Nanostructured Pt-M and Pt-Ru-M (M = Fe, Co and Cu) Catalysts for PEM Fuel Cells

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Introduction

Fuel cells are attractive alternative energy conversion devices due to their higher efficiency and low pollution. It is well-known that the cell voltages of both the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC) are limited by slow reaction kinetics at the oxygen electrode leading to lower overall efficieny. Additionally, the platinum catalysts are expensive. With an objective to lower the cost, other catalysts such as metal oxides, metal porphyrins, and metal alloys have been pursued in the literature over the years, but their electrocatalytic activities are generally less than that of pure platinum.¹⁻³ We present here the synthesis of some carbon supported Pt-M and Pt-Ru-M catalysts with M = Fe, Co, or Cu and their electrochemical performance towards both oxygen reduction and hydrogen oxidation.

Experimental

Pt-M and Pt-Ru-M (M = Fe, Co, or Cu) catalysts (20 wt.%) were prepared in-situ on high surface area Vulcan XC-72R carbon support by reducing a mixture of H₂PtCl₆ and the respective metal salt solutions with sodium formate at about 70 °C. In some cases, a few drops of sodium borohydride solution were added in the beginning to initiate the reduction of the transition metal ions Mⁿ⁺. The samples were characterized by X-ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electrochemical performances were evaluated with circular electrodes consisting of diffusion and catalyst layers towards both oxygen reduction and hydrogen oxidation in 0.5 M H_2SO_4 electrolyte using a pre-calibrated Hg/Hg_2SO_4 , SO_4^{-2-} reference electrode in a three-electrode system. The catalysts were also tested in PEMFC single cells using a commercial fuel cell test station (Electrochem Inc.).

Results and Discussion

X-ray diffraction data indicated the formation of Pt-M and Pt-Ru-M catalysts. In the case of Pt-Fe, the presence of some oxide impurity was noticed possibly due to surface oxidation, which could, however, be eliminated by heating at around 200 °C in a mixture of 95% Ar - 5 % hydrogen. TEM data indicate the dispersion of nanostructured Pt-M catalysts with a size distribution of 1-5 nm in the carbon matrix. Elemental analysis carried out by energy dispersive spectroscopic (EDS) analysis in TEM suggests the presence of both platinum-rich and the transition metal (M)-rich particles apart from alloy particles.

Figure 1 compares the cathodic polarization curves in sulfuric acid medium (for oxygen reduction) of the platinum-based catalysts (20 wt.% on carbon) such as Pt-Fe (1:5), Pt-Co (1:5 and 1:7), and Pt-Cu (1:3) with that of the Pt catalyst (20 wt% on carbon) prepared by a similar procedure. Although, the Pt-Cu catalyst exhibits very low polarization at low current densities compared to all other catalysts, it performs poorly above 200 mA/cm². On the other hand, it is interesting to note that the Pt-Co (1:7) and Pt-Fe (1:5) catalysts containing significantly lower noble metal content exhibit performances similar to that of pure Pt.

Figure 2 compares the galvanostatic anodic polarization curves in sulfuric acid medium (for hydrogen oxidation) of the platinum-based catalysts (20 wt% on carbon) such as Pt-Ru-Co (1:1:1), Pt-Ru-Co (1:1:2), and Pt-Ru-Co (1:1:5) with that of a commercial Pt-Ru catalyst (Etek). As can be seen in Fig. 2, the Pt-Ru-Co (1:1:1) catalysts exhibit very low polarization (only about 60 mV) without iR compensation at room temperature similar to that shown by the commercial Pt-Ru catalyst up to a current density of 0.65 A/cm². The data show that it is possible to reduce further the noble metal content and the cost without sacrificing the catalytic activity by using the ternary alloy catalyst (Pt-Ru-Co).



Fig. 1. Galvanostatic polarization data (without iR compensation) for various platinum based catalysts towards oxygen reduction in 0.5 M H_2SO_4 at room temperature.



Fig. 2. Galvanostatic polarization data (without iR compensation) for various platinum based catalysts towards hydrogen oxidation in 0.5 M H_2SO_4 at room temperature.

References

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