tubing was used for

this work. The quartz tube started at a nominal O.D. of 0.25" and widened to 1.5" at the joint on one side and reduced back from 1.5" to 0.25" on the other half of the tube. A glass frit was placed in one end to support a powder sample evenly across the diameter of the tube, the tube rotated to a vertical position, and a pre-measured quantity of sample was spread evenly covering the glass frit. Spreading the sample across the surface of a glass frit ensured that the H₂S would flow evenly through the powder sample. If this precaution to situate the sample properly was not taken, the H₂S/Ar mixture would pass through only small volumes of the total sample that offered the least resistance to gas flow. Thus, the values of adsorption calculated would be and under estimate the actual mass. The second half of the quartz tube was joined with the lower section forming a gas tight seal at the ground glass joint. The sample tube was placed into a small tube furnace rotated to the vertical position. The surface of the sample was first cleaned by heating the sample to 85°C in flowing UHP N₂ overnight to clean the surface. The sample was cooled to room temperature under flowing UHP N₂ and was plumbed into the H₂S adsorption apparatus such the 1000ppm H₂S would flow through the cleaned sample and then into the ion trap to be measured using the ion probe.

Once the adsorption of H₂S on to the surface of the sample stopped, presumably after complete surface coverage, the slopes of the [S⁻] v. time curves were expected to be parallel if flow rate and H₂S concentrations were identical. The ion trap was prepared in a manner identical to the procedure outlined above with the exception of the addition of 1ml of the 10⁻³M Na₂S solution used to standardize the probe. This was done so that the ion probe would indicate a constant EMF - an EMF versus time with zero slope- prior to H₂S break through.

Membrane Preparation for H₂S Crossover Studies

We employed protonated Nafion® membranes with different thickness into standard fuel cell hardware (50 cm²) 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% H₂O₂ 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 H₂SO₄ and then de-ionized H₂O, 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 50cm² 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 N₂ 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 H₂S (Scott Specialty Gases, certified analysis); for this work, a cylinder of 1030ppm ± 2% H₂S with an Ar balance was used. The side exposed to the H₂S source will always be referred to as Side A.

The humidification of the H₂S 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 N₂ or with forming gas (6%H₂/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.

H₂S Crossover Experiments

Gas flow was controlled using analog MKS mass flow controllers. Dry (or humidified) 1030ppm H₂S source was always passed through the fuel cell hardware on Side A. Dry (or humidified) UHP N₂ 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 H₂S would be dissolved into trap solution before the Ar bubble left the solution. No un-reacted H₂S 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 H₂S 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 H₂S due to adsorption. H₂S has a high affinity for most surfaces. Without the Sulfinert™ tubing, some of the H₂S crossover would not immediately be trapped. The length of tubing was kept as short as possible; e.g. less than 12 inches.

When performing longer H₂S trapping experiments – e.g. overnight or longer- hydrogen was used as the sweep gas. Although UHP N₂ may be used as a sweep gas, longer experiment times increase the probability of oxidizing the antioxidant buffer solution. Unwanted oxidation of the buffer solution becomes evident as the ascorbic acid in the buffer turns from a clear or pale yellow to a dark brown; once the ascorbic acid is consumed, the sulfide ion in solution will oxidize. The use of hydrogen mixtures 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 H₂S/Ar and forming gas were both started simultaneously soon thereafter. The data acquisition continued until termination of the experiment. The start and end times were precisely recorded so that a crossover rate could be calculated.

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 (TGA) 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 Na₂S 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 Na₂S was corrected for water

and sulfate content, calculated S^{2-} concentrations agreed very well with values calculated using titration data.

H₂S adsorption/Surface Area Measurements Using Ag/AgS Ion Probes

The first experiments in a series were to investigate whether sulfur ion probe technique could be used to measure the amount of H₂S adsorbed onto the surface of a material. This task was accomplished by performing two consecutive experiments where in each case, an Ar gas containing a known amount of H₂S was passed through the experiment and then into a sulfur ion chemical trap where all H₂S gas would instantly dissolve and be fully reduced to S^{2-} . By subtracting the measured $[S^{2-}]$ of the first experiment (a blank with no powered sample present) to the $[S^{2-}]$ measured in the second experiment, the amount of H₂S adsorbed onto/into the sample could be calculated by difference.

Figure 2a shows the back-to-back experiments for a 1.1611g sample of neat carbon black XC-72R (Cabot) and a blank run with no sample. Since there may be H₂S adsorption onto surfaces other than the sample, the blank run also serves to quantify this amount of adsorption and subtraction of the blank from an identical experimental run performed on the sample, will serve to reduce this error. Typically, performing a series of blank experiments indicated that the usual amount of error – a sum of calibration error, error in H₂S certification, flow rate, adsorption losses on surfaces other than the sample, etc.) lead to a difference between predicted value of the slope and that calculated from the EMF data of less than 10%. After 40 minutes of H₂S flow time and with nearly identical flow rates (49.95 sccm compared to 50.00 sccm), the slopes were nearly parallel and the difference in concentration, corresponded to a difference of 3.13×10^{-4} g of H₂S captured by the XC-72 or 0.027wt% uptake onto the surface of the carbon.

Figure 2b shows a similar experiment performed using ETEK 20wt% Pt on carbon XC-72. The blank and sample experiments were repeated using 0.2511 g of ETEK Pt (20wt%) supported on XC-72 carbon. The larger quantity of H₂S adsorbed onto the Pt surfaces of the catalyst is obvious from the data; close inspection of Figure 2b shows that no H₂S entered the trap for almost 70 minutes until all the Pt sites available for coverage by H₂S molecules was exhausted. At 100 minutes, we calculated an H₂S uptake of 7.96% on a Pt basis or almost 300 times more H₂S adsorbed onto the Pt than onto the carbon support alone.

H₂S Crossover Studies in Nafion® Membranes Using Ag/AgS Ion Probes

The first sample prepared was of the configuration (metal flowfield)/GDL/Nafion® 117/GDL/(metal flowfield). Before the crossover experiments, H₂S 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 H₂S 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. To increase overall precision, instead of measuring surface as described above, the blank and sample experiments were run for identical amounts of time and the sulfide ion concentration was measured using lead titrations and the Ag/AgS ion probe as an endpoint indicator. Figure 3 shows a typical example of the ion probe EMF response that was used to calculate $[S^{2-}]$ by knowing the $[Pb^{2+}]$ of the titrating solution. For a 50 cm² membrane and GDL, H₂S break-through took approximately 15 minutes using a 1030ppm concentration of H₂S/Ar at flow rate of 50sccm corresponding to 1.96mg of H₂S adsorbed onto all exposed surfaces. Depending on the crossover rate, this amount of H₂S might delay seeing any H₂S crossover (via change in EMF of the ion probe) for a significant amount of time.

After finishing the GDL/flowfield “surface area” characterization, the apparatus was configured for the crossover experiment. A new sulfide ion trap was prepared, and SulfInert™ tubing was used to connect the flowfield outlet of Side B to the trap while Side A remained

connected to the H₂S source. Figure 4 is an illustration of the apparatus used for crossover experiments. In order to insure that all surfaces leading up to the ion trap are prepassivated with H₂S – given the amount of potential H₂S uptake as found in the surface area characterization above – both the 1030ppm H₂S source gas and 6% H₂ sweep gas were flowed across Sides A and B respectively for 72 hours prior to commencement of the trapping experiment. When crossover/trapping experiment was performed, the sweep gas and H₂S 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. The first experiment was performed with a Nafion® 117 membrane and unhumidified gas streams for only less than 550 minutes after which the trap solution was titrated to determine [S²⁻]. An approximate rate of H₂S crossover may be estimated from these data. Taking the measured concentration and converting to a mass and dividing by the total time that the H₂S flowed across Side A of the membrane gave an averaged value of 3.2e⁻⁸ g/min.

The experiment was then repeated using humidified gas streams across both Sides A and B. Both the sweep gas and the H₂S source were humidified by passing the gases through a room temperature water bubbler. Hydrogen sulfide is water-soluble and this amount of time also allowed the amount of H₂S in the bubbler to saturate (approx. pH = 4). The total experiment time was extended to almost 24 hours in order to take advantage of a more pronounced EMF change signaling the endpoint and thus reducing overall error in the titration measurement.

As before, Na₂S 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 3.09e⁻³M Pb(NO₃)₂, and the sulfide ion concentration was found to be 4.07e⁻⁴M [S²⁻]. 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 H₂S 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 H₂S 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⁻⁵M, 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 5 summarizes all three experiments.

To summarize, there is a significantly higher rate of H₂S 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 H₂S 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.

In the last two experiments, a Nafion® membrane and GDL assembly was prepared using 50.8µm thick, 212 membrane. The thinner membrane should have a higher rate of H₂S 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 6 shows the concentration of sulfide ion trapped in the SAOB solution versus time H₂S was flowing across the membrane assembly overlaid with the 117 membrane data shown in Figure 5. In the wet membrane state, there was a substantial increase in the amount of H₂S trapped during the course of the experiment; the average crossover rate over the 1449 min 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 7 shows the same data set as Figure 6 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 sometimes observed in other $[\text{S}^-]$ vs. time plots. A slight change in the slope of the concentration curve is to be expected since the volume of the ion trap is not constant. Loss of volume would cause a positive second derivative since the S^- concentration, $[\text{S}^-]$ would be increasing over time. This behavior was seen in Figure 6 for the humidified membrane. However, the abrupt decrease in crossover rate must be caused by something else.

Further investigation into the cause of this behavior suggested that the most likely reason for changes in crossover rate might be a non-constant partial pressure of H_2S . The source H_2S concentration was verified by performing a blank experiment where the flow rate was set and the H_2S source is bubbled directly into the stirred SAOB trap for a predetermined amount of time. Several blank runs showed that the H_2S concentration would change overtime anywhere between 650 to more than 900ppm apparently depending on the temperature of the source gas bottle. 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 $\text{H}_2\text{S}/\text{Ar}$ 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

Ag/AgS ion probes provide a simple and inexpensive way to study H_2S interactions with PEMFC materials and have proven invaluable in the study of poisoning mechanisms. 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 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 evidence the rate that the sulfide ion trapped was not constant during the experiment. 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 calculated permeation constants were naturally compromised, the relative differences in the sulfide ion concentration curves reflected the trends in crossover rate as a function state of humidification and membrane thickness. Future work will focus on using the experimental

methods developed in this work in conjunction with a new H₂S delivery system that will deliver a constant partial pressure of H₂S to the Nafion® membrane.

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Figures and Captions:

Figure 1. Illustration of the sulfide ion trap (1M Orion SAOB) and sample for quantitative H_2S adsorption studies.

Figure 2a and b. $[\text{S}^{2-}]$ versus time curve for 1.1611g of carbon XC-72 compared and blank (left) and that for 0.2511g of 20wt% Pt ETEK (right).

Figure 3. Measured EMF produced by the ion probe immersed in a 10^{-3}M Na_2S during a titration with a 0.03M $\text{Pb}(\text{NO}_3)_2$ solution. The calculated S^{2-} concentration is overlaid to show the precipitous drop in the amount of sulfide ion in solution due to the formation PbS precipitate. The addition of $\text{Pb}(\text{NO}_3)_2$ solution was halted when $[\text{S}^{2-}]$ fell below the limit of probe sensitivity.

Figure 4. Illustration of the sulfide ion trap (1M Orion SAOB), Ag/AgS ion probe, and fuel cell hardware containing GDL/Nafion®/GDL samples used for H_2S crossover studies.

Figure 5. Plot of calculated sulfide ion concentration versus elapsed H₂S/Ar flow time across Side A for dry and humidified Nafion® 117 membranes.

Figure 6. Plot of calculated sulfide ion concentration versus elapsed H₂S/Ar flow time across Side A for dry and humidified Nafion® 117 and 212 membranes.

Figure 7. Expanded sulfide ion concentration axis showing similar H₂S crossover rates for dry 117 and 212 membranes.