

**Methanol-tolerant Oxygen Reduction
Electrocatalysts based on Carbon-supported
Platinum-Macrocycles**

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Abstract

Methanol crossover from the anode to the cathode through the proton exchange membrane hinders the development of the DMFCs. It leads to the wastage of fuel, suppression of the cathode potential and poisoning of the cathode electrocatalysts. One solution is to find new catalysts for oxygen reduction, which are highly inactive towards methanol oxidation.

As yet, transition metal macrocycles and transition metal chalcogenides have been studied as methanol-tolerant oxygen reduction catalysts. However, their performance is inferior to that of Pt except in the presence of high concentrations of methanol. Especially, their long term stability is in question for practical fuel cell applications.

In this study, we report carbon-supported platinum and iron tetraphenylporphyrin (FeTPP-Pt/C) co-catalysts by the slow adsorption of FeTPP onto commercial Pt/C (20wt% Pt, E-TEK). The resulting materials were heat-treated under argon atmosphere at temperatures from 300 to 900°C. The electrochemical measurements by RDE (Fig. 1) show that non-heat-treated FeTPP-Pt/C co-catalyst has higher methanol tolerance and oxygen reduction activity than the corresponding Pt/C. Using thermal analysis, XRD, TEM (EDX), ICP-AES and XPS characterizations, a possible reaction mechanism of the co-catalysts is illustrated in Fig. 2. The uniform adsorption (figure not shown) of FeTPP over Pt/C allows the access of O₂ to Pt sites, but blocks the larger methanol molecules to stay.

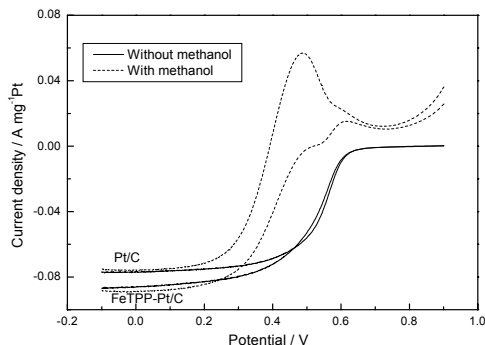


Fig. 1. Polarization curves for oxygen reduction on non-heat-treated FeTPP-Pt/C and Pt/C in O₂-saturated 0.5M H₂SO₄ with and without 1M CH₃OH.

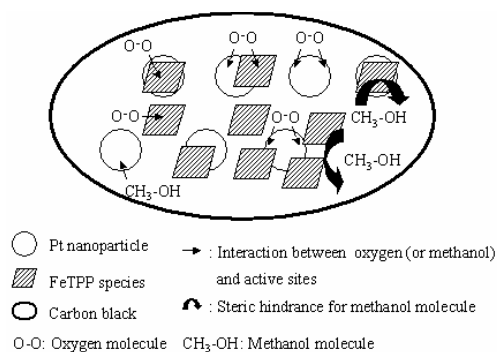


Fig. 2. Schematic illustration of oxygen reduction and methanol tolerance mechanism of FeTPP-Pt/C catalysts.