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Methanol Tolerant FeTPP-Pt/C Co-catalysts for the Electroreduction of Oxygen

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Abstract: It was found for the first time that iron tetraphenylporphyrin (FeTPP)-Pt/C showed the good activity for the electroreduction of oxygen and methanol tolerant ability. Their performances were related to the heat-treatment temperature.

Keywords: FeTPP, Pt, oxygen reduction, methanol tolerant.

Though direct methanol fuel cells have received much attention during the last thirty years[1], their performances are limited by several basic problems. One of them is that methanol in the anode will diffuse through the polymer electrolyte membrane to the cathode, causing the decrease in the electrocatalytic activity of Pt catalyst[2], which is usually used for electroreduction of oxygen. Thus, it is an important project to find an electrocatalyst, which shows the good activity for oxygen reduction and methanol tolerant ability. In this paper, it was reported for the first time that FeTPP-Pt/C co-catalyst had the above ability.

The electrochemical measurements were carried out with CHI602A potentiostat (CH Instrument Co.), Model 616 rotating disk electrode (EG&G PAR Co.). A Pt wire and a saturated calomel electrode were served as the counter electrode and the reference electrode, respectively. The working electrode was a glassy carbon electrode (0.196 cm^2). The FeTPP-Pt/C co-catalyst was obtained when FeTPP was adsorbed on platinum supported on carbon black. The resulting FeTPP-Pt/C was heat-treated at various temperatures in Ar atmosphere for 2 hours. Then, 0.4 mL 5 wt% Nafion® solution (Aldrich Co.) and 5 mg FeTPP-Pt/C catalyst were mixed. 5 μL suspension was placed on the surface of the working electrode and left to dry at room temperature.

Figure 1A compares the polarization curves of Pt/C, FeTPP/C and FeTPP-Pt/C in O_2-saturated 80 mL 0.5 mol/L H_2SO_4 without CH_3OH and O_2-saturated 0.5 mol/L H_2SO_4 with 1 mol/L CH_3OH. **Figure 1A** shows that the electrocatalytic activity of un-heat-treated FeTPP-Pt/C for oxygen reduction is worse than that of Pt/C in the absence of methanol, but better than that of FeTPP/C. In the presence of 1 mol/L CH_3OH, electrocatalytic performance of FeTPP-Pt/C is better than that of Pt/C. For example,

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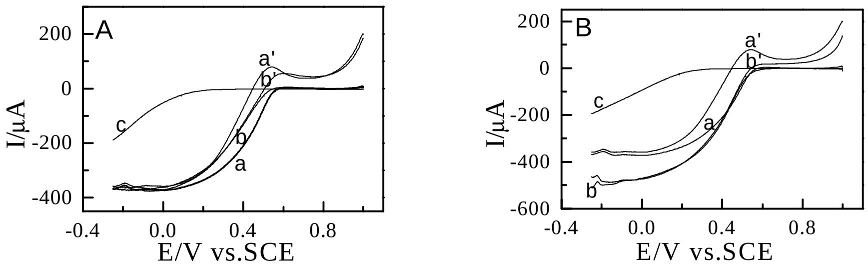
methanol oxidation causes the onset of cathodic current shifts cathodically by 0.07 V for FeTPP-Pt/C, while 0.13 V for Pt/C. The activity of heat–treated FeTPP-Pt/C at 450°C is better than that of Pt/C in the absence of methanol. In addition, the methanol oxidation has little effect on the performance of heat-treated FeTPP-Pt/C at 450°C (**Figure 1B**). The further experiments demonstrated that the methanol tolerant ability of FeTPP-Pt/C increases with increasing the heat-treatment temperature. However, the activity of FeTPP-Pt/C for oxygen reduction decreases gradually above 700°C. The experiment results indicated that heat-treated FeTPP-Pt/C at 450°C had the better catalytic activity and methanol tolerant ability simultaneously.

The sublimation of FeTPP above 400°C will lead to re-dispersion of FeTPP over the surface of co-catalysts, thus makes methanol difficult to access to the Pt atom due to the steric hindrance. It may be the reason for methanol tolerant ability of FeTPP-Pt/C. In addition, because both FeTPP and Pt are active for oxygen reduction, their interaction in FeTPP-Pt/C may increase the electrocatalytic activity for oxygen reduction.

Figure 1 Polarization curves



(A) un-heat-treated FeTPP-Pt/C

(B) heat-treated FeTPP-Pt/C at 450°C

(a) Pt/C, (b) FeTPP-Pt/C, (c) FeTPP/C in O_2-saturated 0.5 mol/L H_2SO_4 ;
(a′) Pt/C, (b′) FeTPP-Pt/C in O_2-saturated 0.5 mol/L H_2SO_4 with 1 mol/L CH_3OH.
Sweep rate: 10 mV/s, rotation rate: 1000 rpm, temperature: 25°C.

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References

1. B. S. Baker, *Hydrocarbon Fuel Cell Technology*, Academic Press Inc., New York, **1965**.
2. A. Kuver, W. Vielstich, *J. Power Sources*, **1998,** *74* (2), 211.

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