

Iron-Phosphate/Pt Nanostructured Electrodes for High-Efficiency Fuel Cells

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The Pt/FePO₄ thin-film electrodes consisting of nanocrystalline Pt and amorphous FePO₄ were fabricated. Nanostructured Pt/FePO₄ thin-film electrodes showed higher catalytic activity and better stability than pure Pt electrodes for methanol oxidation. The electrocatalytic properties of FePO₄/Pt/C nanocomposites were also examined. The FePO₄/Pt/C nanocomposites showed no initial degradation of electrocatalytic properties and exhibited enhanced long-term stability.

Keywords: fuel cell, nanocomposites, phosphate, methanol oxidation, stability

1. INTRODUCTION

Fuel cells are intensively investigated due to their potential for use as power sources of portable devices. However, the low cathode efficiency of the oxygen-reduction reaction (ORR), the loss of Pt activity with long-term operation, and the poisoning by CO should be resolved for fuel-cell commercialization.^[1]

Metal phosphates are of great interest for fuel-cell cocatalysts due to their compatible properties, such as the high proton conductivity, the acid stability, the catalytic activity, etc.^[2-5] In this study, nanostructured Pt/FePO₄ thin films and FePO₄/Pt/carbon nanocomposites are investigated. Various Pt/FePO₄ nanostructures showed the enhanced methanol-oxidation activities. It was also confirmed that well-dispersed FePO₄ nanoparticles prevent both the dissolution and agglomeration of Pt nanoparticles and lead to the long-term stability of the FePO₄/Pt/C nanocomposite.

2. EXPERIMENTAL PROCEDURE

Nanostructured Pt/FePO₄ thin films for the anode of direct methanol fuel cells (DMFCs) were deposited using a radio frequency (rf) magnetron sputtering method. To modify the nanostructures of Pt/FePO₄ electrodes, the sputtering power of the FePO₄ target was varied from 20 W to 60 W while the sputtering power of the Pt target was fixed at 16 W. A three-electrode electrochemical system in a solution of 0.5 M H₂SO₄ and 2 M CH₃OH was used to evaluate the methanol oxidation of the Pt/FePO₄ thin-film electrodes. High-resolution transmission electron microscopy (HRTEM) was used

for a nanostructural analysis of the thin-film electrodes, and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used for the measurement of the actual Fe/Pt atomic ratio in the thin-film electrodes. The chemical-bond states of the thin-film electrodes were analyzed by x-ray photoelectron spectroscopy (XPS).^[6]

For the synthesis of FePO₄/Pt/C nanocomposite electrodes, commercial 20 wt.% Pt-supported carbon catalysts were added to a solution containing FePO₄ nanoparticles. This was mechanically stirred for 1 h and dried at 90°C for 2 days. The FePO₄ molar concentrations of the nanocomposites were varied (0.1, 1, or 10 mM). To evaluate the electrocatalytic properties of the nanocomposite electrodes, a three-electrode electrochemical system in a solution of 0.5 M H₂SO₄ was used. The electrochemical surface area (ESA) changes of the nanocomposite electrodes were measured by the hydrogen desorption method (Pt-H). The Pt, Fe, and P dissolutions into the electrolyte were measured by ICP-AES after 1000 cycles.^[7]

3. RESULTS AND DISCUSSION

3.1. Nanostructured Pt/FePO₄ thin film for a DMFC anode material

Transmission electron microscopy (TEM) images of the nanostructured Pt/FePO₄ thin films were obtained (Fig. 1). It was observed that the nanocrystalline Pt and amorphous FePO₄ were well distributed in the Pt/FePO₄ thin films. Figure 1(a) shows the Pt/FePO₄ thin film consisting of ~5 nm Pt nanocrystals (dark region) and amorphous FePO₄ (relatively bright region). The ICP-AES analysis confirmed that the atomic ratio (Fe/Pt) was 0.12, and the actual amount of Pt incorporated in the Pt/FePO₄ nanocomposites was

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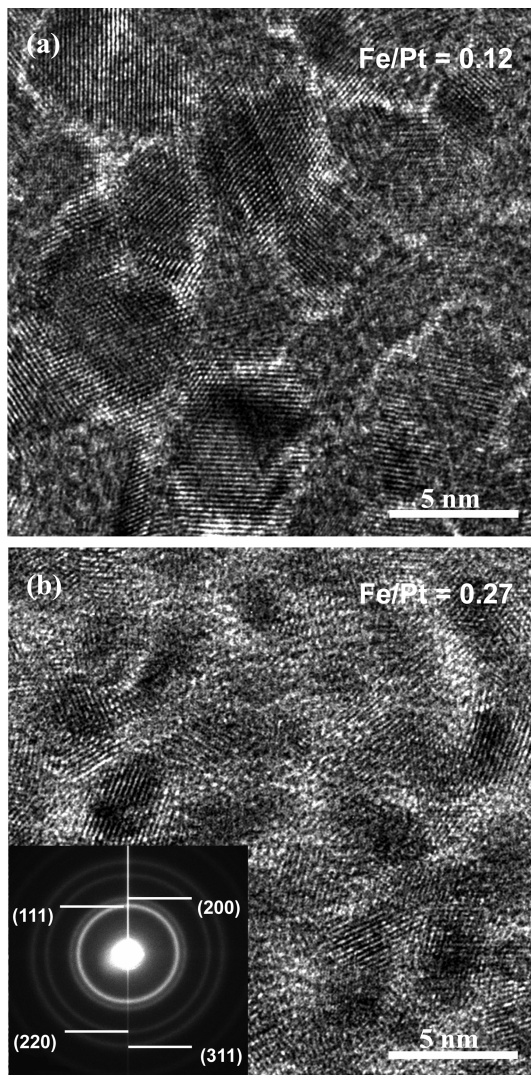


Fig. 1. HRTEM images of the nanostructured Pt/FePO₄ thin films. The inset in (b) shows diffraction patterns of Pt/FePO₄ (Fe/Pt = 0.27). (Reprinted with permission from B. Park.^[6] Copyright 2006, The Electrochemical Society.)

approximately 80 wt.% compared with the pure Pt electrode.

For the Pt/FePO₄ thin-film electrode with an atomic ratio (Fe/Pt) of 0.27, ~3 nm Pt nanocrystals and the FePO₄ matrix were observed by HRTEM (Fig. 1(b)). The Pt nanocrystals representing the (111) planes were observed in the nanostructured Pt/FePO₄ thin-film electrodes. Minimization of the Pt/FePO₄ interfacial energy may cause the Pt nanoparticles to become embedded in the FePO₄ matrix.^[8] The formation of Pt nanophase in the Pt/FePO₄ thin films was confirmed by the diffraction pattern, as shown in the inset of Fig. 1(b). The actual amount of Pt embedded in these Pt/FePO₄ nanostructured thin films was approximately 70 wt.% compared with the pure Pt electrode.

To measure the active surface area of the Pt/FePO₄ nanocomposite thin-film electrodes, cyclic voltammograms

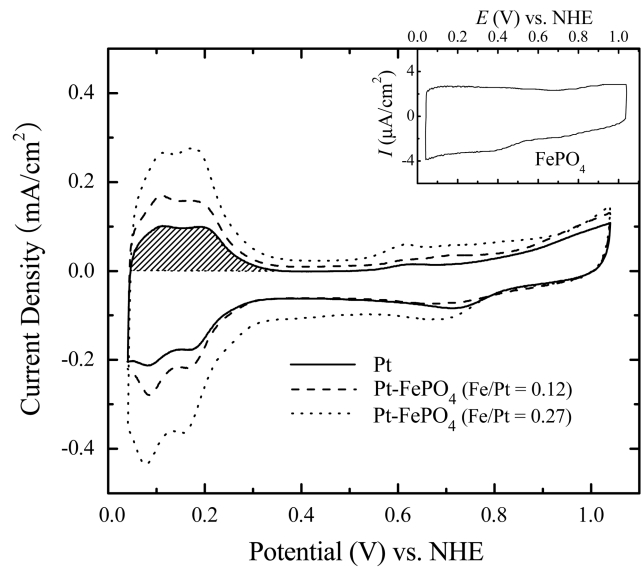


Fig. 2. CVs of the Pt and Pt/FePO₄ thin-film electrodes in the H₂SO₄ solution. The CV data for the pure FePO₄ in H₂SO₄ is shown in the inset. (Reprinted with permission from B. Park.^[6] Copyright 2006, The Electrochemical Society.)

(CVs) were obtained between 0.04 and 1.04 V vs. NHE (normal hydrogen electrode), as shown in Fig. 2. The CV data was measured in the 0.5 M H₂SO₄ solution at a scan rate 50 mV/s, and the electrochemical active surface area of the electrodes was measured by the hydrogen desorption method.^[9] The active surface area (per 1 cm²) was 5.7 cm² and 3.6 cm² for the electrodes with an atomic ratio (Fe/Pt) of 0.27 and 0.12, respectively. The nanostructured Pt/FePO₄ thin-film electrodes showed an increase in the active surface area compared with the pure Pt electrode (2.5 cm²). The very low current density of the FePO₄ thin-film electrodes (in the inset of Fig. 2) indicates that FePO₄ itself is not electrochemically active. The well-dispersed Pt nanoparticles in the Pt/FePO₄ electrodes lead to a larger active surface area, even with a smaller amount of Pt than the pure Pt electrode.

3.2. FePO₄/Pt/C nanocomposite for electrode material

The existence and distribution of FePO₄ nanoparticles in the FePO₄/Pt/C electrodes were examined by z-contrast scanning transmission electron microscopy (STEM) images and energy-dispersive spectroscopy (EDS) mapping, as shown in Fig. 3. The EDS mapping of Pt (closed) and Fe (open) exhibits the uniform distribution of FePO₄ and Pt nanoparticle nanocomposites (Fig. 3(b)).

To examine the catalytic stabilities, the ORR currents of Pt/C and FePO₄(0.1 mM)/Pt/C nanocomposites were obtained in a 0.5 M H₂SO₄ solution. The catalytic behaviors of the Pt/C electrodes and the FePO₄/Pt/C electrodes before 1000 cycles were quite similar, as shown in Fig. 4(a). After 1000 cycles however, the limiting current of the Pt/C was ~70%

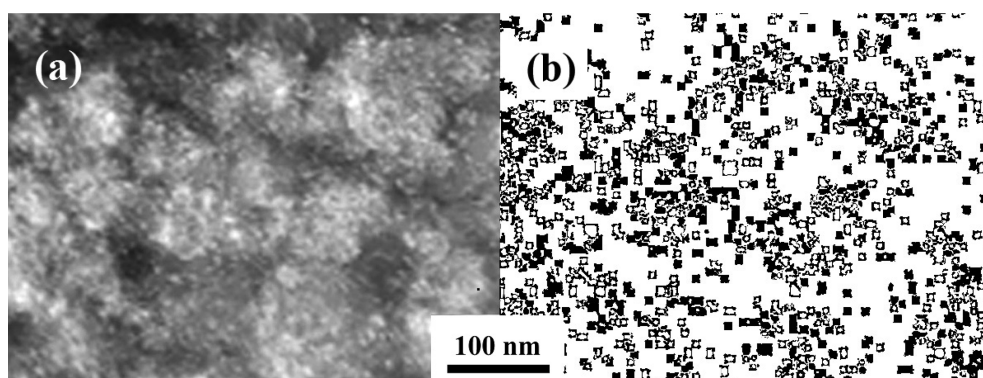


Fig. 3. (a) Z-contrast STEM image of $\text{FePO}_4/\text{Pt}/\text{C}$ nanocomposites. (b) The positions of Pt (closed) and Fe (open) from the EDS mapping. (Reprinted with permission from B. Park.^[7] Copyright 2007, American Institute of Physics.)

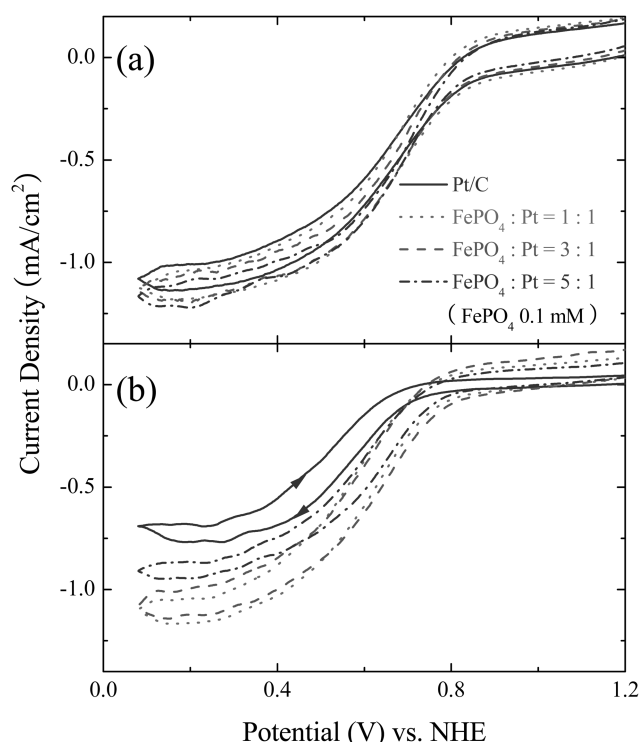


Fig. 4. ORR currents of Pt/C and $\text{FePO}_4/\text{Pt}/\text{C}$ nanocomposites (a) before and (b) after 1000 cycles. (Reprinted with permission from B. Park.^[7] Copyright 2007, American Institute of Physics.)

compared with the $\text{FePO}_4/\text{Pt}/\text{C}$, as shown in Fig. 4(b). Moreover, the ORR onset voltage of Pt/C decreased significantly. The loss of ORR activity in the Pt/C electrodes after 1000 cycles can be attributed to the irreversible oxidation of the Pt surface, while the $\text{FePO}_4/\text{Pt}/\text{C}$ electrodes showed negligible loss of the ORR activity. The enhanced electrocatalytic stability of the nanocomposites may result from the charge transfer at the nanoscale interface of FePO_4 and Pt nanoparticles, which was confirmed by XPS.^[7]

4. CONCLUSIONS

Pt/FePO_4 thin-film electrodes deposited by sputtering exhibited superior activity and stability compared with a pure Pt electrode for methanol oxidation. The $\text{FePO}_4/\text{Pt}/\text{C}$ nanocomposites exhibited enhanced long-term stability for ORR compared with the Pt/C electrode. These experimental results show that fuel cell electrode properties can be improved via appropriate nanostructural control of the iron-phosphate and platinum.

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