Preparation of PtRu/C anode catalyst with a high alloying degree for PEFC and its effect on CO tolerance

1. Introduction

Carbon-supported PtRu catalysts are widely used as the anode catalysts in polymer electrolyte membrane fuel cells (PEMFC) fed with reformed gas due to their superior CO tolerance[1-2]. PtRu alloy are more beneficial to enhance the intimate contact between Pt and Ru and thus improve the CO tolerance according to bi-functional mechanism and electronic effect. However, preparation of well-alloyed nanoparticles of Pt and Ru by reduction in homogeneous solutions represents a major challenge due to the large difference between the redox potentials of the two metals. In this work, the conventional ethylene glycol (EG) method was modified to prepare 45 wt.% PtRu/C catalyst by a two-step, sequential reduction process and boiling the synthesis solution, and the alloying degree of PtRu/C catalyst was greatly improved without the need of additional thermal post-treatment.

2. Experimental

The mixture of RuCl₃·xH₂O, Arabic gum and Vulcan XC-72 (pH~6) dissolved in EG was heated to 150 °C at a rate of 10 °C min⁻¹ under high-purity Ar atmosphere, then the calculated amount of H₂PtCl₆·6H₂O (pH~6) was added into the mixture. The mixture was then heated to 170 °C and maintained at this temperature for 1 hr. The mixture was further heated to the boiling temperature of EG (197 °C) and kept at 197 °C for 1 hr. Then the solution was cooled down and HCl solution was added to the solution to adjust the pH value to about 1 to hydrolyze the Arabic gum and settle the PtRu nanoparticles onto carbon support. Finally, the obtained catalyst was filtered, washed and dried, which was denoted as PtRu/C-H catalyst. For comparison, 45 wt.% PtRu/C was also prepared by co-reduction using the conventional method, and the obtained catalyst was denoted as PtRu/C-L catalyst. The prepared catalysts were characterized by XRD, STEM, CO stripping voltammetry and current-voltage curve measurements.

3. Results and Discussion

Fig. 1 shows the slow scan XRD pattern of Pt (220) peak in two PtRu/C catalysts, and the Pt (220) peak position (2θₑ) was obtained from curve fitting and used for the calculation of lattice parameter (a).

\[
a = \frac{\sqrt{2} \lambda}{\sin \theta_{\text{Max}}} \quad \text{(1)}
\]

The alloying degree of PtRu/C catalyst is defined as the Ru atomic fraction (χₑ) in PtRu alloy, which is related to the lattice parameter by the following equation proposed by Antolini et al.

\[
a = a_p - 0.124 \chi_e \quad \text{(2)}
\]

where \(a_p = 0.39155 \text{ nm}\) is the lattice parameter of carbon-supported platinum. For PtRu/C alloy catalyst with an atomic ratio of 1:1, the theoretical value of \(\chi_e\) is 0.5. The alloying degree of PtRu/C-L catalyst was 0.18, which is similar to the reported result[2], while the alloying degree of PtRu/C-H catalyst was greatly improved and reached 0.44. And the crystallite size of PtRu/C-L and PtRu/C-H catalysts was calculated to be 2.1 nm and 2.8 nm.

Fig. 1 Slow scan XRD pattern and curve fitting for Pt (220) diffraction peaks in two PtRu/C catalysts. The patterns were collected using an acquisition time of 6 s and a step size of 0.01°.

Fig. 2 shows the STEM images and the corresponding size distribution diagrams of PtRu/C-L and PtRu/C-H catalysts. Because PtRu/C-L catalyst was prepared under mild conditions, metal particles had a small size and were uniformly distributed on the carbon support. For PtRu/C-H catalyst, a fraction of
metal particles clumped together to form small aggregates and larger agglomerates structures, and the metal particles were unevenly distributed on the carbon support. However, it can also be observed that the primary particles of PtRu/C-H catalyst remained small as shown in Fig. 2 (b). The mean particle size of PtRu/C-L and PtRu/C-H catalyst was 2.6 nm and 4.1 nm, respectively, which is corresponding to the XRD result.

![Fig. 2 STEM images of PtRu/C-L (a) and PtRu/C-H (b) catalysts.](image)

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Fig. 3 shows the CO stripping voltammetry on both PtRu/C catalysts in 0.5 M HClO$_4$ at 25 °C after saturated adsorption of CO and subsequent purging of the solution with high-purity Ar. PtRu/C-H catalyst yields a lower onset of oxidation and oxidation current peak than PtRu/C-L catalyst. The onset of CO electro-oxidation on PtRu/C-H and PtRu/C-L catalysts is 0.316 V and 0.340 V, while the oxidation current peak on PtRu/C-H and PtRu/C-L catalyst is 0.454 V and 0.536 V, respectively. The number of nucleation sites for the adsorption of oxygen-containing species at low electrode potentials was roughly proportional to the atomic fraction of Ru in the PtRu alloy[1], so PtRu/C-H catalyst showed a better CO electro-oxidation activity than PtRu/C-L catalyst. By calculating from the CO stripping voltammetry, the electrochemical surface area of PtRu/C-H and PtRu/C-L catalysts is 43.51 and 40.71 m$^2$g$^{-1}$ PtRu, respectively. Fig. 4 shows the polarization curves of PEMFC with different PtRu/C catalysts as anode catalyst. When the anode was fed with pure H$_2$, PEMFC with PtRu/C-L catalyst gave a better performance than that with PtRu/C-H catalyst. At a current density of 0.2 A cm$^{-2}$, the cell voltage of PEMFC with PtRu/C-L and PtRu/C-H catalysts is 0.787 V and 0.765 V, respectively, which indicated H$_2$ electro-oxidation on Pt was more facile than on PtRu alloy. When the anode was fed with 500 ppm CO-contaminated H$_2$, PEMFC with PtRu/C-H catalyst showed a greater performance than that with PtRu/C-L catalyst. At a current density of 0.2 A cm$^{-2}$, the cell voltage of PEMFC with PtRu/C-L and PtRu/C-H catalysts is 0.634 V and 0.670 V, respectively. And at higher current densities, the cell voltage difference between the two PtRu/C catalysts is more dramatic.

![Fig. 3 CO stripping voltammetry of PtRu/C catalysts in 0.5 M HClO$_4$ at 25 °C. Scan rate: 10 mV s$^{-1}$.](image)

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