A novel sintering resistant and corrosion resistant Pt₄ZrO₂/C catalyst for high temperature PEMFCs

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Received 8 December 2005; received in revised form 3 March 2006; accepted 5 March 2006
Available online 2 May 2006

Abstract

An novel Pt₄ZrO₂/C catalyst was prepared and compared with 20 wt.% Pt/C in terms of the sintering resistance and corrosion resistance. To evaluate their sintering resistance and corrosion resistance properties, an accelerated ageing test (AAT) was performed. The catalysts before and after AAT were characterized by cyclic voltammetry (CV), rotating disk electrode (RDE) and X-ray diffraction (XRD). After AAT, the dissolution rate of Pt and Zr in H₃PO₄ media (105 wt.%, 204 °C) was characterized by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The electrochemical area (ECA) changes of thin film electrodes based on Pt₄ZrO₂/C and Pt/C catalysts were also evaluated using continuous CV sweep technique. All the results showed that Pt₄ZrO₂/C has higher sintering resistance and corrosion resistance than Pt/C. ‘Anchor effect’ is proposed to explain the enhanced effect of ZrO₂ in Pt₄ZrO₂/C binary catalyst compared with Pt/C that contain platinum alone.

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Keywords: Pt₄ZrO₂/C; Accelerated ageing test; Sintering and corrosion resistance; Anchor effect; High temperature PEMFCs

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) as a clean and efficient power generator for stationary and mobile applications have attracted more and more attentions during the last decades [1–4]. Generally, the PEMFCs use perfluorosulfonic acid polymer such as DuPont’s Nafion as proton exchange membrane. This solid electrolyte needs water to conduct the protons, so the operational fuel cell temperature is limited to be below 100 °C [5]. High temperature PEMFCs use H₃PO₄ doped polybenzimidazole (PBI) [6,7] or modified Nafion membrane [8] as solid electrolyte. Such systems possess many advantages [5,9]: (1) higher catalytic activity and quicker electrode kinetics; (2) less poisonous effect of CO in fuel stream; (3) more convenient for co-generation of heat and power; (4) more simple water and heat management, etc. Although the elevated cell temperature gives great advantages to cell performance and simplifies the fuel cell system design, the common used Pt/C catalyst is apt to agglomerate [10–14] and dissolve [15] under high temperature and acid environment. This will decrease the catalyst activity and the durability of the fuel cells. Therefore, it is very important to develop better sintering resistant and corrosion resistant catalysts for high temperature PEMFCs.

ZrO₂ as a material that has high melting point, outstanding thermal and chemical stability, excellent mechanical properties and biocompatibility has been widely used in many applications. For instance, ZrO₂ is used as a support and oxygen storage material in three-way catalyst [16,17], as an oxygen ion conductor in the electrolyte of solid oxide fuel cells (SOFCs) [18,19] and as a promoter for preferential oxidation of CO [20], etc. It is proved that ZrO₂ has both higher thermal stability and better corrosion resistance. In this paper, ZrO₂ was introduced to the Pt/C catalyst. The novel Pt₄ZrO₂/C catalyst and Pt/C catalyst were compared by AAT method and continuous CV sweep technique. The initial experimental results showed that the novel Pt₄ZrO₂/C catalyst is a very promising catalyst for high temperature PEMFCs.
2. Experimental

2.1. Preparation of Pt$_{4}$ZrO$_2$/C and Pt/C Catalysts

The catalysts were prepared by a modified polyol process [21,22]. First, Vulcan XC-72 (Carbot corp., BET: 235 m$^2$/g, denoted as C) was mixed with water and acetone (volume ratio of 3:1). The appropriate zirconyl nitrate was added, and then excessive NH$_4$OH was added with constant stirring to make a precipitate. The resultant sample was filtered and washed with deionized water, then dried at 100 °C in air for 10 h. This material was finally calcined at 500 °C in N$_2$ for 3 h to get ZrO$_2$/C. The Pt$_4$ZrO$_2$/C and Pt/C were prepared by the reduction of H$_2$PtCl$_6$ in an ethylene glycol (EG) solution on ZrO$_2$/C and XC-72 powders. In the two catalysts, the weight ratio of Pt:C was maintained at 20:80 and in Pt$_4$ZrO$_2$/C the atomic ratio of Pt:Zr was 4:1. The as-received catalysts were identified as Pt$_4$ZrO$_2$/C-A1 and Pt/C-B1. The Pt$_4$ZrO$_2$/C-A and Pt/C-B1 were then calcined at 500 °C in N$_2$ for 3 h, and the two calcined catalysts were named as Pt$_4$ZrO$_2$/C-A2 and Pt/C-B2.

2.2. Accelerated Ageing Test (AAT)

A 100 mg Pt$_4$ZrO$_2$/C-A1 was immersed in 10 g phosphoric acid (105 wt.%) to form a slurry, and then this slurry was disposed at 204 °C saturated with air for 5 h. The same procedure was explored with Pt/C-B1, Pt$_4$ZrO$_2$/C-A2 and Pt/C-B2. It has been reported that the sintering and corrosion of the catalysts under such treatment simulates the actual status after 2000 h of normal phosphoric acid fuel cell (PAFC) operation [23]. Since the circumstance of phosphoric acid doped PBI high temperature PEMFCs is similar to that of PAFC, the same AAT method was used here to verify the durability of the home-made catalysts. After AAT, the explored Pt$_4$ZrO$_2$/C-A1, Pt/C-B1, Pt$_4$ZrO$_2$/C-A2 and Pt/C-B2 were named as Pt$_4$ZrO$_2$/C-A4, Pt/C-B4, Pt$_4$ZrO$_2$/C-A3 and Pt/C-B3, respectively.

2.3. Physical Characterization of Pt$_4$ZrO$_2$/C and Pt/C Catalysts

XRD analyses of all catalysts were performed on a Rigaku Rotaflex (RÜ-200B) using Cu Kα radiation ($\lambda$ = 1.54056 Å) with a Ni filter to characterize the Pt and ZrO$_2$ crystalline structures. The 2θ angular regions were explored between 10° and 90°, and the scan rate was 5° min$^{-1}$ with step of 0.02°.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis with a model TJIA was conducted to determine the concentration of the dissolved Pt and Zr in hot H$_3$PO$_4$ after AAT.

2.4. Electrochemical Characterization of Pt$_4$ZrO$_2$/C and Pt/C Catalysts

2.4.1. CV Test

Electrochemical characterization was performed on an EG&G 273A instrument, and a standard three electrode electrochemical cell was used to test the Pt$_4$ZrO$_2$/C and Pt/C electrodes in sulfuric acid electrolyte. The thin film electrode was used as working electrode, and the thin film catalyst layer on the rotating disk electrode (RDE) was prepared as follows. A mixture containing 5.0 mg Pt/C or Pt$_4$ZrO$_2$/C catalyst, 1.0 ml ethanol and 50.0 μL Nafion (5 wt.%, Dupont corp.) was ultrasonically blended in a weighing bottle for half an hour to obtain a homogeneous ink. A 25 μL paint ink was spread on the surface of a glassy carbon electrode (area: 0.1256 cm$^2$) and the electrode was dried in the air to obtain a thin active catalyst layer. A big platinum foil (3 cm$^2$) and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. All electrode potentials in this paper were quoted to SCE. A solution of 0.5 M H$_2$SO$_4$ was used as electrolyte. The CV data were recorded in the potential range of −0.25 to 1.0 V versus SCE with a scan rate of 50 mV/s. Before the CV test, high purity nitrogen was introduced for 30 min to clean the electrolyte. ECA was determined by integrating the hydrogen adsorption/desorption area of the cyclic voltammogram and dividing the charge over a value of 210 μC/cm$^2$ assuming a monolayer adsorption of hydrogen atom on platinum surface [24].

2.4.2. RDE Test

The RDE test was measured using a RDE system (EG&G model 636) coupled with EG&G 273A instrument. The three electrode configurations and the electrolyte in RDE test is the same with CV tests. The RDE curves were obtained in the potential range of 1.0 to 0 V versus SCE with a scan rate of 5 mV/s. Before the RDE test, the electrolyte was saturated with O$_2$ by bubbling O$_2$ for 30 min.

3. Results and Discussion

Fig. 1 shows the XRD patterns of Pt$_4$ZrO$_2$/C, ZrO$_2$/C and Pt/C. It is obvious that the XRD patterns of Pt$_4$ZrO$_2$/C-A1 and Pt$_4$ZrO$_2$/C-A2 combined the crystalline features of Pt and ZrO$_2$, indicating the coexistence of them both. Pt$_4$ZrO$_2$/C-A3 and Pt$_4$ZrO$_2$/C-A4 show the Pt (1 1 1), (2 0 0), (2 2 0) and (3 1 1)
Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mean particle size by XRD (nm)</th>
<th>Electrochemical surface area (ESA) (m² g⁻¹)</th>
<th>Dissolution of Pt and Zr in 105% H₃PO₄ after AAT (wt.%)</th>
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</thead>
<tbody>
<tr>
<td>Pt/C-B1</td>
<td>1.53</td>
<td>63.1</td>
<td>7.8</td>
</tr>
<tr>
<td>Pt/C-B2</td>
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<td>6.3</td>
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<tr>
<td>Pt/C-B4</td>
<td>2.95</td>
<td>43.6</td>
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</tr>
<tr>
<td>Pt₄ZrO₂/C-A1</td>
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<td>69.5</td>
<td>5.0</td>
</tr>
<tr>
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<tr>
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<td>59.4</td>
<td></td>
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<tr>
<td>Pt₄ZrO₂/C-A4</td>
<td>2.45</td>
<td>54.5</td>
<td></td>
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</tbody>
</table>

peaks, but the crystalline features of ZrO₂ are not evident. The “absence” of the diffraction peaks typical for ZrO₂ could be due to the possibility that the ZrO₂ exists in an amorphous form after AAT [25,26]. The average particle sizes of Pt in the Pt₄ZrO₂/C and Pt/C catalysts were calculated from the Pt (2 2 0) reflections using the Scherer equation [27]. The results were summarized in Table 1.

Fig. 2a and b shows the CVs for Pt/C and Pt₄ZrO₂/C before and after AAT in 0.5 M H₂SO₄ electrolyte at room temperature. The ECA of Pt₄ZrO₂/C-A1 is 69.5 m²/g, which is slightly higher than that of Pt/C-B1 (63.1 m²/g). The possible reason for the increase of ECA is that the first uniformly deposited ZrO₂ on the carbon support serves as the dispersant for the subsequent deposited Pt. After the calcination at 500 °C for 3 h, the ECA of Pt₄ZrO₂/C-A2 and Pt/C-B2 decreased. This bears evidence that the agglomeration of small granular crystallites when the heat treatment is proceeded. After AAT, the ECA of Pt/C-B3 decreased from 58.7 to 50.9 m²/g and that of Pt/C-B4 decreased from 63.1 to 43.6 m²/g. For Pt/C-B3 the rate of the ECA retention is 86.7% and for Pt/C-B4 is 69.1%. After AAT, the ECA of Pt/C-B1 decreased much more than that of Pt/C-B2. This is because Pt/C-B2 has a procedure of calcination and this procedure elevates the interaction of Pt and carbon support. The enhanced interaction between Pt and carbon can restrain the agglomeration and the dissolution of Pt to some extent. Similar results were also found for Pt₄ZrO₂/C. The ECA of Pt₄ZrO₂/C-A3 decreased from 64.8 to 59.4 m²/g and that of Pt₄ZrO₂/C-A4 decreased from 69.5 to 54.5 m²/g. For Pt₄ZrO₂/C-A3 the rate of the ECA retention is 91.7% and for Pt₄ZrO₂/C-A4 is 78.4%. However, it is obvious that after AAT, the ECA of Pt₄ZrO₂/C-A3 and Pt₄ZrO₂/C-A4 is larger than Pt/C-B3 and Pt/C-B4 and the rate of ECA retention is much higher. These results revealed that Pt₄ZrO₂/C exhibited better resistance to sintering at elevated temperatures than Pt/C, which is ascribed to the so-called ‘anchor effect’ of ZrO₂ to Pt on carbon substrates. The existence of oxide or hydroxide can inhibit the agglomeration of catalyst crystallite to some extent, and hence prolong the life of the catalyst [23,28]. When ZrO₂ is present on carbon, the highly dispersed Pt atoms are obstructed by the adjacent ZrO₂ and the agglomeration of Pt particles could be inhibited.

The data in Table 1 also reveal that Pt₄ZrO₂/C has better resistance to sintering and corrosion. From Table 1, it is obvious that the particle size increase of the explored Pt₄ZrO₂/C after AAT is less significant than that of the explored Pt/C. In addition, the rate of Pt dissolution in Pt/C-B1 and Pt/C-B2 is higher than that of Pt₄ZrO₂/C-A1 and Pt₄ZrO₂/C-A2 after AAT. Furthermore, the uncalcined catalysts dissolved much more Pt than the calcined catalysts. The enhanced interaction between Pt and

Fig. 2. Cyclic voltammograms for Pt/C (a) and Pt₄ZrO₂/C (b) catalysts in 0.5 M H₂SO₄ purged with N₂ at room temperature, recorded at 50 mV/s.
carbon due to the calcination may explain this phenomenon. It is speculated that there is a strong interaction between Pt and quadrivalent Zr, which may prevent the dissolution of Pt in the strict acid environment. Pt4ZrO2/C-A1 dissolved more Zr than Pt4ZrO2/C-A2. This is because that the calcination enhanced the interaction of Pt and carbon, and moreover, the interaction of Pt and Zr was also enhanced by the calcination. During AAT, there was an anchor effect of ZrO2 to Pt and meanwhile Pt may anchor ZrO2. It is well known that less noble metal components in the catalysts will dissolve in hot phosphoric acid under PAFC operating conditions. For example, it was reported that over 67 atom percent of V and 37 atom percent of Cr dissolved in phosphoric acid (99 wt.%, 194 °C) at 0.9 V versus RHE [29]. Similarly, 12 and 33 atom percent of Zr in Pt4ZrO2/C-A2 and Pt4ZrO2/C-A1 dissolved after AAT, but the ORR activity of Pt4ZrO2/C-A3 and Pt4ZrO2/C-A4 did not decrease much more in despite of the dissolution of Zr according to Fig. 3b.

The polarization curves towards oxygen reduction in 0.5 M H2SO4 are shown in Fig. 3a and b. Comparison of Fig. 3a with b shows that Pt4ZrO2/C offered larger oxygen reduction current than Pt/C did. ZrO2 has been found to have fairly high oxygen storage capacity, which can thus enlarge the oxygen concentration on the surface of the catalyst, and achieve higher ORR activity while keeping the catalyst at the same oxygen pressure [30,31]. The ORR activity of Pt/C-B2 is higher than Pt/C-B1, because the heat treatment enhances the interaction of Pt with carbon support, which accelerates the transfer of electron, and thus increases the kinetic of ORR. A similar result was also found for Pt4ZrO2/C. But after AAT, the ORR activity of Pt/C-B3 and Pt/C-B4 decreased. It is due to both the conglomerates of Pt particles and the decrease of the actual amount of Pt in Pt/C-B3 and Pt/C-B4. However, the ORR activities of Pt4ZrO2/C-A3 and Pt4ZrO2/C-A4 are similar to Pt4ZrO2/C-A2 and Pt4ZrO2/C-A1. This is owing to the ‘anchor effect’ of ZrO2 to Pt in Pt4ZrO2/C, which inhibits the agglomeration of Pt in Pt4ZrO2/C and slows the dissolution of Pt in hot condensed phosphoric acid. These two factors favor to maintaining the activity of Pt4ZrO2/C. But after AAT, Pt4ZrO2/C-A3 performed higher ORR activity than Pt4ZrO2/C-A4. This trend is in agreement with CV results according to Fig. 2.

![Figure 3. Polarization curves for Pt/C (a) and Pt4ZrO2/C (b) catalysts on rotating disk electrode in 0.5 M H2SO4 saturated with O2 at room temperature and rotated at 2500 rpm, recorded at 5 mV/s.](image)

![Figure 4. Cyclic voltammograms after continuous cycling for Pt/C (a) and Pt4ZrO2/C (b) catalysts in 0.5 M H2SO4 purged with N2 at room temperature, recorded at 50 mV/s.](image)
Fig. 4a and b shows the CVs for Pt/C-B1 and Pt4ZrO2/C-A1 after continuous cycling. In the case of the cycling, the entire active surface of the catalyst is exposed to electrolyte and the transfer of protons is high, which results in more severe circumstance than that of actual PEMFCs. Under such conditions, the degradation of the catalysts is accelerated [32]. The ECA decreases gradually as the cycle number increases. This phenomenon indicates the increase of metal particle size. Fig. 5 shows the ECA as a function of the cycle number for Pt/C-B1 and Pt4ZrO2/C-A1. During the initial cycles, the ECA increases until it reaches a maximum value. The initial increase is due to the initial wetting of the thin Nafion layer covering the catalyst particles. After the ECA gets to the maximum, the surface area starts to decrease. Similar behavior is observed for Pt/C-B1 and Pt4ZrO2/C-A1, but Pt/C-B1 showed much greater decrease of ECA in the first 100 cycles when compared to Pt4ZrO2/C-A1. After 800 cycles, the ECA of Pt4ZrO2/C-A1 and Pt/C-A1 are 25.0 and 17.2 m²/g, respectively. During the whole cycling experiments, the ECA of Pt4ZrO2/C-A1 remains greater than that of Pt/C-A1.

4. Conclusions

In this paper, Pt/C and Pt4ZrO2/C were prepared and the sintering resistance and corrosion resistance properties were evaluated by an accelerated ageing test and a continuous CV test. XRD patterns show that the particle size of Pt4ZrO2/C does not increase too much after AAT. The Pt4ZrO2/C catalyst maintains higher electrochemical area and much more platinum than Pt/C after AAT. The continuous CV tests also give similar results. The preliminary experiments indicate that the addition of ZrO2 into platinum catalysts can significantly improve the durability of the catalyst in terms of the sintering resistance and corrosion resistance. The proposed ‘anchor effect’ of ZrO2 to Pt is responsible for preventing Pt4ZrO2/C catalysts from sintering during the accelerated ageing test. The detailed corrosion resistance mechanism of ZrO2 to platinum catalysts is in progress. The life-time test of Pt4ZrO2/C in H3PO4-doped PBI high temperature fuel cell will be discussed in the future.

Acknowledgements

This work is partly supported by the National Natural Science Foundation of China (Grant No. 50236010) and the Innovation Foundation of Dalian Institute of Chemical Physics.

References