PEM fuel cell performance is limited by three main sources of polarization losses: activation, ohmic and mass transport. Relative magnitudes of these differ depending upon the type of catalyst, membrane and substrate used in the fuel cell. More importantly there can also be a large variation in these losses between cells having the same components, due to the different fabrication techniques used in making the Membrane-Electrode Assembly (MEA). Even for a particular technique like screen-printing, the processing conditions alter the performance due to the different polarization losses (1). These differences become more significant at higher operating cell temperature and lower relative humidity operation. Catalyst coated membranes (CCMs) were made for a PEM fuel cell using screen-printing or the decal transfer method. Fuel cell performance was compared between cells made under different processing conditions. Effects of catalyst drying temperature, amount of propylene glycol in the catalyst ink and membrane used were studied on fuel cell performance.
INTRODUCTION

Proton exchange membrane fuel cells have increasingly received a worldwide attention due to their potential use as the means to utilize the hydrogen economy. High power density makes them suitable for their potential application for stationary power, transportation etc. Over the previous decade efforts have been made to improve the fuel cell performance by optimizing the MEA. Most of this has been focused on improving the electrode structure by changing its composition. Fuel Cell performance depends on the type of components used as membrane, catalyst, substrate etc. But more importantly even if the basic components are kept the same the variation in the performance obtained is huge. One key reason for this variation is the technique used for MEA fabrication. Even for the same technique like screen printing the variation could be because of the presence or the absence of certain processing steps. It is shown that the processing conditions could also alter the losses associated with various sources of polarization, which then affect the fuel cell performance (1). One of the most commonly used techniques is the screen-printing of the catalyst ink onto decals and then the decal transfer onto the membrane by hot pressing. Wilson et al (2,3). demonstrated this technique though many people use it with some variation either in the fabrication procedure or the same process but different processing conditions. This leads to a difference in performance because of the different polarization losses associated with the processing conditions. Activation, ohmic and mass transport are the three main sources of polarization losses in fuel cell all of which can be affected by the change in some of the processing condition. In this work a simplified approach to making MEAs was followed. The Nafion® in the catalyst layer was used in its H+ form and also the membrane was used without any pretreatment. There have been many papers and patents describing the details of the fabrication technique used, but very few on the effect of changing some of the conditions in the technique used (4). This study illustrates the effect of drying temperature of catalyst, effect of changing ratio of Pt/C : propylene glycol and finally the change in membrane electrode interface by changing the membrane on the polarization losses.

EXPERIMENTAL

Membrane Electrode Assembly Preparation

Fig. 1 shows the schematic of MEA fabrication. Catalyst ink was made by mixing Carbon supported noble metal catalyst with 5% Nafion® solution in isopropyl alcohol (EW1100, Solution Technology Inc/ PA). The ink was stirred for 2 hours before adding solvents to the ink. Isopropyl alcohol and Propylene Glycol were used as solvents. The ink was homogenized for about 5 hours using a homogenizer. Before making the decals the ink was dried under N2 to get rid of excess solvents so as to have a desired viscosity. 5 mil Teflon® was used as a blank to make the decals. The cathode catalyst was 46 wt% Pt/C and the anode catalyst was 30.1 wt% Pt-23.3 wt% Ru/C. The Nafion® loading was kept constant at 35 wt% in anode and cathode catalyst. The decals were dried in an oven to remove the solvents. Drying temperature was varied. Both anode and cathode decal were simultaneously hot pressed onto the membrane for 5 minutes at 130°C. The active area
used was 6.25-cm². Nafion®112 and Nafion®-Teflon®-phosphotungstic acid (NTPA) membranes from Ionomem Corp. were used in the cells. Cathode catalyst loading was 0.4-0.5 mg/cm² and anode loading was 0.3-0.4 mg/cm². SGL_10BB gas diffusion layer were used for both the anode and cathode side. The heat-treated catalyst-coated membrane was sandwiched between two gas diffusion layers to obtain a MEA for single cell polarization and voltammetry measurement. The graphite flow field used was a single-serpentine pattern. Incompressible Teflon® gaskets were used as a seal. They were also used to achieve a sufficient amount of compression on the MEA so that all components established intimate contact between each other to minimize contact losses. “Pinch” is defined as the difference between the MEA thickness (catalyst-coated membrane and two GDLs) and the total thickness of incompressible gaskets. A total pinch of 150-μm was used. The torque on all bolts of the cell hardware was 25lb•in.

Polarization Curve Measurement

Polarization curves were measured for the cells using a fuel cell test station (Scribner Associates, model 890C) and a flow loop built in house. The test station was equipped with temperature controllers to control the cell temperature and the relative humidity of the gas going in to the cell. Cell internal resistance was measured at current densities higher than 100 mA/cm² using a current interrupt technique through Scribner software included with the load box. The internal resistance comprises mostly of the membrane ionic resistance and contact resistances if any. The MEAs prepared as described were tested at three different operating conditions listed in table I. The anode and the cathode gas line temperatures were set 10 °C above the cell temperature to ensure no water condensation in the inlet gas lines. Constant reactant utilization conditions were used: 33% hydrogen utilization, 25% oxygen utilization for air, and 5% oxygen utilization for pure oxygen.

Table I. The three operating conditions at 80°C, 100°C, and 120°C, at atmospheric pressure

| T_{cell} | P_{cell} | T_{humidity,cat.} | T_{humidity,an.} | Cathode Inlet R.H. | Anode Inlet R.H | Inlet P_{O2} in Air |
|---------|---------|-----------------|-----------------|-------------------|----------------|-------------------|
| [°C]    | [atm]   | [°C]            | [°C]            | [%]               | [%]            | [atm]             |
| 80      | 1       | 80              | 73              | 75                | 100            | 0.136             |
| 100     | 1       | 90              | 90              | 70                | 70             | 0.064             |
| 120     | 1       | 90              | 90              | 35                | 35             | 0.064             |

Linear and Cyclic Sweep Voltammetry

Two additional diagnostic tests were used besides polarization tests: linear sweep voltammetry (LSV) for a determination of hydrogen crossover through the membrane and cyclic sweep voltammetry (CV) for a determination of electrochemical surface area (ECA) available for hydrogen adsorption. A potentiostat was used for these measurements in which pure hydrogen was used at the anode and pure nitrogen was used at the cathode. The flow rates were set at 200 cm³/min each. The reference and counter electrode leads were connected to the anode while the working electrode lead was
connected to the cathode. For the CV, the sweep rate was 30mV/sec. For the LSV, the sweep rate was 4 mV/s. Both tests were done at 25°C and also at the operating conditions to verify reasonable hydrogen crossover and electrochemical surface area utilized at real operating conditions.

RESULTS AND DISCUSSION

Effect of Propylene Glycol

Propylene Glycol is used as a solvent along with isopropanol in the catalyst ink. One of the key reasons for using it is to obtain a desired viscosity for printing the ink onto a Teflon® blank. Also the propylene glycol can change the pore structure of the catalyst as it has a very high boiling point so the decals made would have propylene glycol, which can later be removed to get a porous electrode structure. Three cells were build with different ratios of Pt/C: Propylene glycol in the catalyst ink. Pt/C: Propylene glycol ratio for B727 and B744 was 1:8 and 1:2 respectively. Cell B752 was made without adding propylene glycol to the catalyst ink. Fig. 2 shows the polarization curve at 80°C cell temperature for the three different builds. The iR-free cell voltage is corrected for voltage loss due to membrane resistance. In the low current range the H₂/Air polarization curves overlap each other indicating similar activation losses for the three cells. But a significant improvement in the mass transport resistance is observed in the high current density region when the Pt/C: Propylene glycol ratio is reduced from 1:8 to 1:2. When no propylene glycol is used for B727 the mass transport losses increase. Mass Transport loss was calculated by taking the difference in the iRFree Cell voltage for H₂/Oxygen and H₂/Air at 400mA/cm². The higher the loss the higher the diffusional resistance in the cathode catalyst layer. Fig. 3 shows mass transport loss for the three cells. Mass transport loss for B744 decreases by about 25mV compared to B752 because of addition of propylene glycol. Propylene glycol probably acts as pore former in the catalyst layer that improves the oxygen diffusion through the catalyst layer. But when the ratio of Propylene glycol used is increased in B727 it is seen that the mass transport loss increase by 35mV compared to B744. All the values were calculated at 400mA/cm².

Effect of Membrane

Three MEAs were made with the same processing conditions, the only difference being the membrane used. The chosen processing conditions were based on optimum performance obtained with a particular variable. In this case catalyst was dried at 130°C, hot pressed at 130°C and Pt/C : Propylene glycol ratio of 1:2. Fig. 4 shows iR-free cell voltage for cells with different membranes. Contrary to the expectation that the cell voltage corrected for membrane resistance would be similar it was found that even the membrane used make a difference in cell performance. Cells made with Nafion®-Teflon®-phosphotungstic acid composite membrane and Nafion®111 membrane were found to have similar performance whereas Nafion®112 was about 30mV lower than the rest. This lower performance for Nafion®112 was found to be the case even for different processing conditions. The difference in cell voltage starts at low current density and is almost constant thereafter. This indicates higher activation losses when Nafion®112 is used. Fig. 5 shows the cell voltage at 10mA/cm² which is an indication of catalyst
activity. Also the Tafel slope for Nafion® 112 was found to be higher than the other two cells. The catalyst utilization was found to be less when Nafion® 112 is used compared to when NTPA and Nafion® 111 are used. The lower utilization of the catalyst explains the lower activity and higher Tafel slope for Nafion® 112. But the difference in catalyst utilization in this case is not a function of the catalyst or the processing conditions because they are kept uniform for all the cells. The only other way the utilization could change is because of the inferior membrane electrode interface for Nafion® 112. SEM micrographs were taken for the cross section of MEAs having Nafion® 112 and NTPA. The sample was made using freeze fracture. Clearly Fig. 6 shows catalyst separation when Nafion® 112 is used as the membrane. The membrane electrode interface is intact and uniform for NTPA. The trend was seen throughout the cross section of the MEA. This explains that the inferior interface for Nafion® 112 with catalyst leads to lowering of the catalyst utilization and higher activation losses. To prove the above conclusion the Fig. 7 was plotted with the current density in terms of mA/cm²Pt. The three curves overlap each other explaining the difference in performance due to difference in catalyst utilization. Nafion® 112 was made using an extrusion process where as the other two membranes are cast membranes. In decal transfer technique the solvent is completely removed before hot pressing the decals onto the membrane surface. To study the effect presence of solvent during the formation of membrane electrode interface MEAs were made by spraying the catalyst ink onto the membrane directly. The membrane was placed in from of a filament lamp to evaporate the solvent. Fig. 8 shows the iR-free polarization curves for H₂/Air at 80°C operating cell temperature for both NTPA and Nafion® 112 using the two fabrication techniques decal transfer and spraying method. Propylene glycol was added to the catalyst ink used for decal transfer whereas that used for spraying was made without adding propylene glycol. As can be seen from the figure there is no difference in performance at low current density for NTPA for either fabrication procedure. At high current density the difference is due to absence of propylene glycol in the ink used spraying. The catalyst utilization was also found to be the same for the two procedures. An increase in catalyst utilization is seen from the ECA measurements for MEA made by spraying the catalyst ink onto Nation® 112 compared to decal transfer on Nafion® 112. This leads to a gain of about 20mV at 400mA/cm².

**Electrode loss at different operating conditions**

Cells B744 and B752 were run at three different operating conditions to compare the ohmic and mass transport losses in the electrodes of the cell. Electrodes for B744 were made by adding propylene glycol to the ink and were dried at 130°C for 30 min before transferring them to the membrane. Electrodes for B752 were made without adding propylene glycol and thus were dried at a lower temperature 65°C before hot pressing the electrodes onto the membrane. Fig. 9 shows the polarization curves for B744 and B752 at the three operating conditions mentioned in table 1. iR-free Cell voltage is corrected for iR loss due to the membrane. The H₂/Air performance at 400mA/cm² is found to be the same for the two cells at all the three operating conditions. Fig. 10a shows that the total loss in the electrodes is similar for the two cells at the three operating condition making the performance similar. Fig. 10b shows the mass transport loss in the electrode and iR loss in the electrode for the two cells at all the three operating conditions. Mass Transport loss was calculated by taking the difference in the iR-free cell voltage for H₂/ Oxygen and H₂/Air at 400mA/cm². Its representative of the mass transport loss in the electrodes.
mainly the cathode side. Ohmic loss in the electrode was determined using the current ratio (current density at a particular cell voltage for H₂/Oxygen and H₂/Air) (5). The total electrode losses would be the sum of above-mentioned losses. From Fig. 10b it can be seen that the mass transport loss for B752 is about 25mV higher than B744 at 80°C operating condition. This difference increases to 50mV at 120°C. Propylene glycol acts as a pore former in B744 decreasing the mass transport loss due to oxygen diffusion in the cathode. But adding propylene glycol and increasing the drying temperature of the catalyst has a deleterious effect on the ohmic loss in the electrode. The ohmic loss in B744 is about 10mV higher than in B752 at 80°C. The difference increases to 57mV at 120°C at 400mA/cm².

CONCLUSION

The impact of processing condition on the different sources of polarization losses in PEM fuel cells is examined using polarization curves (H₂/Oxygen and H₂/Air) at three different operating conditions. Membrane electrode interface was found to be critical factor affecting the catalyst utilization. The properties of the membrane and also the fabrication process used could alter the interface affecting the activation losses in the cell. Propylene glycol used as a solvent was found to have a significant impact on the mass transport resistance in the catalyst layer. But adding propylene glycol and consequently the high drying temperature required increased the iR loss in the electrode layer.

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Screen Print ink onto blank

Blank + ink

Dry Catalyst to remove solvents

Blank + ink

hot Press

Peel off blanks

blank + ink + membrane

blank

Figure 1. Schematic of membrane electrode assembly fabrication procedure.

Figure 2. iR-free Polarization curves at 80°C cell temperature for H₂/Oxygen and H₂/Air for B727 Pt/C: Propylene glycol = 1:8, B744 Pt/C: Propylene glycol = 1:2, and B752 without Propylene Glycol.
**Figure 3.** Mass Transport loss for B727 Pt/C: Propylene glycol = 1:8, B744 Pt/C: Propylene glycol = 1:2, and B752 without Propylene Glycol.

**Figure 4.** Effect of different membranes using same processing conditions on fuel cell performance. iR-free Polarization curves for H₂/Air at 80°C Cell Temperature, 100%RH Anode, 75%RH cathode shown for three different Membranes.
Figure 5. Effect of cells with different membranes on tafel slope and cell voltage at 10mA/cm² (V_{10mA/cm²}).

Figure 6. SEM image for a cross section of MEA with different membranes (a) Nafion® 112 (b) NTPA
Figure 7. iR-free Polarization curves for H2/Air at 80°C Cell Temperature, 100%RH Anode, 75%RH cathode. The current density is plotted in terms of mA/cm²-Pt.

Figure 8. Effect of MEA fabrication technique on fuel cell performance. iR-free Polarization curves for H2/Air at 80°C Cell Temperature, 100%RH Anode, 75%RH cathode shown for MEA made by Decal transfer and Spraying of catalyst on membrane.
Figure 9. iR-free Polarization curves for H₂/Oxygen and H₂/Air for B744 Pt/C: Propylene glycol = 1:2 and drying temperature 130°C, B752 without Propylene Glycol and drying temperature 65°C a) 80°C cell temperature b) 100°C cell temperature c) 120°C cell temperature
Figure 10 a. Total electrode losses at the three operating conditions for B744 and B752 at 400mA/cm².

Figure 10 b. Mass Transport and iR loss in the electrode at the three operating conditions for B744 and B752 at 400mA/cm².