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# Fabrication of a thin catalyst layer using organic solvents

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## Abstract

The effects of various organic solvents on the performance of polymer electrolyte membrane fuel cell (PEMFC) electrode were investigated. The five catalyst inks were prepared by mixing the 20 wt.% Pt/C, 5 wt.% solubilized Nafion, tetrabutylammonium hydroxide (TBAOH), and different organic solvents such as normal butyl acetate, *iso*-amyl alcohol, diethyl oxalate, ethylene glycol and ethylene glycol dimethyl ether. Membrane electrode assemblies were prepared by using a transfer method. From the measurements of performances of single cells, the most suitable solvent was selected and the results were discussed in terms of distribution of Nafion ionomer on Pt particles and robustness of the catalyst structure. In addition, reactant transport through electrodes was discussed in relation with decomposition of the solvents.
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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered to be a suitable candidate for residential, portable and mobile applications, due to their high efficiency and power density, even at low operating temperature [1–4]. Thus, there has been worldwide interest in the development and commercialization of PEMFC.

High performance of membrane electrode assembly (MEA) could be obtained by a good contact between the electrolyte and catalyst along with a high utilization of Pt catalyst [2–4] in the MEA. Wilson et al. [2,3] demonstrated the possibility of high performance catalyzed membranes of ultra low Pt loading. Chun et al. [5] developed a manufacturing process of thin-film catalyzed MEA by using a transfer-printing technique.

It was suggested that the mixture changed into one of the three stages: (i) solution, (ii) colloid and (iii) precipitation, due to the dielectric constant of the organic solvent, when the perfluorosulfonate-ionomer (PFSI) solution, e.g. Nafion solution was mixed with various kinds of organic solvents. It was reported [4] that high performance is achieved by coprecipitation of PFSI colloid and Pt/C and simultaneous cross-linkage of PFSI covered on Pt/C.

In the present study, considering the dielectric constant of the organic solvent, five different solvents were selected such as normal butyl acetate, *iso*-amyl alcohol, diethyl oxalate, ethylene glycol and ethylene glycol dimethyl ether. Catalyst slurries were prepared using the selected solvents and then fabricated into thin catalyzed MEAs using a transfer-printing technique.

For the fabricated MEAs, the performances of single cells were investigated. The results obtained were discussed in terms of distribution of Nafion ionomer on Pt particles along with robustness of the catalyst structure. In addition, the effect of solvent on the oxygen diffusion in the catalytic layer was discussed.

## 2. Experimental

The procedures for the pretreatment of the membrane, the preparation of the MEA, assembly of single cell and fuel cell test station have been described in detail in the previous publication [5]. A brief description is as follows. The pretreatment procedure involved boiling the polymer electrolyte membrane Nafion 115 (DuPont) in aqueous $H_2O_2$ solution, followed by boiling in pure water to clean out the surface and interior of a membrane. The membrane was boiled in NaOH solution to covert a membrane into $Na^+$ form before the transfer-printing. Then, the membrane was boiled in pure water to remove the remaining NaOH on the surface, followed by drying the membrane fixed with a frame in a vacuum oven.

When the Nafion solution was mixed with various kinds of organic solvents, the mixture changed into the follow-

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ing form of solution, colloid, or precipitate depending on their dielectric constants ($\varepsilon$). For the PFSI solution: (i) in the solvents with $\varepsilon > 10$, a solution is formed; (ii) with $\varepsilon$ between 3 and 10, a colloidal solution is formed; and (iii) with $\varepsilon < 3$, a precipitation occurs [4]. The normal butyl acetate ($\varepsilon = 5.01$), iso-amyl alcohol ($\varepsilon = 15.8$), diethyl oxalate ($\varepsilon = 8.10$), ethylene glycol ($\varepsilon = 38.66$) and ethylene glycol dimethyl ether ($\varepsilon = 5.50$) were selected as an organic solvent having different dielectric constants.

The 20 wt.% Pt/C (HiSPEC 3000 fuel cell catalyst, Johnson Matthey) was used as an electrocatalyst both on the cathode and anode. The electrocatalyst slurry mixed with 5 wt.% solubilized Nafion was prepared to provide the more intimate contact between the polymer electrolyte membrane and platinum clusters. The slurry containing Nafion and Pt/C was prepared by first thoroughly mixing the solution using a magnetic stirrer, followed by adding the organic solvents into the slurry. The protonated form of Nafion within the slurry was converted into the $TBA^+$ form by the addition of 1 M TBAOH dissolved in methanol to give thermoplastic property to the constituting Nafion ionomer. About 50% excess TBAOH was added to minimize the thermal degradation of the ionomer. TBAOH solution was not added until the catalyst and Nafion solution were completely mixed (typically a few hours), because addition of more alkaline solutions directly to the solubilized Nafion results in some coagulation. The ratio of supported Pt catalyst to Nafion was maintained at 3:1 (in weight of solids) and the ratio of Pt catalyst to organic solvents at 2:3. In some cases, paintability of the prepared slurries was not good. The paintability of the slurry was improved by the addition of glycerol, in the approximate ratio of 3:5 (in wt.%) with the 5% Nafion solution except the slurry containing ethylene glycol.

The slurry was applied to one side of thin polymer film held in place on a vacuum table by using the screen printer. And then, the coated layer was dried for 4 h in the vacuum oven at 140 °C. The Pt/C electrocatalysts coated on the polymer film were hot-pressed on each side of dried $Na^+$ type membrane for 90 s at 195 °C with a pressure of 77 atm. After hot pressing, the catalyzed membrane was rehydrated and ion-exchanged to the $H^+$ type by immersing into 0.5 M hot sulfuric acid for 60 min, followed by rinsing in the deionized water. A separate teflonized carbon cloth was used as a backing for the thin-film MEA to provide support and hydrophobic distribution network for the gases. The carbon cloth backing was coated by the slurry containing carbon black powder and PTFE emulsion. The Pt loading of 0.7 mg/cm$^2$ was maintained for both anode and cathode surfaces and the thickness of catalyst layer was controlled to be 25 μm.

The single cell was operated at 80 °C under ambient pressure of H$_2$/O$_2$ or H$_2$/air with the stoichiometry of 1.25/2.5. The humidification of the anode/cathode gas streams was accomplished by diverting the streams through heated
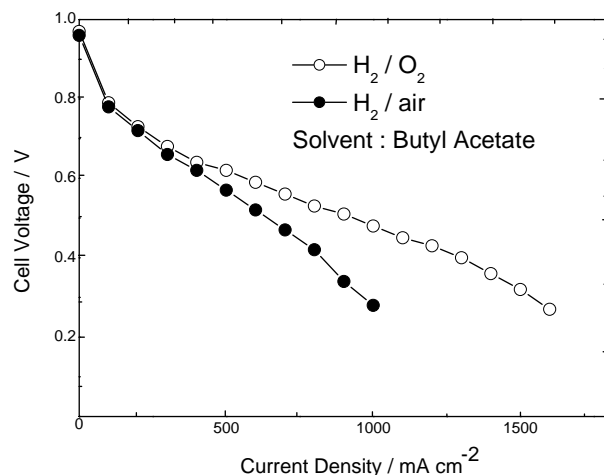


Fig. 1. Polarization curves of the electrode using normal butyl acetate as a solvent at ambient pressure: (○) H$_2$/O$_2$; (●) H$_2$/air. $T_{cell} = 80$ °C and $T_{humidifiers} = 95$ °C.

water-filled bottles that was usually kept at 95 °C for H$_2$ and O$_2$ or air.

## 3. Results and discussion

Fig. 1 shows the polarization curves of the electrode prepared by using normal butyl acetate as a solvent at ambient pressure in H$_2$/O$_2$ and H$_2$/air. The current densities were measured to be 920 mA/cm$^2$ at 0.5 V and 560 mA/cm$^2$ at 0.6 V using H$_2$/O$_2$. The cell performance was determined to be 630 mA/cm$^2$ at 0.5 V and of 430 mA/cm$^2$ at 0.6 V using H$_2$/air. The polarization curves of the electrode fabricated by using diethyl oxalate as a solvent at ambient pressure in H$_2$/O$_2$ and H$_2$/air are demonstrated in Fig. 2. This
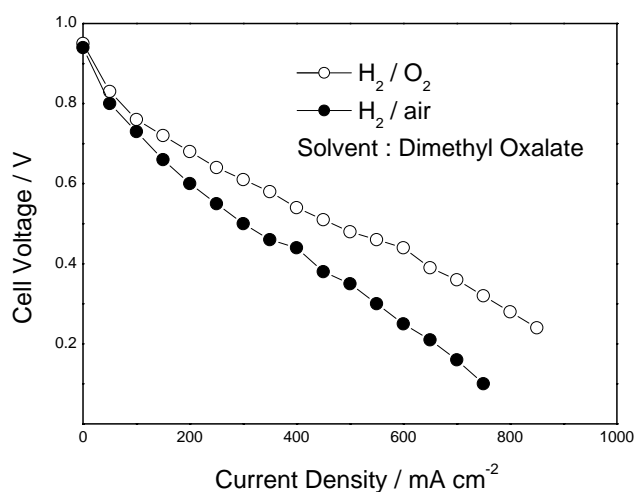


Fig. 2. Polarization curves of the electrode using normal diethyl oxalate as a solvent at ambient pressure: (○) H$_2$/O$_2$; (●) H$_2$/air. $T_{cell} = 80$ °C and $T_{humidifiers} = 95$ °C.

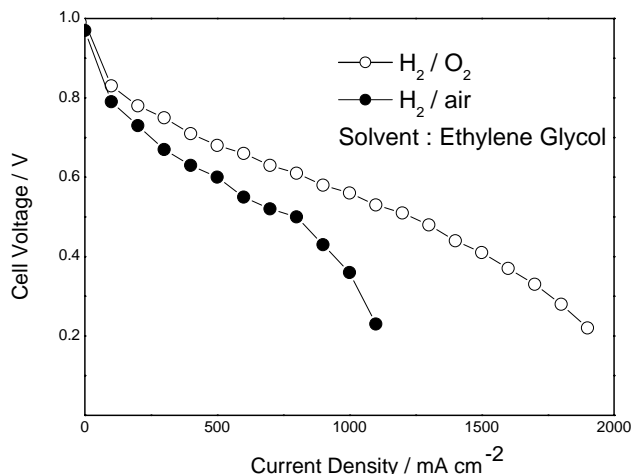Fig. 3. Polarization curves of the electrode using normal ethylene glycol as a solvent at ambient pressure: (○) $H_2/O_2$; (●) $H_2$/air. $T_{cell} = 80\,^\circ$C and $T_{humidifiers} = 95\,^\circ$C.

electrode gave low performance of $465\,\text{mA/cm}^2$ at $0.5\,\text{V}$ and $310\,\text{mA/cm}^2$ at $0.6\,\text{V}$ using cathode $O_2$. With air, it showed the current densities of 300 and $200\,\text{mA/cm}^2$ at 0.5 and $0.6\,\text{V}$, respectively.

The polarization curves of the electrode using ethylene glycol as a solvent at ambient pressure in $H_2/O_2$ and $H_2$/air are shown in Fig. 3. This electrode gave high performance of $1230\,\text{mA/cm}^2$ at $0.5\,\text{V}$ and $840\,\text{mA/cm}^2$ at $0.6\,\text{V}$ in $H_2/O_2$. With air, its performances were determined to be 800 and $500\,\text{mA/cm}^2$ at 0.5 and $0.6\,\text{V}$, respectively. Fig. 4 presents the polarization curves of the electrode using *iso*-amyl alcohol as a solvent at ambient pressure in $H_2/O_2$ and $H_2$/air. The current densities of $360\,\text{mA/cm}^2$ at $0.5\,\text{V}$ and $290\,\text{mA/cm}^2$ at $0.6\,\text{V}$ using $H_2/O_2$ were obtained.

According to suggestions of Uchida et al. [4], it seems that the Nafion solution mixed with solvents of higher dielectric
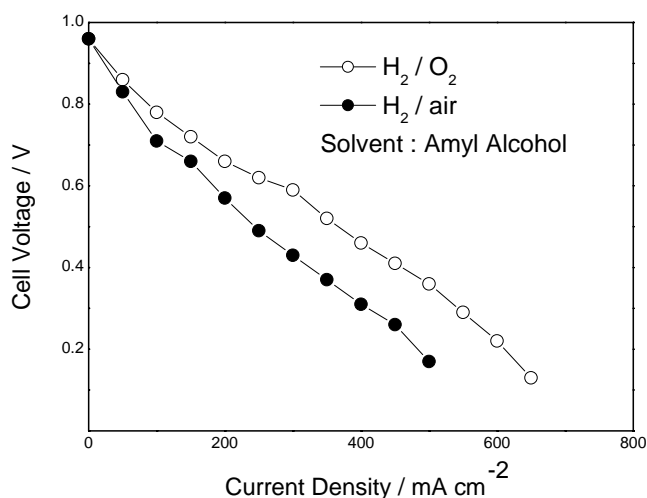


Fig. 4. Polarization curves of the electrode using normal *iso*-amyl alcohol as a solvent at ambient pressure: (○) $H_2/O_2$; (●) $H_2$/air. $T_{cell} = 80\,^\circ$C and $T_{humidifiers} = 95\,^\circ$C.

constants such as ethylene glycol ($\varepsilon = 38.66$) and *iso*-amyl alcohol ($\varepsilon = 15.8$) comes in solution form, whereas the solution mixed with solvents of lower dielectric constants such as normal butyl acetate ($\varepsilon = 5.01$) and diethyl oxalate ($\varepsilon = 8.10$) stays in colloidal form. It was also suggested [4] that the Nafion ionomers in the colloidal form are adsorbed more homogeneously on the Pt/C surface rather than in the solution form. However, the electrode prepared using ethylene glycol which is considered to be in the solution form showed a higher performance than the electrodes fabricated using the solvents of lower dielectric constants.

*Iso*-amyl alcohol seems not to be a good solvent for transfer printing technique due to the difficulty of viscosity control. It seems that the addition of glycerol into slurry as paintability helper increases the dielectric constant of mixture more than 10 and inhibits the colloid formation, thereby decreasing the performance of electrodes prepared by using *iso*-amyl alcohol and diethyl oxalate. In the case of direct coating of electrode prepared by using *iso*-amyl alcohol onto the membrane, much higher performance of $800\,\text{mA/cm}^2$ at $0.6\,\text{V}$ in $H_2/O_2$ is observed compared with the electrode prepared slurry containing *iso*-amyl alcohol and glycerol.

From the Figs. 1–4, oxygen gain ($\Delta V$) is calculated to be as

$$\Delta V = V\left(\frac{H_2}{O_2}\right) - V\left(\frac{H_2}{\text{air}}\right) \tag{1}$$

where $V(H_2/O_2)$ and $V(H_2/\text{air})$ are the cell voltages measured under the application of hydrogen/oxygen and hydrogen/air, respectively. Oxygen gain is another easy measurement for oxygen transport through catalytic layers. Lower oxygen gain means the fast transport of oxygen through the catalytic layer.

Fig. 5 presents the oxygen gain for four kinds of catalytic layers as a function of applied current. It seems that there is no clear correlation between the dielectric constant and oxygen gain. Instead, oxygen gain is seems to be related with the boiling or decomposition temperature of the solvents. The electrodes prepared from solvents having higher boiling temperatures, ethylene glycol ($196\,^\circ$C) and dimethyl oxalate ($163\,^\circ$C), showed higher oxygen gains, comparing to the electrodes fabricated by using the other two solvents (*iso*-amyl alcohol; $102\,^\circ$C, butyl acetate; $124\,^\circ$C). Considering that the temperature during the slurry drying is $140\,^\circ$C, in the case of electrodes prepared from solvents of ethylene glycol and dimethyl oxalate, the pores of micro and macro sizes in the electrodes seem to be partially filled with solvents even after the heat treatment, thereby decreasing the transport of reactant gas through the electrodes. It is well known that microstructure of a catalytic layer strongly affects the gas transport rate in the catalytic layer. Gloaguen et al. [6] suggested that oxygen is first transported through gas pores and then diffuses though the electrolyte phase of the catalytic layer, from the comparative study of macro-homogeneous and agglomerate models for the oxygen reduction in the thin catalytic layer.
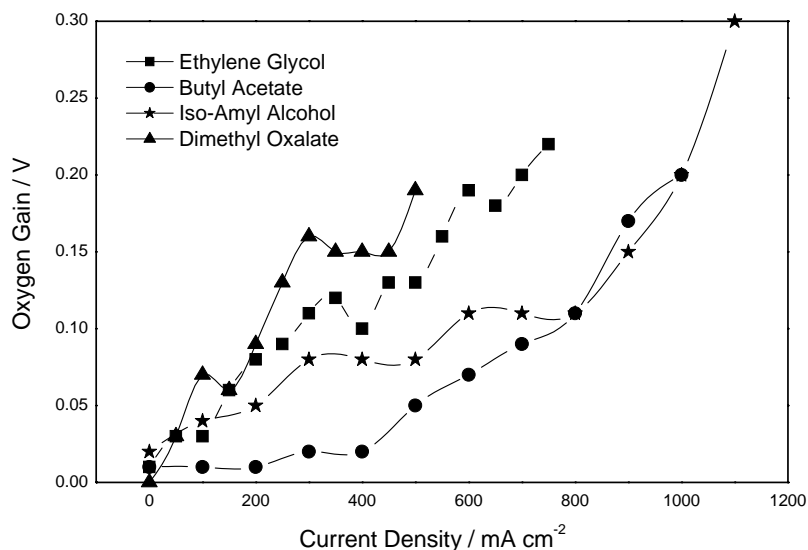
Fig. 5. Oxygen gain for catalytic layers prepared using various solvents.

## 4. Conclusions

The electrode prepared by using ethylene glycol showed a better performance of $840 \, \text{mA/cm}^2$ at $0.6 \, \text{V}$ in $H_2/O_2$ than those by using other solvents. Oxygen gain of the electrodes seemed to be related to the decomposition temperature of the solvents. The pores in the electrodes seemed to be partially blocked by the remaining solvents even after the heat treatment, thereby increasing the oxygen gain.

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