

Development of a Titanium Dioxide-Supported Platinum Catalyst with Ultrahigh Stability for Polymer Electrolyte Membrane Fuel Cell Applications

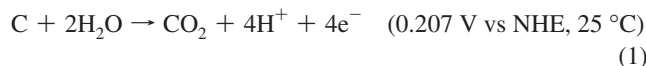
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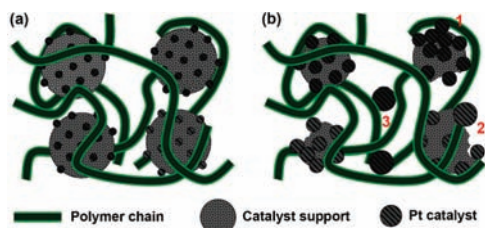
Polymer electrolyte membrane fuel cells (PEMFCs) are emerging as promising candidates in the portable electronics and automobile industries.¹ In contrast to the early development of PEMFCs, current research focuses extensively on the improvement of fuel cell reliability and durability. It has been shown that several factors can reduce the lifetime of PEMFCs, including (1) platinum-particle dissolution and sintering, (2) carbon support corrosion, and (3) membrane thinning.²

Carbon is the typical catalyst support material for PEM-based fuel cells because of its large surface area, high electrical conductivity, and well-developed pore structure. However, during fuel cell start-up and shut-down, the carbon support in the cathode encounters severe corrosion, as indicated by the following reaction:³



Scheme 1 represents the carbon corrosion in the cathode during PEMFC operation. Electrochemical corrosion of the carbon supports causes the agglomeration and sintering of the Pt catalyst particles, which results in decreased electrochemical surface area (ECSA) of the catalyst. Carbon corrosion also leads to electrically isolated Pt particles that are detached from the support. These effects result in a rapid degradation of the Pt catalyst and thus affect its performance. The resulting reduced lifetime of PEMFCs is not appropriate for most of the projected applications. Therefore, it would be desirable to use more robust noncarbon support materials such as metal oxides. However, only a few studies have focused on the development of alternate catalyst supports for fuel cell applications.^{4–6}

Scheme 1. Schematic Representation of the Effect of Carbon Corrosion on (1) Agglomeration, (2) Coalescence, and (3) Loss of Pt Particles in the Membrane Electrode Assembly (MEA) during Operation of PEMFCs: (a) Normal (Corrosion-Resistant) Electrode and (b) Corroded Electrode



Titanium dioxide (TiO₂) is a widely used material with a variety of potential applications in photocatalysis, photovoltaics, water splitting, and gas sensors.⁷ TiO₂ possesses good mechanical resistance and stability in acidic and oxidative environments.⁸ Therefore, it may be considered as an alternative catalyst support. However, its low electrical conductivity prevents its use in fuel

cells. Recently, Debe et al.⁵ and Sung et al.⁶ have investigated the possible use of a nonconductive polymer as a catalyst support material for hydrogen and methanol fuel cells, respectively. The present work reports on the synthesis of TiO₂ and platinum catalyst supported on TiO₂ (Pt/TiO₂). The aim of our study is to demonstrate that the synthesized Pt/TiO₂ electrocatalyst exhibits excellent fuel cell performance as well as ultrahigh stability at high positive potentials.

Mesoporous TiO₂ was synthesized via a template-assisted route. In the synthesis, the porous structure of TiO₂ was tailored by the controlled hydrolysis of titanium isopropoxide in the presence of a surfactant (Pluronic P123). For the preparation of the Pt/TiO₂ catalyst, a solution of NaBH₄, a deaerated suspension of the TiO₂ support and sodium dodecyl sulfate, and a platinum precursor (H₂PtCl₆) were prepared separately. The resulting three solutions were mixed together and then stirred for 2–6 h to allow the adsorption of the colloidal Pt particles onto the TiO₂ support. The resulting Pt/TiO₂ electrocatalyst was filtered, dried at 80 °C for 24 h, and stored for future studies.

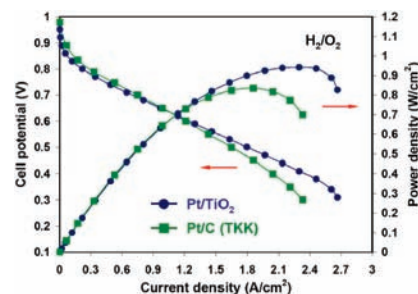


Figure 1. Polarization curves for PEMFCs using the Pt/TiO₂ and Pt/C cathode electrocatalysts. Measurements were taken at 75 °C with fully humidified reactants (the flow rates of H₂ and O₂ were 150 mL/min). Pt loading was controlled at 0.5 mg/cm² at the anodic side (LT140EW, BASF) and 0.4 mg/cm² at the cathodic side. No back pressure was applied during fuel cell operation.

Figure 1 shows the polarization curves of PEMFCs employing Pt/TiO₂ and Pt/C (TKK) as cathode electrocatalysts. The current densities at 0.6 V were 1.24 and 1.22 A/cm² with maximum power densities of 0.94 and 0.84 W/cm² for the Pt/TiO₂ and Pt/C electrocatalysts, respectively. Although the Pt particle size in the Pt/TiO₂ electrocatalyst was large ($d_{\text{Pt}} = 6.2 \text{ nm}$; Table 1), it showed a fuel cell performance comparable to that of the commercial Pt/C (TKK) electrocatalyst. In the case of Pt/C, the catalyst layer thickness was $\sim 11 \mu\text{m}$ at a desired Pt loading of 0.4 mg/cm². In contrast to Pt/C, an ultrathin catalyst layer ($< 3 \mu\text{m}$) could be obtained for the Pt/TiO₂ catalyst at the same Pt loading because TiO₂ has a 2-fold higher density than carbon. This difference was directly reflected in an increase in the current density at potentials lower than 0.7 V due to improved mass transfer kinetics. Therefore,

the high fuel cell performance of the Pt/TiO₂ electrocatalyst can be attributed to the low mass transport limitation in the cathode at high current density (>1.2 A/cm²).

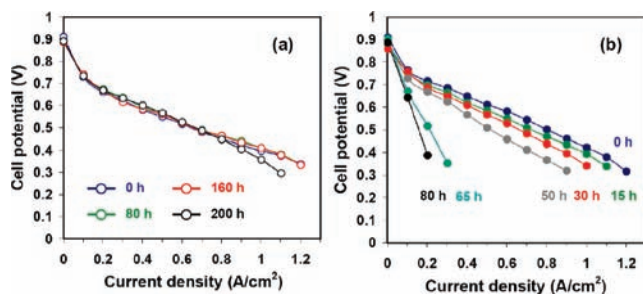


Figure 2. Polarization curves for PEMFCs with (a) Pt/TiO₂ and (b) Pt/C electrocatalysts after the potential was held according to the AST protocol for 0–200 and 0–80 h, respectively. The Pt loading was 0.5 mg/cm² on the anodic side (LT140EW, BASF) and 0.4 mg/cm² on the cathodic side.

The electrochemical stability and performance of the Pt/TiO₂ and Pt/C electrocatalysts were examined using an accelerated stress test (AST) protocol. The protocol was slightly modified from the original protocol suggested for PEMFCs by the U.S. Department of Energy.⁹ The durability and stability of the electrocatalysts were compared by holding the cell potential at 1.2 V according to the modified AST protocol. Figure 2 shows the polarization curves for the Pt/TiO₂ and Pt/C electrocatalysts after the potential was held at 1.2 V for 0–200 and 0–80 h, respectively. In the case of the Pt/TiO₂ electrocatalyst, the polarization curves were similar even after a corrosion time (T_c) of 200 h, while the Pt/C electrocatalyst showed a significant decrease in performance after $T_c = 50$ h due to carbon corrosion and subsequent detachment and agglomeration of catalyst particles.

Table 1. Particle Size (d_{Pt}) and ECSA Measured for Two Pt Electrocatalysts after the Potential Was Held at 1.2 V for 0 and 80 h

catalyst	d_{Pt} (nm)		ECSA (m ² /g)	
	0 h	80 h	0 h	80 h
Pt/TiO ₂	6.2	7.8	13.8	11.0
Pt/C	2.5	11.5	53.1	3.8

Table 1 summarizes the size of the Pt particles and the ECSA measured for the two Pt electrocatalysts at $T_c = 0$ and 80 h. There was a slight increase of the Pt particle size for the Pt/TiO₂ catalyst ($d_{Pt} = 7.8$ nm) at $T_c = 80$ h relative to the initial particle size of 6.2 nm. However, in the case of the Pt/C electrocatalyst, a 4-fold increase in the particle size ($d_{Pt} = 11.5$ nm) relative to the initial value ($d_{Pt} = 2.5$ nm) was observed. This result is due to carbon corrosion and migration and agglomeration of Pt particles.

Figure 3a compares the normalized ECSA of the two electrocatalysts as a function of T_c . Both catalysts exhibited a decrease in ECSA with increasing corrosion time. However, the Pt/C electrocatalyst showed a more rapid decay (93% after $T_c = 80$ h). The significant decrease in ECSA is due to the corrosion of the high-surface-area carbon support at high positive potentials. As described in Scheme 1, electrochemical corrosion is one of the most important issues that affects the long-term stability of PEMFCs. For the Pt/TiO₂ electrocatalyst, the total loss of ECSA is ~20% after $T_c = 80$ h, indicating that it is electrochemically more stable than the Pt/C electrocatalyst. The smaller decrease in ECSA for the Pt/TiO₂ electrocatalyst during holding of the potential can be attributed to

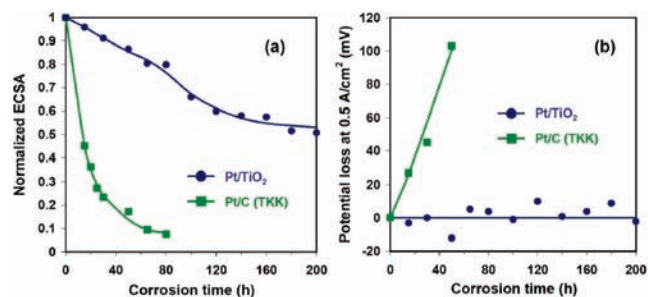


Figure 3. (a) Normalized ECSA and (b) potential loss at 0.5 A/cm² as a function of corrosion time (T_c) for Pt/TiO₂ and Pt/C electrocatalysts.

the stability of the TiO₂ support at high positive potentials. Figure 3b compares the potential loss at 0.5 A cm⁻² for Pt/TiO₂ and Pt/C as a function of T_c . Significant potential loss (~100 mV) was observed for the Pt/C electrocatalyst at $T_c = 50$ h, whereas no loss was observed in the case of the Pt/TiO₂ electrocatalyst even at $T_c = 200$ h. The ultrahigh stability of the Pt/TiO₂ electrocatalyst can be attributed to a strong metal support interaction (SMSI) between the Pt particles and the TiO₂ support. It has been reported that TiO₂ can anchor the Pt particles by interacting with Pt and thereby inhibit Pt migration and agglomeration.¹⁰ This explanation was confirmed by XRD analysis (Table 1) of the Pt/TiO₂ and Pt/C catalysts after the potential holding experiment.

In conclusion, a novel TiO₂-supported Pt electrocatalyst was synthesized and investigated as a possible cathode catalyst for PEMFCs. The excellent fuel cell performance of the Pt/TiO₂ electrocatalyst was attributed to the low mass transport limitation in the cathode catalyst layer. The AST results indicated an ultrahigh stability of the Pt/TiO₂ electrocatalysts. The SMSI and corrosion resistance of the TiO₂ support enhanced the stability of the Pt catalysts. On the basis of the experimental results reported above, this Pt/TiO₂ electrocatalyst can be considered as an alternative cathode electrocatalyst to improve the reliability and durability of PEMFCs.

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

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