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

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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-
trolled nanometer-sized materials with many peripheral ionic exchange COOH groups. This study reports the effects of introducing nanometer-sized dendrimer electrolytes into the catalyst 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/isopropl 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, pore volume, and pore size distribution of the Pt-C sample were determined by applying the Barret-Joyner-Halenda method 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

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**Table I. Properties of the PAMAM Dendrimers**

<table>
<thead>
<tr>
<th>Generation</th>
<th>Molecular Weight (g/mol)</th>
<th>Estimated Diameter (nm)²</th>
<th>Number of Surface Groups (-COONa)</th>
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</thead>
<tbody>
<tr>
<td>1.5</td>
<td>2,935</td>
<td>2.9</td>
<td>16</td>
</tr>
<tr>
<td>3.5</td>
<td>12,931</td>
<td>4.5</td>
<td>64</td>
</tr>
</tbody>
</table>

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