

## Effect of Water Electrolysis Catalysts on Carbon Corrosion in Polymer Electrolyte Membrane Fuel Cells

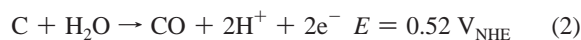
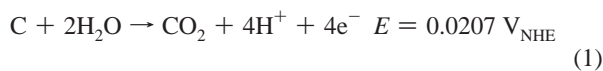
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**Abstract:** A new approach to preventing electrochemical carbon corrosion in the cathode of polymer electrolyte membrane fuel cells (PEMFCs) was developed. The addition of 2 wt % IrO<sub>2</sub> (0.016 mg cm<sup>-2</sup>) to the catalyst layer of the cathode was demonstrated to reduce the electrochemical corrosion of carbon by 76% at 1.6 V<sub>NHE</sub> and 70 °C compared with a commercial Pt/C catalyst of the same Pt loading of 0.4 mg cm<sup>-2</sup> and under the same test conditions. The IrO<sub>2</sub> was shown to behave as a catalyst for water electrolysis, thereby removing water from the catalyst layer, which promoted electrochemical carbon corrosion.

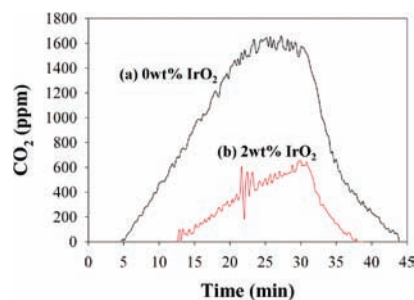
The issue of electrochemical carbon corrosion has received much attention because it is considered to be one of the critical determinants of the lifetime of polymer electrolyte membrane fuel cells (PEMFCs). According to the mechanism of electrochemical carbon corrosion, carbon reacts with water and produces CO<sub>2</sub> which is the main product of carbon corrosion and CO as shown in the following reactions:



Although this equilibrium potential implies that electrochemical carbon corrosion is thermodynamically favored under normal PEMFC operational conditions, severe carbon corrosion is not observed due to slow electrochemical kinetics. However, it has been reported that during abnormal operational conditions, such as fuel starvation or the formation of an air/fuel boundary due to the repeated start up/shut down cycles, the potential of electrodes increases higher than the open-circuit voltage (OCV).<sup>1-3</sup> Such a high potential accelerates the kinetics of electrochemical carbon corrosion and deteriorates both the performance and durability of the fuel cell.

To solve this problem, several recent studies have concentrated on developing materials that exhibit corrosion resistance including corrosion resistant metal oxides<sup>4</sup> and graphitized forms of carbon. Of these materials, carbon nanofibers,<sup>5</sup> carbon nanotubes,<sup>6</sup> and carbon nanocages<sup>7</sup> have been explored extensively. Rolled graphene sheets with a few dangling bonds or defects hinder the attack of oxidative atoms/groups on the closed structure, resulting in significantly improved resistance to carbon corrosion. However, none of the carbon materials reduce the electrochemical corrosion of carbon sufficiently at a highly corrosive potential.

In the present study, we adopted a new strategy for tackling the carbon corrosion problem especially occurring at the cathode. Unlike previous approaches, in which corrosion-resistant materials were developed, this method was designed to remove water from the catalyst



**Figure 1.** Comparison of CO<sub>2</sub> mass spectra for the MEAs (a) without IrO<sub>2</sub> and (b) with 2 wt % IrO<sub>2</sub> in the cathode catalyst layer of the PEMFC. Corrosion tests were performed at 1.6 V<sub>NHE</sub> with a humidifier temperature of 70 °C. The flow rate of H<sub>2</sub> (anode side) and N<sub>2</sub> (cathode side) were 20 and 30 ccm, respectively. The pressure was 1 atm.

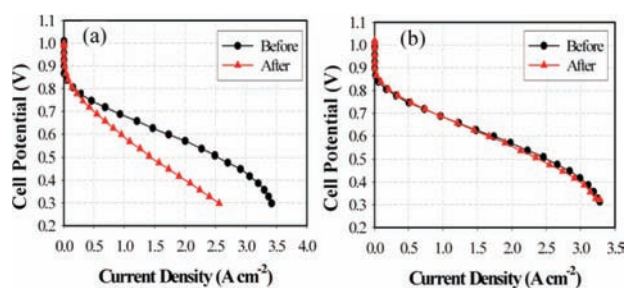
layer of a PEMFC. In our previous study, the presence of water was found to be indispensable for electrochemical carbon corrosion.<sup>8</sup> No electrochemical carbon corrosion occurred under dry conditions, even at a high oxidative overpotential. Based on this result, the addition of iridium oxide (IrO<sub>2</sub>) to the catalyst layer of the cathode was proposed as a method of removing water. IrO<sub>2</sub> promotes oxygen evolution, which is the anodic reaction during water electrolysis.<sup>9</sup> The presence of IrO<sub>2</sub> in the cathode catalyst layer of PEMFC was hypothesized to decompose water molecules around the carbon supports if the potential was increased under carbon corrosion conditions. As a result, electrochemical carbon corrosion was expected to be suppressed. When a water oxidation catalyst is added to the anode of PEMFC, it was known to mitigate cell reversal due to fuel starvation.<sup>10</sup> In this case, carbon is protected by promoting water oxidation to sustain the current flowing through the fuel cell.

IrO<sub>2</sub> was synthesized using a modified Adams-type fusion reaction of the iridium salt under nitrate flux.<sup>11</sup> The physical mixture of prepared IrO<sub>2</sub> and the commercial corrosion-resistant Pt/C catalyst from Tanaka Co. (50 wt % Pt) were used for the cathode. For the anode, a commercial Pt/C from Johnson Matthey Co. was used. The catalysts were mixed with 5 wt % Nafion ionomer in isopropanol under ultrasonication and then spray-deposited onto a 5 cm<sup>2</sup> Nafion 212 membrane in order to prepare membrane electrode assembly (MEA). According to the previous report, the commercial corrosion-resistant Pt/C catalyst used in this study displayed high corrosion resistance in the corrosion test at 1.4 V<sub>NHE</sub>.<sup>12</sup> The total Pt content was fixed at 0.4 mg cm<sup>-2</sup>. The amount of IrO<sub>2</sub> added was 2 wt % of Pt/C, which corresponded to 0.016 mg cm<sup>-2</sup>. A corrosion test was conducted by application of a 1.6 V constant potential to the cathode electrode of PEMFC for 30 min. CO<sub>2</sub> emission during the corrosion test, which is direct evidence of carbon corrosion, was quantified as a function of time using online mass spectrometry.

Figure 1 shows a mass spectrogram indicating CO<sub>2</sub> production during the corrosion test in the presence and absence of IrO<sub>2</sub> in the

catalyst layer. The MEA without IrO<sub>2</sub> displayed CO<sub>2</sub> evolution 5 min after the start of the corrosion test. The concentration of CO<sub>2</sub> increased to 1600 ppm and then decreased after the corrosion test was terminated. In contrast, the MEA containing IrO<sub>2</sub> began to release CO<sub>2</sub> 12 min after the start of the corrosion test and showed considerably less CO<sub>2</sub> generation. The total amount of CO<sub>2</sub> generated (248 μL) was less than that generated by the MEA without IrO<sub>2</sub> (1018 μL) by a factor of 4.1. This observation indicated that electrochemical carbon corrosion was substantially inhibited by the addition of IrO<sub>2</sub>.

The effect of carbon corrosion on the performance of the PEMFC was examined by plotting the polarization curves before and after corrosion tests, and the results are shown in Figure 2. The initial current densities at 0.6 V were 1.73 and 1.74 A cm<sup>-2</sup> for the MEAs with and without IrO<sub>2</sub>, respectively. Because IrO<sub>2</sub> is inert with respect to the oxygen reduction reaction, the addition of IrO<sub>2</sub> did not contribute to the enhanced performance of the fuel cell. After the corrosion test, the MEA without IrO<sub>2</sub> showed a considerable performance degradation of 44.9% (from 1.73 to 0.95 A cm<sup>-2</sup>) at 0.6 V, whereas the performance of the MEA containing 2 wt % IrO<sub>2</sub> did not drop significantly from its initial performance and showed only a 4% performance degradation at 0.6 V (from 1.74 to 1.67 A cm<sup>-2</sup>).

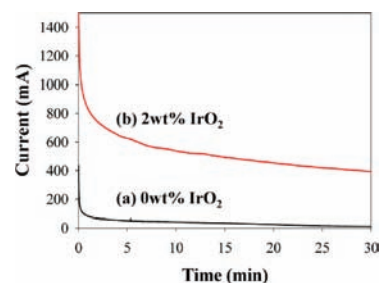


**Figure 2.** Comparison of MEA performances before and after the corrosion tests using (a) MEA without IrO<sub>2</sub> and (b) MEA containing 2 wt % IrO<sub>2</sub>. Measurements were performed at a cell temperature of 75 °C under ambient pressures with O<sub>2</sub> at the cathode (150 ccm) and H<sub>2</sub> at the anode (150 ccm).

To examine the changes in the Pt active surface areas, cyclic voltammetry (CV) tests were performed before and after the corrosion experiments (Figure S1). The CV of the MEA without IrO<sub>2</sub> showed a decrease of the Pt active surface area by 32.9% from 31.6 to 21.2 m<sup>2</sup> g<sup>-1</sup> after the corrosion test. This observation indicated that electrochemical carbon corrosion decreased the amount of carbon available for Pt loading, which forced the Pt nanoparticles to migrate on the carbon surface, resulting in aggregation at relatively stable sites. This explanation was supported by the CV measurements performed on the MEA containing IrO<sub>2</sub>. The CV did not show significant changes in the specific surface area of Pt after the corrosion test. Impedance analysis was performed to examine the effect of carbon corrosion on resistance changes in fuel cells (Figure S2). It was found that the addition of IrO<sub>2</sub> does not affect the ohmic resistance of the electrode. Under conditions where carbon corrosion occurs, the charge transfer resistance increases by 92.5%. On the other hand, the IrO<sub>2</sub>-containing electrode showed no significant changes.

During the corrosion test, the oxidation current was measured as a function of time. The oxidation current included two contributions, the oxidation of carbon and that of water. As shown in Figure 3, the MEA without IrO<sub>2</sub> generated a low oxidation current, whereas the MEA with IrO<sub>2</sub> generated a much higher oxidation current. The higher oxidation current from the MEA containing IrO<sub>2</sub> is attributed to the oxidation of water. The amount of water decomposed by electrolysis was quantified by measuring the amount of O<sub>2</sub> using

mass spectrometry during the corrosion test (Figure S3). The total amount of O<sub>2</sub> generation was 40 990 μL with IrO<sub>2</sub>, while it was 1446 μL without IrO<sub>2</sub>. It implies that the rate of water electrolysis is enhanced by 28 times in the presence of IrO<sub>2</sub>. According to the linear sweep voltammetry as shown in Figure S4, IrO<sub>2</sub> shows a high activity with respect to oxygen evolution so that water electrolysis is initiated around 1.45 V<sub>NHE</sub>, which is lower than the potential applied during the corrosion test.<sup>13</sup> In contrast, Pt has a relatively lower activity toward water electrolysis, resulting in a high onset potential for water electrolysis to occur at about 1.6 V<sub>NHE</sub>.<sup>14</sup> Therefore, the addition of IrO<sub>2</sub> is observed to be a very effective way of removing water from the catalyst layer.



**Figure 3.** Comparison of the oxidation current during the corrosion test for MEAs (a) without IrO<sub>2</sub> and (b) with 2 wt % IrO<sub>2</sub> in the catalyst layer in the PEMFCs.

In conclusion, a new approach based on the addition of IrO<sub>2</sub> to the electrocatalyst was suggested to prevent electrochemical carbon corrosion in PEMFCs under severely corrosive conditions. The IrO<sub>2</sub> in the catalyst layer behaved as a catalyst for water electrolysis. Water electrolysis eliminated water, which was essential for electrochemical carbon corrosion, from the catalyst layer. As a result, the electrochemical carbon corrosion was considerably decreased by 76%, even using just 2 wt % IrO<sub>2</sub> (0.016 mg cm<sup>-2</sup>).

**Acknowledgment.** This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (2009-0093823) and the National Research Foundation of Korea (NRF-2009-0092926) funded by the Ministry of Education, Science, and Technology.

**Supporting Information Available:** Experimental details and supporting figures are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA104672N