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Journal of Power Sources 94 (2001) 78–84

JOURNAL OF
**POWER
SOURCES**

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Optimal composition of polymer electrolyte fuel cell electrodes determined by the AC impedance method

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Received 22 February 2000; received in revised form 3 July 2000; accepted 9 October 2000

Abstract

A proton exchange membrane fuel cell (PEMFC) electrode having a modified morphology of conventional Teflon (PTFE) bonded electrodes was studied using the AC impedance method. The electrode differs from other types of electrodes in the presence of a thin catalyst-supporting layer between the gas diffusion backing and the catalyst layer. The thickness and composition of the supporting layer were optimized on the basis of the information from AC impedance measurements. The optimal thickness of the supporting layer and its PTFE content turned out to be approximately 3.5 mg cm^{-2} and 30 wt.%, respectively. The catalyst layer was cast on top of the supporting layer, from solution that has the proper ratio of ionomer Nafion and Pt/C catalyst. The optimal amount of the ionomer in the catalyst layer was approximately 0.8 mg cm^{-2} when Pt loading was kept at 0.4 mg cm^{-2} . These values are rationalized in terms of the catalyst active area and the transport of the involved species for the electrode reaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: AC impedance method; PEMFC; Pt/C electrode; PTFE; Nafion

1. Introduction

The economic future of proton exchange membrane fuel cells (PEMFC) for applications such as transportation [1,2] critically depends on efficient utilization of the platinum catalyst. Major breakthroughs have been made with respect to lowering the amount of the catalyst loaded on the PEMFC electrode. They include the method for impregnating the catalyst side of the electrode with a solubilized form of the ionomer Nafion [3–6]. More recently, a drastic reduction in the Pt loading was achieved by fabricating separately the catalyst layer and PTFE (polytetrafluoroethylene) containing diffusion layers [7–12]. Low Pt loading was also achieved by a process that features cross-linking carbon-supported Pt (Pt/C) with perfluorosulfonate ionomer during its coagulation from the colloid [13,14]. Improvements in utilization were also made by methods such as sputter-deposition of the catalyst directly on the carbon surface [15,16] or the membrane surface [17,18], or electrodeposition of the catalyst through the Nafion onto the electrode [19]. These methods aimed at minimizing the catalyst loading must also satisfy other criteria, which are proton

access, gas access, and electronic path continuity. A common strategy to meet these requirements is to separate PTFE from the catalyst layer. Although PTFE plays the role of hydrophobicity in the gas diffusion regime of the electrode, it does not have to be present in the immediate vicinity of the catalyst sites [8]. The hydrophobic treatment of a carbon paper or cloth, which is used as the starting material of the gas diffusion backing, often includes the infiltration of a PTFE/carbon mixture into the porous body of the backing and subsequent baking and sintering [2].

In our study the gas diffusion backing of the cell electrode was treated in two steps, a small modification of conventional methods [20]. The carbon paper first underwent the hydrophobic treatment, through Teflon resin wetting and sintering. Then a thin PTFE/carbon film was cast on its treated surface, from an alcoholic suspension. This film plays the role of supporting the catalyst layer such that the catalyst particles do not fall into the pores in the backing. This layer, then called the catalyst-supporting layer, will be actively involved with the electrode reaction, imparting hydrophobicity to and maintaining a proper water balance in the interface. The interface between the carbon backing and the polymer electrolyte, with or without the supporting layer, is depicted in Fig. 1. The insertion of the thin supporting layer between the backing surface and the catalyst film can be advantageous not only in supporting the

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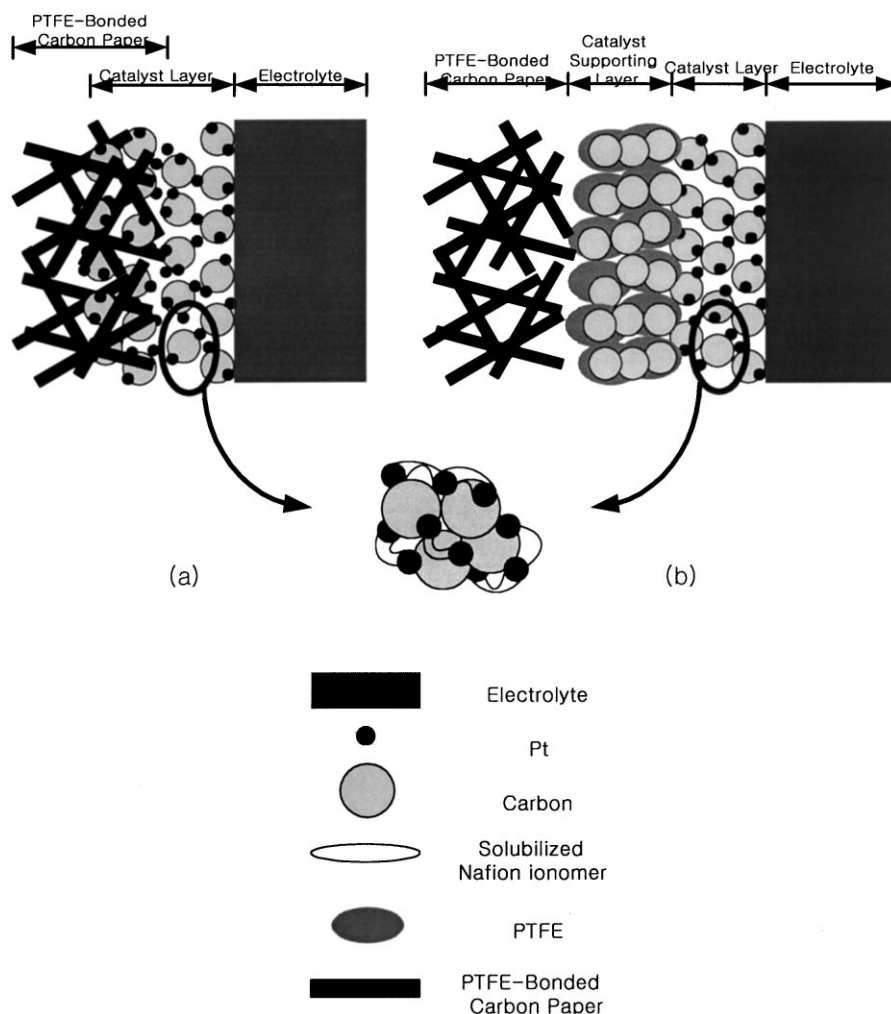


Fig. 1. Schematics depicting the electrode: (a) without the catalyst-supporting layer; (b) with the catalyst-supporting layer.

catalyst film but also in that the diffusion control of the reacting species is limited mainly to the narrow region provided by the supporting layer. But the separation of the catalytic layer from the hydrophobic supporting layer could impede the drain of the water generated at the catalyst layer. Unless the catalyst film is very thin and uniform, even the gas access to the catalytic site will be greatly impeded [8]. Recently a similar method to ours was reported [21] which uses an intermediate hydrophobic carbon layer, similar to the supporting layer in our terms. They claimed that the layer helps improve gas and water management.

In this work, we studied the characteristics of such an interface using AC impedance method, examining the frequency response of the cathodic oxygen reduction reaction. The study was aimed at finding optimal conditions for some important fabrication parameters of the electrodes. Earlier AC impedance studies on the electrodes having thin film catalyst layer showed that the transport of air through such backing develops a lower frequency loop due to gas-phase transport limitations through the backing [7]. Thus, in

our study we used oxygen gas in order to minimize any complexity originated from such limitations and to emphasize the dependence of the frequency response on morphology of the electrodes, particularly of the supporting layer. By using oxygen gas we also attempted to explore the lower frequency region below 1 Hz at which water-related limitation can appear [22].

2. Experimental

The complete fabrication of gas diffusion electrodes (GDE) is basically a three-step process; carbon paper first undergoes hydrophobic treatment, then a thin PTFE/carbon layer is cast onto the treated surface, and lastly the catalyst layer is cast onto the surface of the supporting layer. The starting material for GDE is Toray carbon paper, a bundle of carbon fibers.

For PTFE hydrophobic treatment, the carbon paper was wetted with Teflon resin (Teflon 30-J, Du Pont), then dried at 180°C for 30 min and sintered at 330°C for 30 min.

The treated (wet-proofed) surfaces of the carbon electrodes were examined by SEM (JSM-5800LV, JEOL Ltd.).

A homogeneous 2-propanol suspension composed of the Teflon resin and the carbon powder (Vulcan XC-72) was placed on the surface of the wet-proofed carbon backings. The Teflon concentration in the suspension was varied between 10 and 40 wt.%. Again it was baked and sintered under the same conditions as in the hydrophobic treatment. The total amount of the loaded PTFE/carbon was adjusted to have three different values, at 1.5, 3.5 and 10.0 mg cm⁻².

The catalyst layer was cast onto the PTFE/C layer surface from the catalyst suspension that was prepared by dissolving 20 wt.% Pt/C (E-TEK) and 5 wt.% Nafion[®] solution in 2-propanol solvent. The ionomer Nafion concentration in the catalyst layer was varied between 0.2 and 2.0 mg cm⁻². But the Pt loading in the catalyst layer was fixed at 0.4 mg cm⁻². This was accomplished by changing the concentration of 20 wt.% Pt/C catalyst and 5 wt.% Nafion solution in the suspension and adjusting the amount of them, after expelling the solvent, left on the supporting layer surface. After the catalyst loading, the electrodes were cured at 80°C for 2 h.

The Nafion[®] 115 membrane was boiled in 3 wt.% H₂O₂ solution for 1 h. Then, it was rinsed in boiling deionized water for 2 h. In order to remove metallic contaminants on the membrane surface and exchange Na⁺ for H⁺ in the membrane, it was boiled in 0.5 M H₂SO₄ for 1 h. Finally, it was rinsed again in boiling deionized water for 2 h.

The pretreated membrane and electrodes of a 1 cm² cross-sectional area were bonded together by hot pressing them under 70 kg_f cm⁻² for 90 s, maintaining the temperature at 120°C. A Teflon gasket, carbon block, and copper current collector were secured to both sides of the membrane and electrode assembly, using bolts and nuts. Mass flow controllers (SAM SFC280E) were used to keep the flow rate of pure hydrogen and oxygen gas at 150 ml min⁻¹. The gases were passed through humidifiers before being fed into the cell. Insulation and heating maintained desired temperatures in the cell and in the humidifiers on the cathode and anode sides at 60, 65 and 70°C, respectively.

The electrochemical impedance spectra were recorded in the 1 mHz ≤ *f* ≤ 10 kHz frequency range using the frequency response detector (EG&G Model 1025) and potenti/galvanostat (EG&G Model 263A). The amplitude of the sinusoidal modulation voltage did not exceed 10 mV. The pressure of the oxygen and hydrogen gas supplied into the cathode and anode, respectively, was set at 1 atm. The anode at which hydrogen oxidation takes place was used as the reference and also as the counter electrode of the AC measurements (the cathode was used as the working electrode). For cyclic voltammetry, the Pd/H₂ electrode was used as the reference. The electrode was made of palladium wire of 100 μm diameter (99.9%, Aldrich), which was then loaded electrochemically with hydrogen. The loading was confirmed by measuring the electrical resistance of the wire. Before the electrochemical loading, the wire was coated with PVdF (polyvinylidene fluoride, Kynar 741,

Elf Atochem) film. The working electrode was purged with nitrogen gas. The cell temperature was fixed at 60°C.

3. Results and discussion

3.1. Introduction of the catalyst-supporting layer

The thickness of the PTFE/C layer and the catalytic film, both measured by their loading per unit surface area, were approximately 50 and 30 μm, respectively. We first examined the effect of the supporting layer thickness on the electrode performance. Fig. 2 shows the *i*-*V* curves of the PEMFC whose MEA (membrane-electrode assembly) incorporates electrodes with several thickness of the supporting layer. The thickness expressed in the PTFE/C loading per unit area of the electrode varied from 1.5 to 10 mg cm⁻² while all other conditions were fixed (for example, the composition of PTFE at the layer was fixed at 30 wt.%). From Fig. 2 it is seen that the cell performance peaks at 3.5 mg cm⁻² loading. A further increase in the thickness of the supporting layer is detrimental to cell performance, suggesting that there is an optimal thickness of the layer. The inferior performance of the cell incorporating the electrode without the supporting layer can be explained by the reduction of available catalyst sites. Elimination of the supporting layer should allow part of the catalyst region to penetrate deep inside the backings thus, that region becoming inaccessible to the gas or the proton. (but the Tafel type plotting (*E* versus log *i*) of the curves of Fig. 2 shows that they all exhibit the linear region, the slope of which is 76 ± 4 mV/decade). The reduction of the available catalyst site with a decrease in the thickness of the supporting layer is evident from the cyclic voltammogram (CV) of the cathode shown in Fig. 3. The available area of the Pt sites, which is estimated from the hydrogen absorption-desorption peak, reaches its maximum value at 3.5 mg cm⁻². The reduction of the available Pt sites with

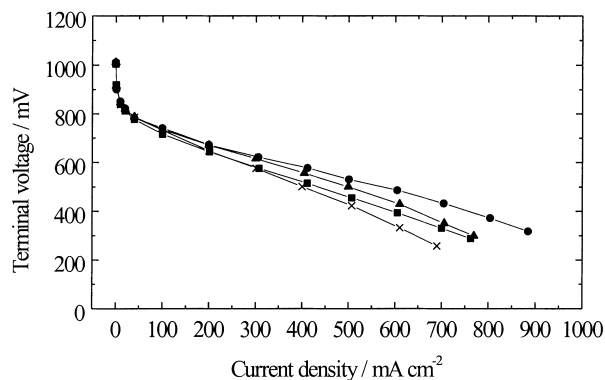


Fig. 2. The *i*-*V* curves of the fuel cell incorporating electrodes with several different loadings (expressed in mass per unit area) of the catalyst-supporting layer: (■) 1.5; (●) 3.5; (▲) 10.0 mg cm⁻²; and (×) no supporting layer. The layer contains 30 wt.% PTFE.

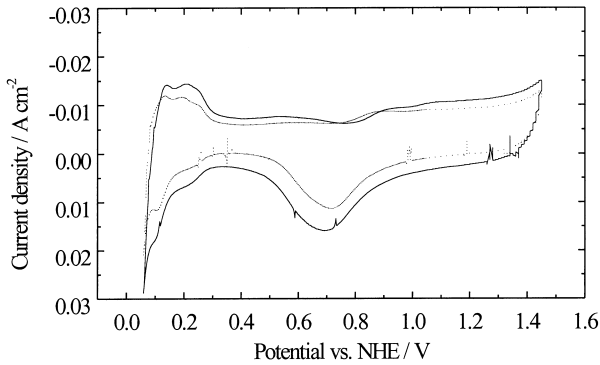


Fig. 3. Cyclic voltammograms of the electrode with two different loadings of the catalyst-supporting layer: (.....) 1.5; (—) 3.5 mg cm⁻². Scan rate was 50 mV s⁻¹.

a further increase beyond the optimal thickness is not clearly understood.

AC impedance spectra for the cathodic reaction of the cell (the potential of which is 0.5 V) also confirm the existence of an optimal thickness of the supporting layer. Fig. 4 shows that the diameter of the higher frequency arc (greater than 1 Hz) representing the faradaic impedance has a minimum value at 3.5 mg cm⁻², implying that at this loading the electrode has the maximum available surface area. As the layer gets thinner (1.5 mg cm⁻² loading and no loading) the spectrum develops a lower frequency arc (more properly a distortion), which should be related to some kind of transport limitations. Thus, the optimal thickness of the supporting layer is related to the maximum active area of Pt in the catalyst film.

3.2. Variation of some fabrication conditions associated with the supporting layer and the catalyst film

Now, the PTFE concentration in the supporting layer was varied while the loading of the supporting layer was fixed at 3.5 mg cm⁻². The *i*-*V* curves for a family of cells, each having a different PTFE concentration, are shown in Fig. 5. It is seen that the optimal concentration of PTFE in the supporting layer is 30 wt.%. The *i*-*V* performance of the cell made of electrodes with the 40 wt.% layer is similar to that made of electrodes with the 10 wt.% layer. The AC impedance spectra for the oxygen reduction reaction (ORR) at different cathodic potentials are shown in Fig. 6 for the same family of cells (the ohmic resistance of the electrodes of

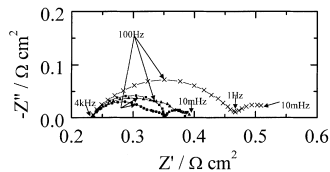


Fig. 4. Impedance spectra for the oxygen reduction reaction at the cell potential of 0.5 V. The electrode has several different loadings of the catalyst-supporting layer: (■) 1.5; (●) 3.5; (▲) 10.0 mg cm⁻² and (×) no supporting layer.

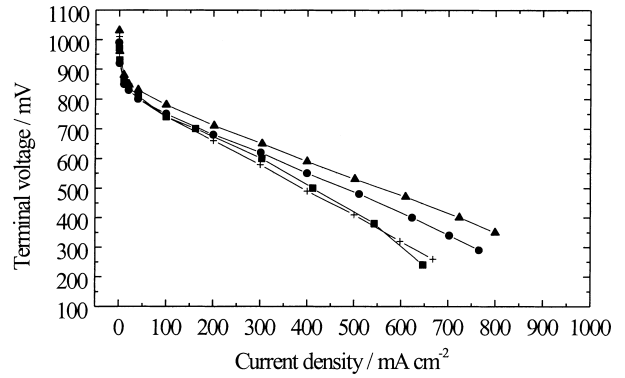


Fig. 5. The *i*-*V* curves of the cell incorporating electrodes with the supporting layer containing various PTFE concentrations: (■) 10; (●) 20; (▲) 30; (+) 40 wt.%.

Fig. 6 falls in the range of 0.25–0.3 Ω cm²). At low overpotential (~0.8 V) the diameter of the high frequency arc registers the minimum value at 30 wt.%. The existence of an optimal PTFE content is partly attributed to the efficiency of water management [21]. The water transport through the supporting layer should be impeded with increase in PTFE loading while the water generated in the cell cannot be effectively removed if PTFE loading is too low.

With the increase of the cathodic overpotential (equivalent to decrease of the cell potential) the diameter of the higher frequency arc decreases due to the increasing driving force as seen in Fig. 6(b) and (c). But the minimum diameter is always demonstrated by the cell incorporating electrodes with the 30 wt.% (PTFE) layer. At higher overpotentials,

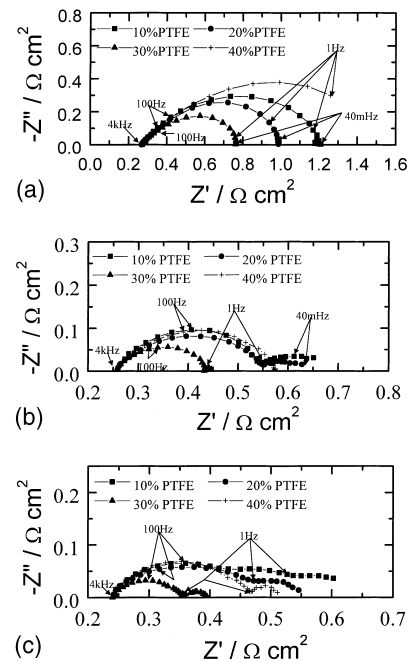


Fig. 6. Impedance spectra for the oxygen reduction reaction at three different cell potentials: (a) 0.8 V; (b) 0.7 V; (c) 0.6 V. The catalyst-supporting layer (3.5 mg cm⁻² loading) of the electrode contains various concentrations of PTFE: (■) 10; (●) 20; (▲) 30; (+) 40 wt.%.

even the optimized cells with respect to the supporting layer thickness develop the lower frequency arc. From Fig. 6 it is seen that the growth of this arc with the increase in the overpotential is sensitive to the PTFE concentration in the supporting layer. The cell using electrodes with 10 or 20 wt.% (PTFE) layer demonstrates, even at a medium overpotential (0.7 V), a clear growth of the lower frequency loop. At a high overpotential (0.6 V), every cell, including the 30 wt.% cell, shows the lower frequency distortion to some extent. The severe distortion of the spectra in the lower frequency region is believed to reflect water-related transport limitations [22]. It was observed that the cell showing such distortion sometimes failed to perform due to a sudden collapse of the cell current during current-potential measurement [23]. But elucidation of such transport limitation requires much more creative investigations in both mathematical modeling and experimental measurements.

Water content at the interface contributes to the transport of the involved species in many different ways. At extremity a high water level can block the oxygen transport. The increased concentration of the water, due to the generation at the cathode, can directly affect the ORR kinetics and also contributes indirectly to the state of contact between the Pt catalyst and the ionomer. With a significant drop in the water concentration at the interface there is a possibility of ionomer shrinkage, reducing both the surface contact of the catalyst with the ionomer and the proton conductivity of the ionomer. The related CV measurements actually demonstrated a substantial decrease of the Pt active area for the electrode with 40 wt.% PTFE in the supporting layer. If such reduction in the active surface area is caused by low water content at the interface, an increase in the humidifier temperature should improve cell performance, since it can restore the proper water content, both in the ionomer and in the supporting layer. The i - V curves shown in Fig. 7

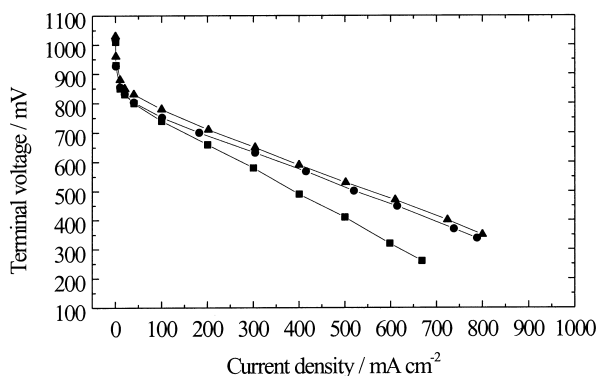


Fig. 7. The i - V curves of the cell incorporating electrodes with the supporting layer containing 40 wt.% PTFE. The temperature of the humidifier on the cathode side was maintained at: (■) 65°C; (●) 80°C. For comparison is shown the curve of the cell that incorporates electrodes with the supporting layer containing 30 wt.% PTFE and was operated with the temperature of the humidifier on the cathode side maintained at 65°C (▲).

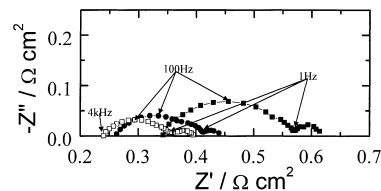


Fig. 8. Impedance spectra for the oxygen reduction reaction at the cathodic potential of 0.6 V. The catalyst-supporting layer (3.5 mg cm^{-2} loading) of the electrode contains 40 wt.% PTFE. The temperature of the humidifier on the cathode side was maintained at: (■) 65°C; (●) 80°C. For comparison is shown the spectra of the electrode with the supporting layer containing 30 wt.% PTFE and with the temperature of the humidifier on the cathode side maintained at 65°C (□).

demonstrates that the performance of the cell utilizing 40 wt.% PTFE electrodes, with the temperature of the cathodic side humidifier maintained at 80°C, did improve remarkably, almost to the level of the 30 wt.% PTFE electrode operated at 65°C. The impedance spectra of the 40 wt.% PTFE electrode shown in Fig. 8 confirm that the arc diameter does decrease with the increase of the humidifier temperature. We can conclude that the large effective charge transfer resistance demonstrated by the electrode in excessive PTFE content (40 wt.%) is attributed to reduced water content at the interface.

Some portion of the catalytic film cast on the supporting layer surface can penetrate the inside of the surface layer. Thus, the question arises regarding whether such intimate contact between the catalyst and the PTFE brings any beneficial effect. To examine this aspect we cast the catalytic film directly onto the electrolyte membrane surface. The results of the i - V curve and the impedance spectra did not change significantly compared to the case in which the catalyst film was cast on the surface of the supporting layer. Just at high overpotential the cell with the film cast directly on the electrolyte delivered a somewhat smaller current. Thus, this is another demonstration of the non-necessity of placing the catalyst site right into the Teflon body.

3.3. Effect of ionomer concentration in the catalyst layer

In the final adjustment, the effect of the ionomer concentration in the catalyst layer on electrode performance was examined while other variables were kept at their optimal values. Past studies on the influence of Nafion loading on cell performance revealed that the optimal amount of the Nafion ionomer is about 0.8 – 1.0 mg cm^{-2} in the case of the carbon-supported platinum [13,24–26]. But the optimal amount should depend on the Pt catalyst loading in the catalyst layer [20].

In our experiment the ionomer loading in the catalyst layer was adjusted subject to the condition that the Pt loading in the catalyst layer was kept at 0.4 mg cm^{-2} (this condition was maintained throughout this study). The effect

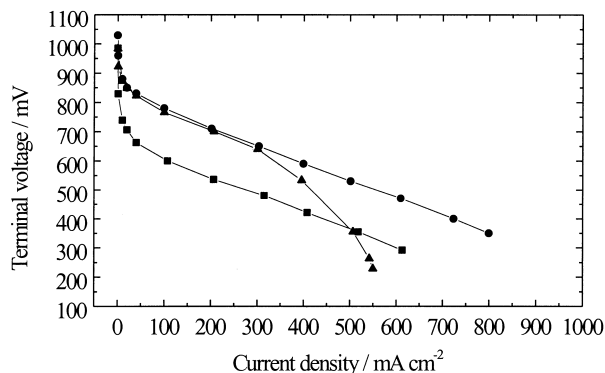


Fig. 9. The i - V curves of the cell incorporating electrodes with the catalyst layer containing various Nafion ionomer concentrations: (■) 0.2; (●) 0.8; (▲) 2.0 mg cm^{-2} .

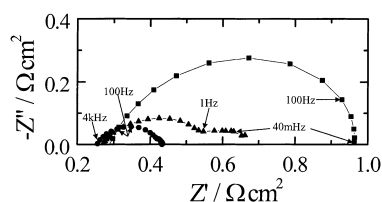


Fig. 10. Impedance spectra for the oxygen reduction reaction at the cathodic potential of 0.6 V. The catalyst layer of the electrode contains various Nafion ionomer concentrations: (■) 0.2; (●) 0.8; (▲) 2.0 mg cm^{-2} .

of the ionomer loading in the cathode on the i - V curves is shown in Fig. 9. As expected, the 0.8 mg cm^{-2} ionomer cell showed the best performance. It is striking that the performance of the 2.0 mg cm^{-2} ionomer cell drops sharply as the current is drawn over 300 mA cm^{-2} . (The linear Tafel zone of the cell of 2.0 mg cm^{-2} ionomer survives short due to the mass transport limitations. Other cells exhibit similar Tafel slope to those of Fig. 2). Such a sudden drop in the cell performance is also well demonstrated in the AC impedance spectra of the cell (Fig. 10). Among three cells having different ionomer loading, only the 2.0 mg cm^{-2} ionomer cell developed the lower frequency arc. This confirms that an increase in the ionomer loading in the catalyst layer retards the oxygen transport, particularly when the current density is high. The transport limitation results from the increase in the distance, through which the gas has to permeate, diffuse or migrate. The CV measurements for the electrodes confirmed that the catalyst active area drops sharply when an insufficient ionomer is used.

4. Conclusions

The electrode for the proton exchange membrane fuel cell (PEMFC) was fabricated by placing a thin catalyst-

supporting layer on top of the gas diffusion backing and casting the catalyst layer from a solution on top of the supporting layer surface. The structure and composition of the electrode was optimized using the information from AC impedance and the cell current-potential measurements. The optimal values of the thickness of the supporting layer, its PTFE concentration and the Nafion ionomer concentration in the catalyst layer were approximately 3.5 mg cm^{-2} , 30 wt.% and 0.8 mg cm^{-2} , respectively, when the Pt loading in the catalyst layer was kept at 0.4 mg cm^{-2} . AC impedance spectrum of the electrode with a low concentration of PTFE in the supporting layer showed clearly a lower frequency arc at high overpotentials, which is believed to reflect water-related transport limitations. Forced increase in the water concentration at the electrode assembly improved the performance of a high PTFE electrode, possibly by increasing the Pt active area.

Acknowledgements

This work was financially supported by the Alternate Energy Program through the Republic of Korea Ministry of Trade, Industry and Energy and the Institute for Advanced Engineering. The authors are grateful to Dr. In-Hwan Oh of KIST for providing us with experimental materials.

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