Studies on the effect of \( \text{H}_2\text{S} \) poisoning of the catalyst in PEM fuel cells utilizing electrochemical methods

Project as requirement for the course ECHE 789B

By

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Abstract

The project studies the effects of \( \text{H}_2\text{S} \) poisoning of the catalyst on membrane electrode assembly (MEA) using cyclic voltammetry. A Literature survey reveals rarity of work that has been done on studying \( \text{H}_2\text{S} \) poisoning of the platinum on MEAs. Understanding \( \text{H}_2\text{S} \) poisoning of the platinum on MEAs is studied at different concentrations of \( \text{H}_2\text{S} \).

Introduction

\( \text{H}_2\text{S} \) has been reported repeatedly to severely poison the platinum catalyst. Testing of effect of \( \text{H}_2\text{S} \) on the platinum has been carried in both the gas and the aqueous phase. The hydrogen chemisorption capacity decreased during \( \text{H}_2\text{S} \) poisoning. Studies showed evidence of presence of polysulfides or neutral sulfur when a Pt electrode was sulfided with \( \text{H}_2\text{S} \) in the aqueous medium[A. Contractor et al]. When supported platinum catalysts were subjected to \( \text{H}_2\text{S} \) in the gaseous phase, adsorbed sulfur is observed on the platinum due to the dissociation of \( \text{H}_2\text{S} \). The following mechanism has been suggested for \( \text{H}_2\text{S} \) adsorption on platinum[M. Mathieu et al].

\[
\text{H}_2\text{S} \pm \text{Pt} \rightarrow \text{Pt} \pm \text{S} + \text{H}_2
\]

\[
\text{H}_2 + 2\text{Pt} \rightarrow 2\text{PtH}
\]

\[
\text{Pt} \pm \text{H} + \text{H}_2\text{S} \rightarrow \text{Pt} \pm \text{S} + 3/2\text{H}_2
\]

Therefore, the poisoning effect of the \( \text{H}_2\text{S} \) on the platinum is due to the formation of sulfur that behaves as a structure blocker for hydrogen to adsorb on the platinum.

\( \text{H}_2\text{S} \) effect of the performance of PEM fuel cells (PEMFCs) has been only recently reported [Uribe F. et al]. Subjection of the MEA only to concentrations of
H₂S down to 1 ppm is claimed to decrease the performance of the cell considerably. Therefore, the main aim in this work is evaluation of the cell performance when the MEA is exposed to H₂S at several concentrations. The decrease in the performance of the cell is measured with time. Cyclic voltammetry is used for studying poisoning of the platinum sites.

**Experimental**

The MEA used is the Gore PRIMEA® Series 5561, the active area on the MEA is 22.03 cm². The catalyst on the MEA is Pt-Ru. The gas diffusion layer used is CARBEL CL. The same kind of the GDM is used for both the anode and the cathode. Schematic of the cell used is shown in figure (1).

![Figure (1): Single Fuel Cell Assembly](image)

The experiment comprise of steady state and transient part. The current-voltage polarization curve is measured at an operating cell temperature of 70 °C in neat
hydrogen before the MEA is poisoned with H\textsubscript{2}S. The anode and the cathode humidifier temperatures are 85 and 75 °C respectively. After recording the current-voltage polarization curve, the MEA is poisoned with 93 ppm of H\textsubscript{2}S in 99.0\% H\textsubscript{2} and 0.99\% N\textsubscript{2} at 70 °C. The performance curve with time is recorded by setting a current value of 13.33 A and reading the cell potential. After the steady state conditions are attained the normal fuel cell operation is interrupted by flowing H\textsubscript{2} on the cathode side and N\textsubscript{2} on the anode. Cyclic voltammetry is carried out using EG&G Instruments model 283 potentiostat after reducing the cell temperature to 25 °C (the reason for this is that no hydrogen or H\textsubscript{2}S peaks could be detected at 70 °C). The CV is applied in the potential range of 0.05 to 0.9 V at a scanning rate of 20 mV/sec. The cathode is conditioned as a counter/reference electrode by first purging the air with N\textsubscript{2} and then flowing H\textsubscript{2} into it. The normal fuel cell operation is restored by flowing H\textsubscript{2} on the anode side and purging the cathode with N\textsubscript{2} followed by flowing air to it. The change of the cell performance with time is recorded. The MEA is then poisoned with 1014 ppm of H\textsubscript{2}S in 9.89\%N\textsubscript{2} and 99.0\% H\textsubscript{2} for 2 min and the CV is recorded according to the procedure mentioned earlier. This is followed by flowing neat H\textsubscript{2} on the anode side. Furthermore the MEA normal performance is interrupted by poisoning it with pulses of 10,014 ppm H\textsubscript{2}S in balance N\textsubscript{2} without running the fuel cell at normal operation. Several CVs were collected. The fuel cell performance is again restored and neat H\textsubscript{2} is fed to the anode and the cell performance is recorded with time.
Results and discussion

The transient of 93 ppm H\textsubscript{2}S poisoning is shown the next graph.

From the previous figure, the rate of potential drop is equal to 0.014 V/hr. The drop of the cell voltage from 0.69 V to 0.16 V shows and confirms H\textsubscript{2}S poisoning effects on the MEA. However, it must be noted that the cell voltage drop rate is considered low compared with the MEA CO poisoning rates at different CO concentrations [W-k Lee et al].

The CV data shows that no peak for H\textsubscript{2}S oxidation is observed, the only peak present is the hydrogen peak comprising of the H atoms adsorbed at 0.18 V as shown in figure(3).
Though transients collected from the normal performance of the fuel cell show strong poisoning of the catalyst by H$_2$S as shown by figure(2), H$_2$S adsorption peak in the CV is absent. This can be explained that sulfur is reported to show an oxidation peak at about 0.97 V corresponding to weakly adsorbed sulfur and a peak at 1.3 V corresponding to weakly adsorbed sulfur [Contractor et al]. However, since the catalyst on the MEA used consists of Ru that is oxidized at potentials higher than 0.90 V, the applied potential should not exceed values higher than 0.90 V. Also a close look at the CV curve shows that the CV is irreversible.

The CV obtained after the MEA has been poisoned in 1014 ppm shows absence of the sulfur adsorption peak as shown in figure(4).
When the cell is purged with 10,014 ppm of H$_2$S in N$_2$, the H$_2$ peak disappeared as the CV shows in the next graph.

A broad peak is observed at potentials ranging from 0.40 to 0.70 V. This peak is not known whether or not it is related to the adsorption of H$_2$S. However, H$_2$S peak occurring in the range between 0.50 and 0.6 V has been recorded after bubbling H$_2$S in the acidic solutions with platinum electrode[N. Ramasubramanian]. Therefore further testing of MEAs at several operating
temperatures and \( \text{H}_2\text{S} \) concentrations is suggested in order to clarify the source of this peak.

**Conclusions**

Effect of \( \text{H}_2\text{S} \) poisoning on the performance of PEM fuel cell has been studied by running the fuel cell at normal conditions and by using cyclic voltammetry. The data collected reveals that the rate of poisoning of the MEA catalyst with \( \text{H}_2\text{S} \) is lower than the corresponding value for CO poisoning. Cyclic voltammetry shows no \( \text{H}_2\text{S} \) adsorption peak. However, a broad peak is observed only when the cell is poisoned with 10,014 ppm \( \text{H}_2\text{S} \) in the balance of \( \text{N}_2 \). This peak is suspected to correspond to \( \text{H}_2\text{S} \) adsorption on platinum.

**Future research**

Investigating the effect of hydrogen sulfide on the PEM fuel cell performance at steady state and transient conditions at different \( \text{H}_2\text{S} \) concentrations and cell temperatures is suggested for the future. Cyclic voltammetry will be employed for estimating hydrogen sulfide chemisorption on the platinum on the MEA.

**References**


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