

Effects of Polyamidoamine Dendrimers on the Catalytic Layers of a Membrane Electrode Assembly in Fuel Cells

Jin Hwa Lee and Jongok Won*

Department of Applied Chemistry, Sejong University, Seoul 143-747, Korea

In Hwan Oh, Heung Yong Ha, and Eun Ae Cho

Korea Institute of Science and Technology, Seoul 136-791, Korea

Yong Soo Kang

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

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Abstract: The transport of reactant gas, electrons and protons at the three phase interfaces in the catalytic layers of membrane electrode assemblies (MEAs) in proton exchange, membrane fuel cells (PEMFCs) must be optimized to provide efficient transport to and from the electrochemical reactions in the solid polymer electrolyte. The aim of reducing proton transport loss in the catalytic layer by increasing the volume of the conducting medium can be achieved by filling the voids in the layer with small-sized electrolytes, such as dendrimers. Generation 1.5 and 3.5 polyamidoamine (PAMAM) dendrimer electrolytes are well-controlled, nanometer-sized materials with many peripheral ionic exchange, -COOH groups and were used for this purpose in this study. The electrochemically active surface area of the deposited catalyst material was also investigated using cyclic voltammetry, and by analyzing the Pt-H oxidation peak. The performances of the fuel cells with added PAMAM dendrimers were found to be comparable to that of a fuel cell using MEA, although the Pt utilization was reduced by the adsorption of the dendrimers to the catalytic layer.

Keywords: PAMAM dendrimer, MEA, fuel cell, catalytic layer.

Fuel cells convert chemical energy directly into power. Proton exchange membrane fuel cells (PEMFC) consist of a solid polymer membrane electrolyte and catalyst electrodes. There have been many studies of such membranes and catalysts with a view to commercializing PEMFCs.¹⁻⁵ The use of expensive platinum or platinum-rich alloys as catalysts is necessary in cells with an acid electrolyte and a relatively low operating temperature. The connectivity of fuel gas, electrons, and protons across the three interfaces between the reactant, polymer electrolyte, and catalyst in the region of a porous electrode must be optimized to provide efficient transport to and from the electrochemical reactions. The limitations on the contact between the solid polymer electrolyte and the catalyst restrict the performance of PEMFCs in comparison with that of aqueous electrolyte fuel cells. This means that their Pt catalyst utilization is low, so a high loading of catalyst is required. Many studies have been carried out with a view to obtaining effective transport across

the electrolyte-catalyst-gas phase boundaries, which has resulted in better catalyst utilization including the use of carbon-supported Pt catalysts.⁶⁻¹²

The contact between the ionomer additive and catalyst can be improved by increasing the volume of the conducting medium and by the thorough dispersion of the ionomer throughout the catalyst layer. It was obtained by blending the solubilized ionomer (e.g., Nafion) and the platinized carbon into a homogeneous "ink". However the presence of voids or unfilled pores in such a catalyst layer lowers its ionic and electronic conductivity. Further, since gas diffuses nearly as readily through hydrated ionomer as through water pockets, it is advantageous for the voids to be filled with small ionomer materials. The optimal catalyst layer can be obtained by the possessing a high volume density of small catalyst particles, and the remainder of the volume is filled with ionomer in order to reduce transport losses occurring between the three phases. Among the candidates for filling the voids are the commercial polyamidoamine (PAMAM) dendrimer electrolytes,¹³⁻¹⁵ which are well-con-

*Corresponding Author. E-mail: jwon@sejong.ac.kr

trolled nanometer-sized materials with many peripheral ionic exchange COOH groups. This study reports the effects of introducing nanometer-sized dendrimer electrolytes into the catalytic layer of a PEMFC.

Experimental

Materials. Commercial Nafion 115 membranes (125 μm , equivalent weight of 1100, Du Pont) were cleaned using a multistep procedure (*vide infra*). 20 wt% Pt on Vulcan xc-72 (Pt-C) was purchased from E-TEK for use as the catalyst. 5 wt% of Nafion solution in isopropyl alcohol (Aldrich) and solutions of generation 1.5 (20 wt%, FW = 2,935) and generation 3.5 (10 wt%, FW = 12,931) poly(amidoamine) (PAMAM) dendrimers in methanol (Aldrich) containing 16 and 64 surface carboxylate groups, respectively, were purchased and used as received. The characteristics of the PAMAM dendrimers are shown in Table I.¹³

Substitution and Impregnation Method. The generation 1.5 (G1.5) and generation 3.5 (G3.5) commercial PAMAM electrolyte dendrimers have a different number of -COONa surface groups. These surface groups have to be converted into protonic form to promote proton transport. The conversions of the PAMAM electrolyte dendrimers were performed using an ion exchange column. The commercial G1.5 and G3.5 PAMAM dendrimers were kept in columns filled with the ion exchange resins for 30 min, and the substituted PAMAM dendrimers were then collected.

Preparation of Membrane Electrode Assemblies (MEAs). Each Pt-C/PAMAM dendrimer slurry was prepared by first mixing Pt-C with the protonated PAMAM dendrimer solution at the appropriate concentration, then this slurry was dried in an 80°C convection oven for 2 days. The Nafion ionomer/Pt-C/PAMAM dendrimer slurry was prepared by adding Nafion ionomer/isopropyl alcohol solution into the Pt-C/PAMAM dendrimer mixture. These solutions were mixed using ultrasonication for 1 hr. The resulting catalyst inks were then cast onto carbon paper to prepare the catalyst layers.

The MEAs are based on the condition for Nafion 115 membranes. The catalyst layers of the reference MEA consisted of 20 wt% Pt-C with platinum loadings of 0.4 and 0.7 mg/cm² for the anode and cathode respectively. Before assembling each MEA, the Nafion 115 polymer electrolyte membranes were cleaned in various solutions in order to

remove any organic and inorganic contaminants and to change their form. The pretreatment procedure involved boiling the Nafion 115 membranes in 5 wt% aqueous H₂O₂ solution for 1 hr, followed by boiling for 1 hr in pure water. The membrane was then boiled for 1 hr in 1 N H₂SO₄ solution, followed by further boiling in water for 1 hr. On completing the purification procedure, the membranes were soaked in deionized water at room temperature overnight and washed acid-free. The prepared catalytic inks were then cast using screen printing equipment over the carbon paper to make the electrodes. The MEAs were prepared by placing the above electrodes on either side of the pre-treated Nafion 115 membrane, followed by hot pressing at 140°C and 200 atm for 90 s. The effective electrode area was 25 cm². MEA samples were prepared with various amounts of PAMAM in the catalytic layers.

Characterization. Hydrogen gas and a sufficient amount of oxidant (oxygen) gas were humidified and fed to each electrode. The cell was maintained at 80°C and the operating pressure was atmospheric. Reactant humidification was achieved using a water-bubbler. The potential-current density characteristic curves of the cells were measured using a dc electronic load (Dae Gil, Korea). An impedance analyzer (IM6, Zahner Elektrik, Germany) was used to measure the resistance of the membrane electrode assemblies at 0.85 V under operating cell conditions. The reference and counter electrodes were connected to the hydrogen electrode and the working electrode was linked to the oxygen electrode. The current responses with respect to a 5 mV sine wave were evaluated in the frequency range 10 mHz to 100 kHz.

The BET surface area,¹⁶⁻¹⁹ pore volume, and pore size distribution of the Pt-C sample were determined by applying the Barret-Joyner-Halenda method²⁰ to the desorption branch of the isotherm measured by nitrogen adsorption-desorption at 77 K using a ASAP2010 (Micromeritics) instrument.

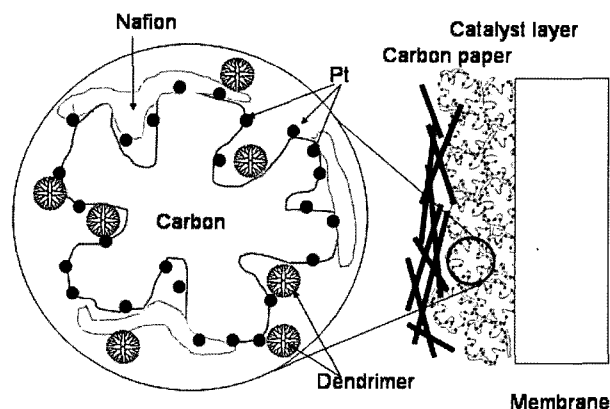
Cyclic voltammetry measurements were conducted at 80°C to determine the electrochemically active surface area of the Pt electrocatalyst. The measurements involved hydrogen and nitrogen at the counter electrode (anode) and working electrode (cathode), respectively, with a potential range of 0.04 to 1.4 V vs. RHE and a sweep rate of 50 mV/s.

Results and Discussion

Before the addition of the PAMAM dendrimers, a BET analysis of the 20 wt% Pt-C was performed to investigate its pore size distribution, which is crucial for determining the optimum size of each PAMAM dendrimer. The BET analysis results showed that the adsorption average pore diameter of the carbon support is 6.31 nm. The size of the PAMAM dendrimers is in the range 2-5 nm, which is small enough to fill the pores of the carbon support. The possible locations of the dendrimer in the Pt-C material are presented in Scheme I. It is expected that the PAMAM dendrimers are

Table I. Properties of the PAMAM Dendrimers

Generation	Molecular Weight (g/mol)	Estimated Diameter (nm) ¹³	Number of Surface Groups (-COONa)
1.5	2,935	2.9	16
3.5	12,931	4.5	64



Scheme I. Polyamidoamine dendrimers were applied into the catalyst layer. The dendrimers reduced the Pt catalyst surface area and thus resulted in a decrease in the utilization of Pt, but at the same time improved the transport by filling the voids between the carbon support and the Nafion ionomers, and overall resulted in equivalent cell performance.

located both inside and outside the carbon support (or attached to the surface of the Pt particles). It is expected that the dendrimers inside the pores will enhance the contact between the three phases, whereas dendrimers attached to the Pt catalyst surfaces will reduce the utilization of Pt.

We aimed to compare the effects of the dendrimers filling the ionomers in a catalyst ink on the performance of the PEMFC. Since the concentration of Nafion in the catalyst layer was found to be optimal at 6.7 mg/cm^2 for a Pt loading of 0.4 mg/cm^2 in our previous experiments,²¹ the concentration of Nafion used in this study was reduced with the addition of the dendrimers in order to avoid blocking the sites for electrochemical reactions. The total concentration of ionomers was fixed at 6.7 mg/cm^2 .

We ignored the differences between the equivalent weights and pKa of $-\text{SO}_3\text{H}$ (1.2×10^{-2}) and $-\text{COOH}$ (1.8×10^{-3})²² in this study because it is difficult to quantify the effects of these differences.

Figure 1 presents the series of polarization curves obtained for the MEAs in test fuel cells operating at 80°C for various concentrations of G3.5 in the catalyst ink. Similar behavior was found for the MEAs with different concentrations of dendrimers, which was also similar to that of the reference

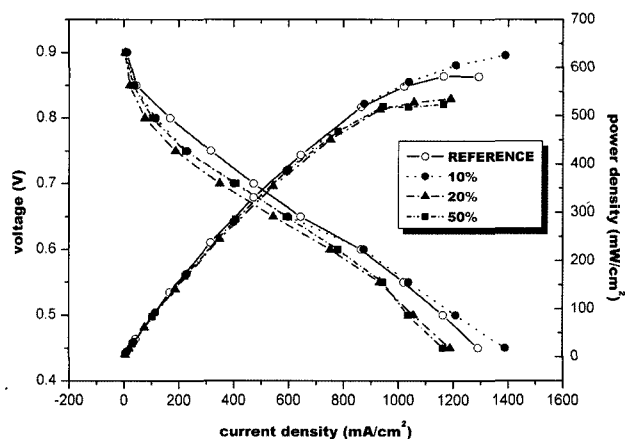


Figure 1. Effect of PAMAM loading in the catalytic layers on cell performance.

MEA without PAMAM in the catalyst layer. Therefore, the PAMAM dendrimers act as ionic conductors inside the catalytic layers of the MEA. At low current density, the values for the MEAs with PAMAM are lower than those for the conventional MEA.

In the high current density region, increases in the PAMAM content have positive effects on the fuel cell performance for concentrations of dendrimer up to 10%; above this concentration the performance starts to decrease rapidly with increasing PAMAM concentration. The current density values at 0.6 V are shown in Table II. The current density did not change significantly with increasing amount of ionomer in the catalytic layer, which is interesting since the amount of Nafion in the catalyst ink with added PAMAM dendrimers was decreased from 6.7 to 3.3 mg/cm^2 . It is also interesting that comparable cell behavior was also observed at a dendrimer loading of 50%, considering that the half amount of optimum Nafion and the lower pKa values of $-\text{COOH}$ compared to $-\text{SO}_3\text{H}$.

The cell potential (E) vs. current density (i) data were analyzed to obtain information about the activation overpotential, the resistance to the flow of ions in the electrolyte, and the electrical resistance of the electrodes. The following equation was used in this analysis:²³

$$E = E_0 - b \log(i/i_0) - R_i i$$

Table II. Characteristics of MEAs with Different Amounts of Ionomers in Their Catalytic Layers

ID	Nafion (mg/cm^2)	Dendrimer G3.5 (mg/cm^2)	Dendrimer % in Catalytic Layer	Current Density at 0.6 V (mA/cm^2)	E_0	B (V/dec)	R_i (Ωcm^2)
ref.	6.7	0	0	864	0.994	0.087	0.267
10 %	6	0.33	5.3	874	0.942	0.071	0.236
20 %	5.2	0.67	11	752	0.959	0.085	0.255
50 %	3.3	1.7	33	780	0.965	0.080	0.278

where E and i are the experimentally measured values of the cell potential and the current density, b is the Tafel slope for this reaction, R_i is the slope of the linear region of the E vs. i plot, E_0 is the reversible open circuit voltage, and i_0 is the exchange current density for the oxygen reduction reaction. This equation assumes that mass transport limitations and the activation overpotential at the hydrogen electrode are negligible.²³

The parameters E_0 , b , and R_i were evaluated using linear least squares fitting. The electrode kinetic parameters were derived from the performance data of several cells using this equation and are summarized in Table II.

The calculated values of the Tafel slopes show some variation (0.071–0.085 V/dec), and are lower than or comparable to that of the conventional MEA (0.087 V/dec). These lower Tafel slope values indicate that the electrode kinetics is fast. This outcome is probably due to the extension of the three dimensional reaction zone in the catalyst layer with PAMAM dendrimers.

The important influences on R_i are the ionic resistances of the electrolyte, the electronic resistances of the electrodes and their contacts with the current collectors, the charge transfer resistance of the hydrogen electrode, and the mass transport resistance, which makes only a small contribution. The reduced differential resistance of the MEA with 10% PAMAM indicates that ion transport in the catalyst pores is improved by the impregnation of the catalytic layer with PAMAM dendrimer.

Typical cyclic voltammograms for the PEMFCs with the various catalytic compositions are shown in Figure 2. The catalytic activity of the electrodes was analyzed using cyclic voltammetric techniques. By integrating the Pt-H desorption peak, the charge of hydrogen desorption was calculate, which is indicative of the electrochemically active surface area. From the columbic charge required for hydrogen adsorption or desorption per unit geometric area (1 cm²) of the electrode, and by assuming a coulombic charge of 0.21 mC/cm² for

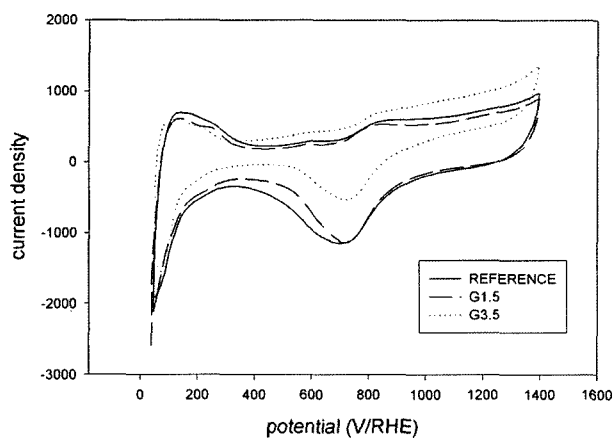
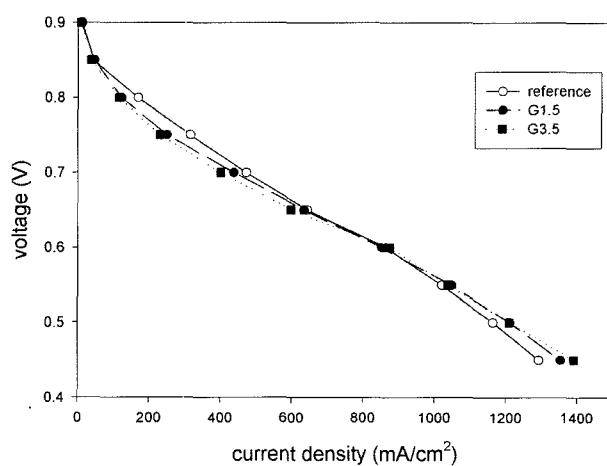


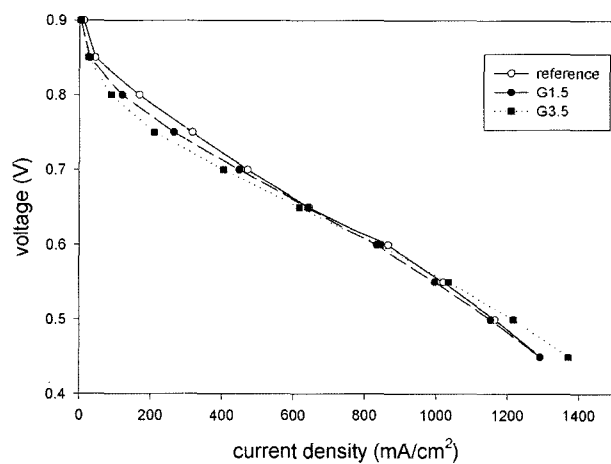
Figure 2. Cyclic voltammograms for fuel cell cathodes in PEMFCs with dendrimers.

these processes on a smooth platinum surface, the roughness factors were calculated.²⁴ The Pt utilization in controlled MEA was 34%. From the roughness factors and the estimated surface areas, the Pt utilization percentage was calculated.^{25–27}

In order to see the effects of the concentrations of the PAMAM dendrimers on cell performance, the concentration of Nafion was fixed for the samples, and the results are shown in Figure 3(a). In here, therefore, the total amount of ionomer in catalyst layer was increased in the 10% samples. The result is compared to the samples in which the total ionomer amount was fixed (Figure 3(b)). The characteristics of the MEAs are summarized in Table III. As shown in Figure 3, the behavior of all the samples is similar; all values are lower than those of the reference MEA at low current density, and there is a positive effect at high current density independent of the size of the PAMAM. With the addition of PAMAM, the utilization of Pt was found to decrease sig-



(a)



(b)

Figure 3. Effect of PAMAM loading in the catalytic layers on cell performance (a) at a fixed Nafion concentration and (b) at a fixed ionomer concentration.

Table III. Characteristics of MEAs with Different Generation and Amount of PAMAM in Their Catalytic Layers

	Current Density at 0.6 V (mA/cm ²)	Pt Utilization (%)	E_o	B (V/dec)	R_i (Ω cm ²)
Fixed amount of Nafion					
G1.5	851	14	0.997	0.092	0.244
G3.5	875	14	0.983	0.088	0.261
Fixed amount of total ionomers					
G1.5	830	29	0.943	0.067	0.272
G3.5	842	18	0.942	0.071	0.236

nificantly from 34 to 14%; however, the cell performance was comparable to that of the reference MEA. This decrease may be due to the loss of electrochemically active area that results from inhibition of the hydrogen adsorption reaction on to the Pt by PAMAM. The addition of the dendrimers thus reduces the active surface area of the Pt particles as expected.

Figure 3(b) shows the cell performances of the MEAs with a fixed amount of ionomer, which are similar to those shown in Figure 3(a). Thus although the addition of small amounts of PAMAM dendrimers reduces the utilization of Pt significantly because of the adsorption of dendrimers onto the Pt surfaces, the electrode kinetics must be faster because of the extension of the three-dimensional reaction zone, as can be seen from the consistency of these cell performances.

Much research has been conducted into improving the utilization of the Pt catalyst, in particular to provide as many catalyst sites as possible by increasing the surface area of Pt by reducing the particle size. However, our result that cell performance can be maintained despite the reduction of utilization of Pt suggests that Pt utilization may not be the only factor affecting the enhancement of cell performance.

The volume fraction and the distribution of the ionomeric electrolyte within the electrode structure are important. The performance of cells based on filling the voids in the catalyst layer is likely to further improve if the dendrimer is fixed onto the carbon support, preventing it from adsorbing onto the Pt catalyst surface. Further experiments aimed at addressing these issues are in progress.

Conclusions

The performance of a test fuel cell constructed by filling the voids in the catalytic layer with nanometer-sized dendrimers was found to be comparable to but not notably superior to that of a cell based on the reference MEA due to the significant adsorption behavior on the surface of Pt.

The results presented here indicate that the addition of the nanometer-sized dendrimers reduced the Pt catalyst surface area and thus resulted in a decrease in the utilization of Pt, but at the same time improved the transport in the three phases by filling the voids between the carbon support and

the Nafion ionomers, and overall resulted in equivalent cell performance. Therefore, it may be more efficient to improve the phase contact within the three phase reaction zone, rather than to improve the utilization of the Pt catalyst.

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