A NEW GAS DIFFUSION ELECTRODE (GDE) WITH A BETTER O₂ REDUCTION ELECTROCATALYSTS WITH VERY LOW PT CONTENTS VIA NANO-SIZED PT-COATED NAFOION

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ABSTRACT
In the present study, a new gas diffusion electrode (GDE) (based on Pt/Nafion membrane) is fabricated. The electrochemical results show that the new GDE has the highest electrochemical activity toward the oxygen reduction reaction (ORR) among the three electrodes. The SEM and XRD findings show that a platinum layer can be attached to Nafion membrane closely and firmly with a strong peak corresponding to (111) crystalline face. The results illustrate that placing a Pt monolayer on a Nafion membrane is an attractive way of designing better O₂ reduction electrocatalysts with very low Pt contents. Under optimum conditions, Tafel slope, exchange current density ($i_0$), and charge transfer resistance ($R_{ct}$) are obtained to be respectively equal to 85 mV dec⁻¹, 2×10⁻³ A, and 8 Ω. For this electrode, the platinum particle size is 4 nm.

Keywords: Oxygen Reduction Reaction, Nafion Membrane, Platinum Monolayer, Gas Diffusion Electrode, SEM, XRD

INTRODUCTION
Fuel cell systems must overcome economic obstacles to become commercially viable. For proton exchange membrane fuel cells (PEMFC), the cost of platinum catalyst has always hindered their commercialization. The kinetics of oxygen reduction reaction (ORR) in the PEMFC requires a precious platinum catalyst due to its lower activity [1, 2]. Since platinum is a very rare and expensive metal, it is necessary to have low platinum in the electrode [3-5]. In addition to the high cost of platinum, the problem related to the thick catalyst layer is another reason to fabricate new MEA with a low loading of platinum. Catalyst layers with shorter thickness produce better performance due to lower diffusion barriers and better catalyst addition [6-9].

The electrocatalytic reduction of molecular oxygen on a platinum catalyst can be largely affected by catalyst particle size and surface structure [10, 11]. Bett et al. [12] found that Pt atoms at the corners, edges, and kink sites or dislocations showed less ORR activity than those on the crystallite faces. It has also been demonstrated that variables such as membrane modification, heat treatment, the time of platinum deposition, different reducing agents, and the concentration of platinum salt play important roles in the modification of the
morphology of the Pt deposition and improvement in the catalytic activity of the Pt deposition [13-16]. To alleviate these impediments, we have developed a new approach to design the low-Pt electrocatalysts for the electrode. This approach involves pressing Pt-coated Nafion membrane on diffusion layer to prepare a new electrode with low platinum loading. In this work, platinum electrocatalyst is deposited on the Nafion surface instead of using Pt/C (10% or 20%) in the catalyst layer as used in conventional methods.

EXPERIMENTAL

Nafion Treatment

Before the deposition of platinum on a Nafion membrane 117-surface, the Nafion membrane was treated by immersing them at 80˚C for more than 1 hr in 3% H2O2, deionized water, and 0.5M H2SO4 solutions.

Platinum Deposition

Platinum deposition of Nafion membrane was achieved by an impregnation/reduction method. In this method, the treated Nafion membranes were immerged in the different concentrations of an H2PtCl6 solution. After the platinum deposition, the Pt-Nafion membrane was hot pressed on gas diffusion layer (GDL) to make a gas diffusion electrode. The loading of platinum for GDE1, GDE2 and GDE3 were 0.2, 0.28 and 0.12 mg cm⁻² respectively. Table 1 summarizes the conditions of the chemical deposition of the analyzed GDE’s discussed in this work. The platinum precursor was H2PtCl6.6H2O and the reductant was NaBH4/NaOH.

Analysis

The morphology of the new GDE’s was characterized via scanning electron microscopy. The electrochemical behaviors of the GDE’s were investigated by electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and cyclic voltammetry (CV) measurement in 2M H2SO4 (SEM) and X-ray diffraction (XRD).

RESULTS AND DISCUSSION

SEM Results

The characteristics of platinum coated on the Nafion membrane were examined by means of scanning electron microscopy (SEM). Figure 1 shows the scanning electron micrographs of GDE’s.

It was believed that some of the cracks had been probably caused by the residual stress between the Pt layer and Nafion membrane. After removing the Nafion membrane from water and drying it, the membrane shrinks. As a result, some cracks are eventually developed in the Pt-films. Figure 1 b shows scanning electron micrograph of GDE2. The scanning electron microscopy analyses indicate a good adhesion between the metallic electrode and the Nafion polymer. From Figure 1 b it can be observed that the platinum particles are uniformly distributed on the membrane indicating the uniformity of the activation of the membrane surface.

XRD Results

The XRD diffractogram of GDE2 is shown in Figure 2. The XRD patterns manifest the metallic polycrystalline platinum peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[H2PtCl6]/M</th>
<th>Time of deposition (min)</th>
<th>Platinum Deposition Temperature (°C)</th>
<th>Loading of Platinum [mg.cm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDE1</td>
<td>0.05</td>
<td>10</td>
<td>40</td>
<td>0.2</td>
</tr>
<tr>
<td>GDE2</td>
<td>0.01</td>
<td>30</td>
<td>70</td>
<td>0.28</td>
</tr>
<tr>
<td>GDE3</td>
<td>0.005</td>
<td>30</td>
<td>70</td>
<td>0.12</td>
</tr>
</tbody>
</table>
This electrode shows a strong peak at 39.5° (2Ѳ) corresponding to Pt (111). The characteristic diffraction peaks of the FCC Pt highlights the successful reduction of Pt precursor to metallic form. Amorphous band at ca. 18° is related to the crystalline peak of Nafion. Considering the Pt (111) peak, it can be seen that this peak is wide and thereby indicating that the procedure is good enough to form nanoclusters of metallic platinum. The Scherer formula is used to assess the particle size:

$$t = \frac{n\lambda}{b\cos \theta}$$  

(1)

$n$ is a constant coefficient which is equal to 1 herein. $\lambda$ stands for wavelength and for Cu Kα1 it is 1.54056 Å (1.54x10^{-10} m). $b$ represents peak breadth in radian.

From the extent of the line broadening of (111) at 2Ѳ of 39.5°, the average platinum particle size of this sample was estimated to be about 4 nm.

The size of particles can be controlled by manipulating the synthesis temperature. By increasing the temperature a smaller particle size can be achieved [5]. From the XRD diagrams of GDE1 and GDE3, the platinum particle size for GDE1 and GDE3 are calculated to be 6 and 8 nm respectively. Moreover, the XRD results are in good agreement with the SEM results. Both techniques suggest that high temperature and long deposition time have a good effect on the chemical characteristics of the new electrode. The surface of GDE2 shows better structural characteristics alongside the other electrodes.

**Electrochemical Measurements**

In order to investigate the electrochemical characteristics of the electrodes, the AC impedance spectrum of each electrode is obtained at the potential of 0.3 V. AC impedance measurements were carried out in the presence of O₂. The Nyquist plots of electrodes are shown in Figure 3. As can be seen, the spectrum of each electrode takes the form of a single semicircular curve. However, the diameter of the semicircle of GDE2 is smaller than that of the other electrodes.
This means that this electrode has lower charge transfer resistance ($R_{ct}$) and a better performance compared to the other electrodes. The charge transfer resistance ($R_{ct}$) of this optimum electrode is 8 Ω. Figure 4 shows the polarization curves for the GDE’s. It is seen in this graph that GDE2 has a higher current at -220 mV compared to the other electrodes. This result confirms the data obtained by the impedance technique.

The kinetic parameters of the ORR for the electrodes can be obtained from the polarization data. The kinetics data were obtained using the below semi-empirical equations:

\[ E = E_0 - b \log i - R_{ct} \]  
\[ E_0 = E_r + b \log i_0 \]  

where, $E_r$ is the reversible potential of the electrode; $i_0$ stands for the exchange current density of the ORR; $b$ and $i$ are the Tafel slope and the current density respectively; $R$ represents the total contributions of polarization components. The kinetic parameters of the GDEs are listed in Table 2.

According to Table 2, GDE2 with a lower Tafel slope and $R_{ct}$ has the highest electrochemical performance.
activity toward the ORR among the three electrodes. The open circulate voltage (OCV) value of this optimum electrode is 0.819 V.

CONCLUSIONS

In the present study, a new GDE (based on Pt/Nafion membrane) is fabricated. The electrochemical results showed that GDE2 has the highest electrochemical activity toward the oxygen reduction reaction among the three electrodes. The results show that the deposition effects on the electrochemical behavior of the Nafion/Pt/GDL electrode. These data suggests enhancing the electrode performance by increasing platinum deposition temperature and decreasing platinum particle size. The SEM and XRD findings show that the platinum layer is closely and firmly attached to Nafion membrane with a strong peak corresponding to (111) crystalline face. The results illustrate that placing a Pt monolayer on a Nafion membrane is an attractive way of designing O₂ reduction electrocatalysts with very low Pt contents. Under optimum conditions, Tafel slope, exchange current density (i₀), and charge transfer resistance (Rₜₐ) are obtained to be Respectively equal to 85 mV dec⁻¹, 2×10⁻³ A, and 8 Ω. For this electrode, the platinum particle size is 4 nm.

ACKNOWLEDGEMENTS

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NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>b</td>
<td>Tafel slope</td>
</tr>
<tr>
<td>CA</td>
<td>Chronoamperometry</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>Er</td>
<td>Reversible potential of the electrode</td>
</tr>
<tr>
<td>FCC</td>
<td>Face centered cube</td>
</tr>
<tr>
<td>GDE</td>
<td>Gas diffusion electrode</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>i₀</td>
<td>Exchange current density of the ORR</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circulate voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
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<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>R</td>
<td>Total contributions of polarization components</td>
</tr>
<tr>
<td>Rₜₐ</td>
<td>Charge transfer resistance (Ω)</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength (here Cu Kα₁= 1.54056 Å)</td>
</tr>
</tbody>
</table>

REFERENCES


