Polyol synthesis of highly active PtRu/C catalyst with high metal loading

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Received 5 October 2005; received in revised form 10 February 2006; accepted 5 March 2006
Available online 30 May 2006

Abstract

Highly loaded PtRu/C catalyst with high activity toward methanol electrooxidation was synthesized via a modified polyol process. XRD patterns indicated that the prepared catalyst was highly alloyed and TEM results showed that the metal nanoparticles were small and uniformly distributed on the carbon support despite the high metal loading. EDX results suggested that the two metals distributed uniformly in the catalyst. Electrochemical characterization and single cell test jointly showed that the prepared 40–20 wt.%PtRu/C catalyst possessed high activity toward methanol electrooxidation.

Keywords: Direct methanol fuel cells; Methanol electrooxidation; Anode catalyst; PtRu/C; High loading

1. Introduction

There are growing interests in the use of direct methanol fuel cells (DMFCs) as power sources for portable electronic devices. However, it is still far from practical application due to three drawbacks: (i) slow reaction kinetics on both anode and cathode side, (ii) methanol crossover, and (iii) the CO-poisoning problem at the anode [1]. Lots of efforts have been devoted to resolving these above-mentioned problems.

In a DMFC, it is methanol oxidation at the anode catalyst rather than the oxygen reduction at the cathode catalyst that limits the performance of the fuel cell compared with PEMFC. The main reason for DMFC anode rate limitation is apparently the sluggish electrooxidation of adsorbed carbon monoxide, an intermediate product of anodic methanol oxidation. Supported or unsupported PtRu catalyst have been considered as the most active catalyst for methanol electrooxidation. It is known that the activity of the catalyst is greatly dependent on the preparing procedure. Various methods for the preparation of PtRu catalyst have been put forward to enhance its activity or stability recent years [2,3]. As is known, for fuel cell, especially DMFC, the catalyst loading must be very high to reduce mass transfer resistance. However, it is by no means easy task to obtain high metal loading with high dispersion of nanoparticles.

The common criteria for a high performance anode catalyst for DMFC are: (1) a narrow particle size distribution, (2) a uniform composition throughout the nanoparticles, (3) a fully alloyed degree, and (4) high dispersion on carbon support at high metal loading.

Intensive efforts have been put on the preparation and characterization of PtRu/C catalyst. Various methods have been developed for the synthesis of PtRu/C catalyst, such as the impregnation method [4–7], the colloidal method [8,9] and microemulsion method [10,11]. However, most of the metal loadings in the present literatures are below 40 wt.%. There are few investigations on the synthesis of PtRu/C catalyst with high metal loading.

Polyol process has been proved to be an effective method for the preparation of nano-sized Pt/C catalysts [12]. In this presentation, bimetallic PtRu/C catalyst with Pt/Ru ratio of 1/1 and high metal loading up to 60 wt.% was synthesized by a modified polyol method. The morphology and structure of the catalyst were characterized with transmission electron microscopy (TEM) and X-ray diffraction (XRD). Its activity toward methanol electrooxidation was tested by electrochemistry method and single cell test.
2. Experimental

2.1. Catalyst preparation

H₂PtCl₆·6H₂O and RuCl₃·xH₂O were used as precursors of PtRu catalysts. Vulcan XC-72R carbon black (Cabot) was used as catalyst support. The preparing procedure is typically as follows: The required amount of metal precursors was added to a solution of ethylene glycol (EG) and water to obtain a mixture with 2 mg metal/ml solvent. The required amount of support was added to the mixture with vigorous stirring. The mixed solution was stirred for about 30 min to obtain a homogeneous solution. The pH value of the mixture was adjusted to above 13 with suitable amount of sodium hydroxide. Then the mixture was heated to 170 °C in an oil bath and maintained at this temperature for 3 h to ensure total reduction of the precursors. After the black mixture was cooled to room temperature it was filtered, washed with copious de-ionized water, and dried at 80 °C for 8 h in a vacuum oven.

2.2. Physical characterization of PtRu/C catalyst

XRD patterns were recorded with a Rigaku Rotaflex (RU-200B) X-ray diffractometer using Cu Kα radiation with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2θ angular regions between 15° and 85° were explored at a scan rate of 5° min⁻¹. Transmission electron microscopy (TEM) investigations were carried out using a JEOL JEM-2000EX microscope operating at 100 kV. HRTEM images were taken on JEOL JEM-2010F with resolution of 0.102 nm operating at 200 kV. The EDX analysis was performed with an OXFORD Inca Energy TEM200 System attached to the microscope.

2.3. Electrochemical characterization and single cell test

Electroactivities towards methanol oxidation of PtRu/C electrodes were measured by CV and LSV experiments using an EG&G model 273A potentiostat/galvanostat and a three-electrode test cell at room temperature. The working electrode was a thin layer of Nafion impregnated PtRu/C composite cast on a vitreous carbon disk electrode. The electrode was prepared as follows: a 5.0 mg catalyst sample was suspended in 1.0 ml of ethanol, and 10.0 wt.% Nafion was added as adhesive and proton conductor. The mixture were ultrasonically scattered for 10 min to form homogeneous ink. Then 25 μl of ink was pipetted on a vitreous electrode with 4 mm diameter to act as the working electrode. The supporting electrolyte was 0.5 M H₂SO₄ + 2.0 M CH₃OH. The counter electrode was a Pt wire. The reference electrode was a saturated calomel electrode (SCE).

The gas diffusion electrodes and MEAs were fabricated according to literatures [13]. The metal loading of the electrodes was 2 mg cm⁻² on the anode and 1 mg cm⁻² on the cathode. MEAs were tested on a homemade 4 cm² single cell using an

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**Table 1**

<table>
<thead>
<tr>
<th>XRD crystalline size (nm)</th>
<th>2θ (°) Peak position</th>
<th>Lattice parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>2.4</td>
<td>68.7</td>
</tr>
<tr>
<td>Homemade</td>
<td>2.1</td>
<td>68.6</td>
</tr>
</tbody>
</table>

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**Fig. 1.** XRD patterns of homemade and commercial 40–20 wt.%PtRu/C catalyst. (1) Homemade; (2) commercial.

**Fig. 2.** TEM image and size distribution of homemade 40–20 wt.%PtRu/C catalyst.
MTI test bench. The cell was composed of a pair of metal plates with linear flow-fields. The load was varied using a rheostat when voltage \((E)\)–current density \((j)\) curves were collected. The MEAs had been activated by 1 M methanol at 75 °C for 2 h before all the data were collected. The \(E=f(j)\) and \(P=f(j)\) curves were recorded using a high power potentiostat interfaced with a PC.

3. Results and discussion

There have been intensive investigations on the synthesis of supported or unsupported PtRu electrocatalyst. However, most of the reported metal loadings are lower than 40 wt.%. As we know, for direct alcohol fuel cells (DAFCs), the metal loading...
must be very high to achieve acceptable performance, due to the sluggish kinetics of the methanol electrooxidation on the anode side. And also, higher metal loading will be favorable for mass transportation.

Fig. 1 compares the XRD patterns of the homemade and the commercial (Johnson Matthey HiSPEC 10100) 40%Pt 20%Ru/C catalyst. Both catalysts show the characteristic of Pt fcc crystal structure. No diffraction peak of ruthenium was found. The broadening diffraction peak suggests that both catalysts have small crystalline size. The particle size and crystalline parameter are calculated according to Scherrer’s formula and Vegard’s law. The Pt(2 2 0) peak was chosen because it is isolated from the carbon support graphite diffraction peaks [14,15]. The calculation results are listed in Table 1. The results in Table 1 clearly show that the XRD particle size and the crystalline parameter of the homemade catalyst and the commercial catalyst do not have large difference and the two catalysts have comparable alloy degree.

TEM characterization was conducted to further study the morphology of the PtRu/C catalysts. Fig. 2 shows the representative TEM image and the particle size distribution of the synthesized 40%Pt 20%Ru/C catalyst. As can be seen the metal nanoparticles are very small and distribute uniformly on the support despite the high metal loading. The average size of the particles is calculated to be 2.6 nm. While for the commercial catalyst (shown in Fig. 3), the particle size is larger and there exists obvious agglomeration of metal particles. The particle size calculated from TEM image is about 5.0 nm. Obviously, for the commercial catalyst, the TEM result does not agree with the XRD result. The reason is as follows: XRD is a bulk method, and the calculated particle size is the average crystalline size [16]. So it cannot reflect the actual morphology of the catalyst. Furthermore, it should be pointed out that the commercial catalyst employs a carbon support (AC01) with large surface area, while the homemade catalyst using Vulcan XC72 as the support.

It is generally accepted that methanol electrooxidation on PtRu catalyst follows the bi-functional mechanism [17]. That is, methanol dehydrogenation on Pt sites to form CO-like species and water dissociate on Ru sites to form oxygen-containing species, and then the CO-like species react with the oxygen-containing species to form the final product. To fulfill this mechanism, it is desirable that the Pt sites are adjacent with the Ru sites. Therefore it is of importance to prepare PtRu catalyst in which the two elements form uniform distribution on carbon support without segregation. EDX analysis was performed to study the element distribution of the homemade PtRu/C catalyst. Shown in Fig. 4(a) and (b) are the EDX spectroscopy on many particles analysis (average information of composition) and single particle analysis (information of composition in one particle) respectively. Both the many particles analysis and single particle analysis show that the platinum to ruthenium molar ratio in the homemade catalyst is near to the nominal ratio 1:1, which suggests the homogenous distribution of the two metals.

The electrochemical activity of the PtRu/C catalyst was evaluated by cyclic voltammetry in 0.5 M H₂SO₄/2 M CH₃OH at room temperature. Fig. 5 shows the cyclic voltammograms and linear sweep voltammograms of the homemade and commercial catalyst. It can be seen from the CV results that although the peak current density of the homemade catalyst is a little lower than the commercial catalyst, its methanol initial oxidation potential is much lower (about 50 mV) than that of the commercial catalyst, which suggests that methanol is more easily oxidized on the homemade catalyst. From the LSV results (Fig. 5(b)), at potential of 0.3 V versus SCE, the mass activity of the homemade catalyst and the commercial catalyst is about 23 and 16 mA/mg PtRu, respectively, suggesting that the methanol electrooxidation activity of the homemade catalyst is higher than the commercial catalyst.

Fig. 6 is the single DMFC cell performance with the homemade catalyst as the anode catalyst. The cathode catalyst is the 20 wt.%Pt/C from Johnson Matthey company. The catalyst loadings at anode and cathode were 2 mg PtRu/cm² and 1 mg Pt/cm². In accordance with the electrochemical results, the homemade catalyst performs better than the commercial one. This is due to its smaller particles size, uniform distribution on the support and uniform composition.
4. Conclusions

In this presentation, highly dispersive 40–20 wt.%PtRu/C catalyst was synthesized via a modified polyol process. XRD results indicate it has comparable alloy degree with the commercial catalyst. TEM analysis shows the homemade catalyst has smaller particles size and much more uniform distribution. EDX analysis shows that the metal composition is uniform throughout the nanoparticles. Electrochemical characterization and single cell test jointly show that the homemade catalyst is more active that the commercial catalyst for methanol electrooxidation.

Acknowledgements

This work was financially supported by Innovation Foundation of Chinese Academy of Science (K2003D2), Hi-Tech Research and Development Program of China (2003AA517040), Key Technologies R&D Programme (2004BA907A43), the Graduate Innovation Research Foundation of Chinese Academy of Science and Samsung-DICP Joint Research Programme.

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