Performance Improvement of Electrode for Polymer Electrolyte Membrane Fuel Cell

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Abstract–The very high power density output available from polymer electrolyte membrane fuel cells combined with low cost has high potential for commercialization. Such high power densities are attained via better utilization of Pt crystallites in the reaction layer. This enhanced performance can be achieved by making a thin catalyst layer on the membrane surface. The robustness in the front surface catalysts is essential to minimize the coagulation of Pt particles when the fuel cells are subjected to long-term operation. This robustness of the catalyst structure depends on the manufacturing processes and also the organic solvents used to make the slurry. In this work, five different electrodes were fabricated by using different fabrication procedures, and the poison effect of CO was investigated at the anode interface.

Key words: PEMFC, Catalyst, MEA, CO Poison

INTRODUCTION

Since fuel cells enable one to directly convert the stored chemical energy to electrical energy without the intermediate generation of thermal energy, they are not limited by the Carnot cycle, unlike heat engines. Thus energy-conversion efficiencies for fuel cell systems (45-65%) are generally two times higher than those for heat engines [Warshay and Prokopious, 1990; Lemons, 1990]. Consequently, there is a worldwide interest in the development and commercialization of polymer electrolyte membrane fuel cell (PEMFC) for vehicular and stationary applications.

One of the main problems with PEMFC performance has been the high Pt loading and another major concern is CO tolerance. It is reported [Kumm, 1990] that coating the catalyst slurry on the membrane leads to a thinner reaction layer at the membrane surface, which not only enhances the high oxygen reduction rate but also results in good contact between membrane and electrode. This has resulted in the reduction of Pt loading from 4 mg to 0.4 mg per cm^2 with only a small loss in cell performance [Srinivasan et al., 1988]. The small concentration of CO in reformed gas acts as a poison of the Pt catalyst in the anode. It is reported that PtRu alloys are the most effective electrocatalysts for the total electrooxidation of CO, and the best Ru content on the electrode surface was 50% for CO oxidation. In addition, the robustness in the front surface catalysts is essential to minimize the coagulation of Pt particles when the fuel cells are subjected to long-term operation. This robustness of the catalyst structure depends on the manufacturing processes and also the organic solvents used to make the slurry.

In the present investigation, five different interfaces or surfaces were fabricated by using different fabrication procedures. The results obtained using these procedures are discussed. The poison effect of CO was investigated at the anode interface. The concentration

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of CO was maintained at 100 ppm, that is, the concentration of CO normally present in reformate gas.

EXPERIMENTAL

In polymer electrolyte membrane fuel cells where catalyst slurry is coated directly on the membrane, the spreadability of catalyst slurry and thickness of layer depend strongly on viscosity and dielectric constant of the medium. This leads to a thinner reaction layer at the membrane surfaces as the bulk of the current is generated close to the front surface of the electrode. It has been demonstrated that the localization of Pt particles near the front surface exhibits improved oxygen reduction kinetics, which manifests itself in terms of a several-fold improvement of current density even at higher cell voltage [Srinivasan et al., 1988].

When organic solvents of different dielectric constant are mixed with Nafion solution [Uchida et al., 1995], the resulting solution will be either one of the following form: solution, colloid, or precipitate. In the present investigation, solvents were selected with dielectric constants greater than 10, except butyl acetate (5.01 at 20 °C). However, isopropyl alcohol (18.1) was mixed with butyl acetate in such a manner that the dielectric constant of the resulting mixture was more than 10 and the slurry remained in solution.

Five different interfaces were prepared with different solvents and fabrication procedures by using 30 wt% Pt/Ru (1 : 1) in Vulcan XC-72 (E-Tek, Inc, USA) for anode sides and 40 wt% Pt/C (E-Tek, Inc., USA) for cathode sides. In all five electrode surfaces, the Pt loading of 0.7 mg/cm^2 were maintained for both anode and cathode surfaces. Nafion 115 from Dupont, 125 μm thick was used. The Nafion membrane was pretreated in a standard way. The cell was operated at 100% humidity. Self-made diffusion layer with 30 wt% PTFE was used. Paste method was applied to coat the catalyst slurry on the membrane for interface I to IV and for interface V, the catalyst slurry was coated on the backing layer which was hot pressed on the membrane. The active electrode area was maintained at 50

cm² for all experiments.

Interface I was made by using the catalyst slurry coated directly on the membrane. The slurry was made by using 30 wt%Pt/Ru for anode interface and 40 wt% Pt/C for cathode interface. For both interfaces Nafion ionomers (5 wt% solution), butyl acetate and isopropyl alcohol were added and sonicated for one hour. For interface II, the chemical composition and preparation procedures were same as interface I except the 3-methyl butanol was used instead of butyl acetate and other solvents remained the same. Interface II was coated directly on the membrane, like interface I.

Interface III was made by using 5 wt% Nafion ionomer, dimethyl sulphoxide, isopropyl alcohol and 10 wt% NaOH solution with 30 wt% Pt/Ru for the anode interface and 40 wt% Pt/C for the cathode interface. The membrane was ion-exchanged into Na$^+$ before coating the slurry on the membrane. The coated membrane was baked at 150 °C under vacuum for 3 hours and finally ion exchanged to H$^+$ form before use.

Interface IV was prepared the same as interface III where ethylene glycol was used instead of dimethyl sulphoxide. The treatment procedure and the other ingredients were same as interface III.

Interface V was made by using carbon cloth from M/S Textron Specialty Materials, USA, as electrode backing material. A gas diffusion layer was sprayed onto the carbon cloth, by using Teflon as binding material, to a final concentration of 0.5 mg C/cm². Then the Pt catalyst was coated onto the diffusion layer. The slurry was made by using 30 wt% Pt/Ru, 5 wt% Nafion solution, glycerol, isopropyl alcohol and 10% NaOH solution for anode interface and 40 wt% Pt/C with the same solvents for cathode interface. The electrode was baked at 150 °C for 3 hours under vacuum. Before hot pressing, the electrode was converted to H$^+$ form by treating with 0.5 M H$_2$SO$_4$.

In all protocols, the weight ratio of Pt/C and Nafion ionomer was maintained at 3 : 1 as reported by Gottesfeld and his group [Wilson et al., 1995]. For interfaces I to IV, the diffusion layer was inserted as such. For interface V, the catalyst slurry was coated over the diffusion layer and then the electrode was hot pressed into the membrane at 140 °C for 5 minutes under pressure before MEA was assembled into the single cell fixtures. The experiments were carried out initially by using H$_2$/O$_2$ and then H$_2$/air; subsequently, the behavior of the electrode was studied by using H$_2$ containing 100 ppm CO. In all experiments, the polarization data were recorded at various current densities at different temperatures.

RESULTS AND DISCUSSION

Fig. 1 shows the polarization curves for interface I using Nafion 115 with H$_2$/O$_2$, H$_2$/air, H$_2$+CO/O$_2$ and H$_2$+CO/air. Interface I was prepared by coating the catalyst slurry directly on the membrane. The maximum current density of 1,100 mA/cm² at 0.5 V at 80 °C was obtained by using H$_2$ and O$_2$; and 640 mA/cm² at 0.5 V at 80 °C was obtained by using H$_2$ and air at ambient pressure.

The behavior of the electrode was investigated by introducing a small amount of CO (100 ppm) in the H$_2$ compartment by using oxygen in the cathode compartment. There was small decay in cell performance when oxygen was used in the cathode compartment; however, a large decay in cell performance was observed when air was used instead of oxygen. This decay in cell performance was due to the partial pressure of oxygen in air at the cathode side and poisoning of the electrode surface by CO on the anode side [Rohland and Plzak, 1999; Schmidt et al., 1994].

The polarization curves for interface I with Nafion 115 with H$_2$/O$_2$, H$_2$/air, H$_2$+CO/O$_2$ and H$_2$+CO/air are demonstrated in Fig. 2. Interface II was prepared by coating the slurry directly on the membrane. It gives high performance of 1,200, 800 mA/cm² at 0.5 and 0.6 V at 80 °C and ambient pressure using cathode O$_2$. With air, it
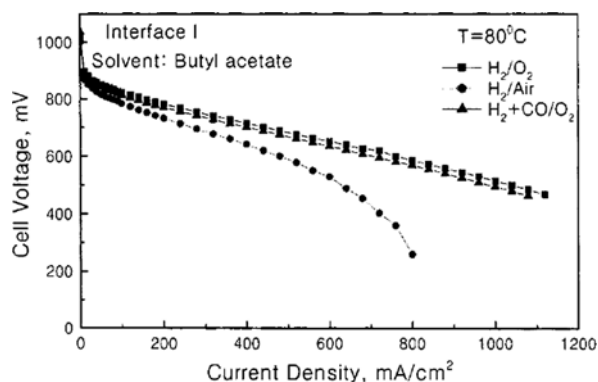

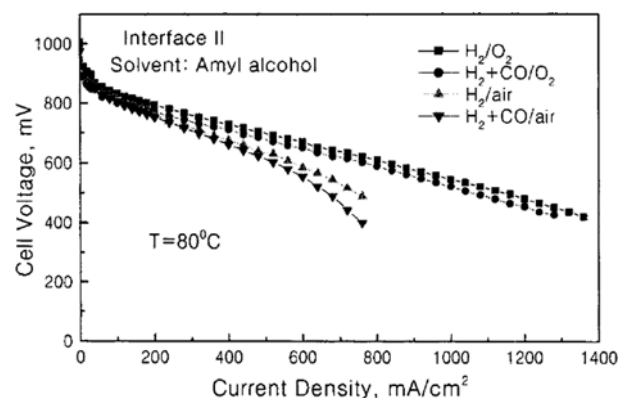Fig. 2. Polarization curves for interface II for Nafion 115 with H$_2$/O$_2$, H$_2$/air, H$_2$+CO/O$_2$ and H$_2$+CO/air.

Fig. 1. Polarization curves for interface I using Nafion 115 with H$_2$/O$_2$, H$_2$/air and H$_2$+CO/O$_2$.
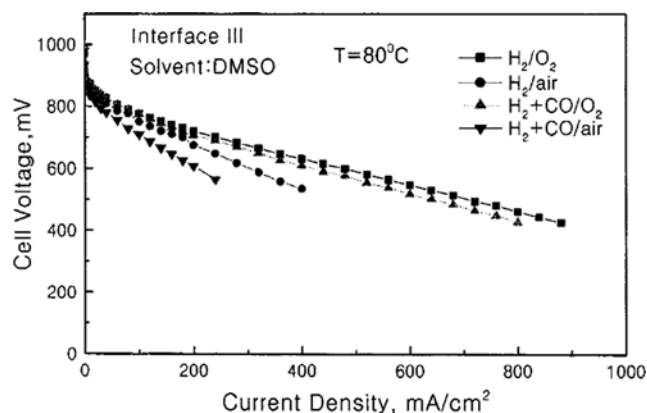
Fig. 3. Polarization curves for interface III for Nafion 115 with H$_2$/O$_2$, H$_2$/air, H$_2$+CO/O$_2$ and H$_2$+CO/air.
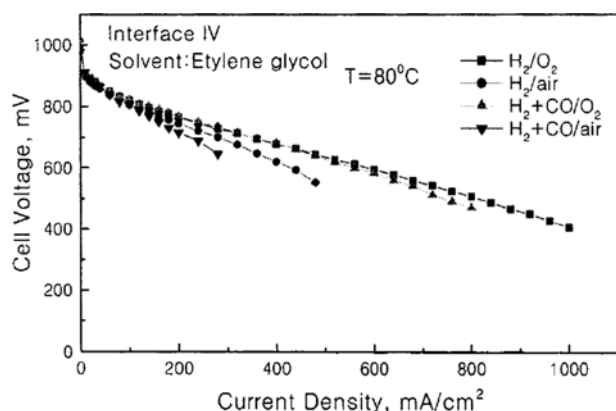
Fig. 4. Polarization curves for interface V for Nafion 115 with H_2/ O_2, H_2/air, H_2+CO/O_2 and H_2+CO/air.

gives a current density of 700, 500 mA/cm^2 at 0.5 and 0.6 V, respectively, at 80 °C and ambient pressure as shown in Fig. 2. Experiments were also conducted with H_2 containing CO as anode gas and oxygen or air as cathode gases. The variation of cell performance using pure hydrogen and hydrogen mixed with CO was about 2% for oxygen and 7% for air.

Fig. 3 shows the polarization data for interface III coated on the membrane directly. It gives current density of 720 mA/cm^2 for H_2/ O_2 and 480 mA/cm^2 for H_2/air at 0.5 V at 80 °C and ambient pressure. The performance using hydrogen mixed with CO decays only 2% for H_2/O_2 from 60 to 80 °C and 8% for H_2/air.

Fig. 4 shows the polarization curves for interface IV at 80 °C for H_2, H_2+CO with O_2 and air prepared by coating the membrane. The fabrication procedure of Interface IV was similar to interface III. A current density of 800 mA/cm^2 for H_2/O_2 and 520 mA/cm^2 for H_2/ air was obtained at 0.5 V at 80 °C and ambient pressure.

The polarization data for interface V with H_2/O_2, H_2/air, H_2+CO/ O_2, H_2+CO/air at 80 °C and ambient pressure are shown in Fig. 5. Interface V was prepared by hot pressing the electrode with membrane. This interface was different from the other interfaces where the slurry was coated directly on the carbon cloth substrate material. The maximum current density of 800 mA/cm^2 at 0.5 V at 80 °C for H_2/O_2 and 480 mA/cm^2 at 0.5 V at 80 °C for H_2/air at ambient pressure was observed. When CO was mixed with the anode com-
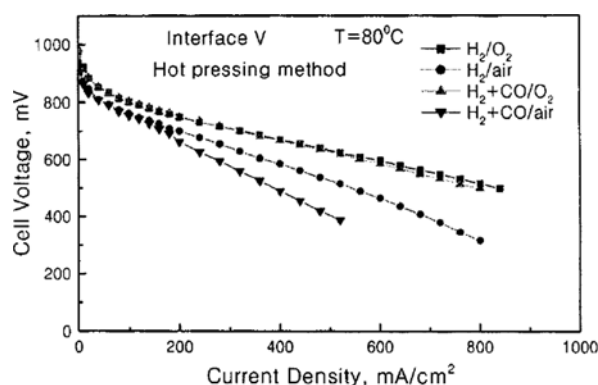

Fig. 5. Polarization curves for interface IV for Nafion 115 with H_2/ O_2, H_2/air, H_2+CO/O_2 and H_2+CO/air.

Table 1. Electrode kinetic parameters for various interfaces for H_2/O_2 and 80 °C

Interface	Tafel slope, mV dec^{-1}	Cell resistance, Ω cm^2
I	77.8	0.29
II	54.0	0.25
III	105.9	0.35
IV	94.9	0.36
V	103.0	0.33

partment, a slight decay in cell performance (about 3%) similar to other interfaces I-IV was observed by using the O_2 cathode. When air was used, decay in cell performance was 9%.

Interface II gives better performance of 1,200, 800 mA/cm^2 at 0.5 and 0.6 V at 80 °C and ambient pressure by using H_2/O_2 than any other interface. This means that the addition of 3-methyl butanol as a solvent minimizes the agglomeration of Pt particles increasing the utilization of catalyst, and that the catalyst layer contacts better with polymer electrolyte membrane by direct coating method than by hot pressing method.

In all polarization curves, the cell potential, V, versus cell current density, i, showed an initial curve downwards due to the over potentials of the two electrode reactions, followed by a linear decline in cell potential with increasing current density. These linear features may be due to ohmic resistance (r_{ms}), which is the overall resistance of electrolyte, ionic and electronic. The equation for this expression, from a current density of zero to the value at the end of linear region, is

$$E = E_0 - b \log i - i r_{ms},$$
$$E_0 = E_r + b \log i_0$$

Here, E is the potential from experimental observation and i is the current density. The parameters b and E_r are the Tafel slope and reversible potential for the single cell, respectively. i_0 is the exchange current density and r_{ms} represents the cell resistance which causes the linear variation of potential with current. The calculated kinetics parameter for various interfaces for H_2/O_2 at 80 °C is given in Table 1. The order of Tafel slope was determined to be 54.0, 77.8, 94.9, 103.0 and 105.9 mV dec^{-1} for interface II, I, IV, V, and III, respectively. The lowest value of 54.0 mV dec^{-1} for interface II means that this interface has better performance than any other interface. This is good agreement with the results of polarization data.

The cell resistance was determined to be about 0.25 to 0.36 Ωcm^2. The cell resistance is mainly influenced by the membrane thickness. The expected resistance values for Nafion 115, calculated for Nafion conductivity of 0.17 Ω^{-1}cm^{-1} at 80 °C and thickness of 160 μm, are about 0.12 Ωcm^2 lower than the values obtained from experimental data. This difference may be attributed to the contact resistance between electrode and membrane and resistance of other cell components such as backing, flow plates and current collectors.

CONCLUSIONS

Five different electrodes were fabricated by using butyl acetate, 3-methyl butanol, dimethyl sulphoxide and ethylene glycol as a solvent and different MEA fabrication method. Interface II which was prepared by coating the catalyst layer directly on Nafion membrane,

and using 3-methyl butanol as a solvent gives higher performance of 1,200 mA/cm^2 at 0.5 V and 800 mA/cm^2 at 0.6 V than any other interface due to the minimization of agglomeration of Pt particles.

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