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Stabilization of platinized carbon catalysts for PAFC

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1. Introduction

In phosphoric acid fuel cells operating with oxygen and hydrogen it is well known that the activation overpotential for oxygen reduction at the cathode is far larger than that for hydrogen oxidation at the anode. This is because the exchange current density for the oxygen electrode is as low as 10^{-10} mA cm^{-2} at room temperature, whereas that for the hydrogen electrode is as high as 10^{-4} mA cm^{-2}. It is also the case that only a few metals are suitable for use as an electrode for oxygen reduction. This is because most metals and their alloys, except those of the platinum group, are not stable at the potential of oxygen reduction, especially in acidic electrolytes. Even when platinum group metals are used as cathodic materials, their corrosion and sintering tend to increase during cell operation. This can lead to reduction in the cell output and, hence, in the overall operational efficiency.

With the objective of solving such problems, a wide variety of studies have been made on carbon-based electrodes carrying platinum with other metals, such as platinum–vanadium [1], platinum–chromum [2], platinum–chromum–cobalt [3], platinum–palladium and platinum–ruthenium [4, 5] and platinum–ruthenium–niobium–nickel [6]. None of these catalysts, however, is completely satisfactory. Some of them have a sufficiently high initial activity, but they tend to lose activity over a relatively short time, and others maintain activity for a long time, but the level of activity is insufficient. Work in the authors' laboratories has shown that a platinum alloy with iron and/or cobalt can provide electrocatalysts free from the drawbacks mentioned above [7, 8].

2. Experimental details

2.1. *Pt/C catalyst preparation*

27 g of CO_2-treated acetylene black prepared as reported previously [9] with a surface area of 104 m^2 g^{-1} were made into a slurry with 200 ml deionized water and 200 ml isopropanol. An aqueous solution of $H_2PtCl_6.2H_2O$ containing 3.0 g Pt was then added with constant stirring.

The slurry temperature was gradually raised to about 95 °C with progressive addition of 30 g of 3 wt% formic acid as a reducing agent. The slurry was kept at 95 °C for 30 min and then cooled to room temperature, filtered and washed with deionized water. The filter cake was dried at 95 °C for 16 h in flowing nitrogen to provide a platinum on carbon supported catalyst with 10 wt% Pt.

2.2. *Pt–Fe–Co/C alloy catalyst preparation*

7 g of the supported platinum catalyst was dispersed in 50 ml deionized water and 50 ml isopropanol. The mixture was blended at high speed for 20 min. 20 ml of an aqueous solution containing iron as ferric nitrate and cobalt as cobaltous nitrate were added to the slurry with constant stirring. A very dilute hydrazine aqueous solution was added slowly until a pH of 7.0 was obtained. Under these conditions the iron and cobalt species were adsorbed completely on the supported platinum catalysts. Stirring was continued for 30 min. The slurry was then filtered and the solids were dried at 95 °C in nitrogen and then heat-treated at 750 °C in a flowing gas stream (7 vol% H_2, balance N_2) for 40 min. The formation and particle size of the platinum–iron–cobalt alloy were determined by X-ray diffraction (D/MAX-IIIAXRD, Rigsku, Co., Japan).

2.3. *Pt–Fe/C alloy catalyst preparation*

A Pt–Fe/C alloy catalyst was prepared in accordance with the experimental procedure outlined in Section 2.2 except that ferric nitrate alone was deposited on the carbon supported platinum catalysts. The presence of Pt_3Fe superlattice was confirmed by X-ray diffraction.

2.4. *Pt–Co/C alloy catalyst preparation*

A Pt–Co/C alloy catalyst preparation in accordance with the experimental procedure of Section 2.2 was repeated except that the cobaltous nitrate alone was deposited on the carbon supported platinum catalysts. The presence of a Pt_3Co superlattice was also confirmed by X-ray diffraction.

2.5. *Electrode fabrication*

The electrode manufacturing technique was described previously [9]. Carbon supported platinum catalyst prepared as described in Section 2.1 was ultrasonically dispersed in an aqueous polytetrafluoroethylene suspension containing 30 v/v of isopropanol and a calculated amount of ammonium bicarbonate to adjust the porosity of the catalyst layer. The mixture was homogenized with strong stirring to yield a workable paste, which was spread uniformly onto a wet-proofed graphite paper to obtain a catalyst layer carrying a platinum loading of 0.5 mg cm^{-2}. The resulting paper was then dried and sintered according to the following steps. First, the temperature was increased slowly to 100 °C and held at 120 °C until no white gases were evolved and then to 320 °C for 20 min. The catalyst layer and gas diffusion layer were cut to an appropriate size. A platinum screen set between the catalyst layer and the diffusion layer served as a current collector. The laminated layers were pressed into one unit under a pressure of 80 kg cm^{-2}. The resulting cathode is identified as E-1.

The above steps were repeated except that the Pt–Fe–Co/C, Pt–Fe/C and Pt–Co/C were utilized in place of Pt/C. The resulting cathodes were identified as E-2, E-3 and E-4, respectively.

2.6. *Accelerated ageing test (AAT)*

0.3 g of each catalyst was immersed in 20 g of 105% phosphoric acid to form a slurry that was saturated with air at 204 °C for 5 h under open-circuit conditions. It has been reported [10] that sintering of the platinum catalyst under such treatment simulates the sintering that occurs after 2000 h of normal PAFC operation. After cooling to room temperature, the slurry was washed with deionized water and filtered. The solid residue was washed thoroughly with deionized water and the amount of platinum dissolving in the filtrate was analysed by spectrophotometry (model 7211, Shanghai, China). Stannous chloride was used as the coloring reagent [11]. The coagulation of platinum in each catalyst after such ageing was re-examined by X-ray diffraction.

3. Results and discussion

The results of an accelerated ageing test for each catalyst are summarized in Table 1. The influence of heat treatment of the catalyst on corrosion resistance and particle size was reported previously [7]. It has been shown that the heat treatment is so critical that it plays a decisive role in producing a successful platinum alloy electrocatalyst.

In the present paper, only the catalysts which were properly heat-treated are reported. As can be seen from Table 1, the platinum alloy catalysts have higher stability (less tendency for platinum to dissolve out into the electrolyte and less change in metal particle size) than the catalyst containing platinum alone. This remarkable effect is ascribed to the so-called ‘anchor effect’ of iron and/or cobalt to platinum on carbon substrate. Both platinum and platinum alloys have a face-centered cubic lattice structure as shown in Figure 1. It is well known that iron and cobalt have a strong tendency to alloy with carbon, the substrate material on which catalyst metals are dispersed. Therefore, the platinum atoms are bonded more strongly to the carbon substrate through the bridges of iron and/or cobalt atoms compared with platinum alone on carbon substrate. This is demonstrated schematically in Figure 2.

The cathodic performance of the studied electrodes together with the electrode carrying platinum alone for purposes of comparison are shown in Figure 3. This indicates that the cathodes made from carbon-supported platinum alloy catalysts show a 20 mV to 40 mV lower polarization than the cathode using carbon-supported platinum alone over a wide range of current densities.

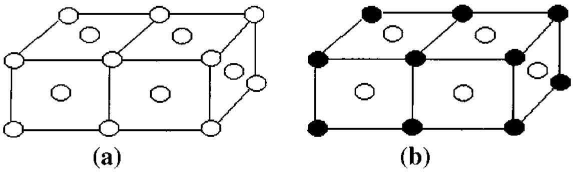

Fig. 1. Supperlattice of platinum (a) and platinum alloy (b). Key: (○) Pt and (●) Fe/Co.

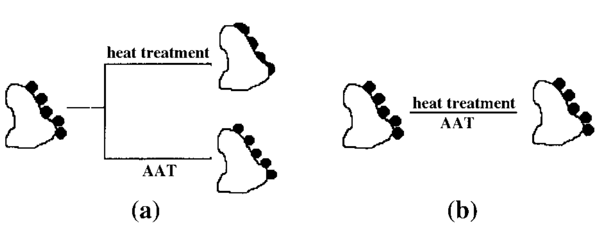

Fig. 2. Schematic drawing of carbon-supported catalysts after heat-treatment and accelerated ageing test. (a) Pt/C (b) $Pt_3(FeCo)/C$.

Table 1. Stability of catalyst powders before and after AAT

Sample	Catalyst	Temp./°C	Dissolution of Pt in H_3PO_4 after AAT/wt %	Metal particle size/nm	
				Before AAT	After AAT
1	Pt/C	95	28.7	7.5	12.2
2	Pt/C	750	2.1	35.8	36.3
3	$Pt_3(FeCo)/C$	750	4.5	13.6	13.1
4	Pt_3Fe/C	750	9.2	13.5	12.7
5	Pt_3Co/C	750	7.9	13.3	13.0

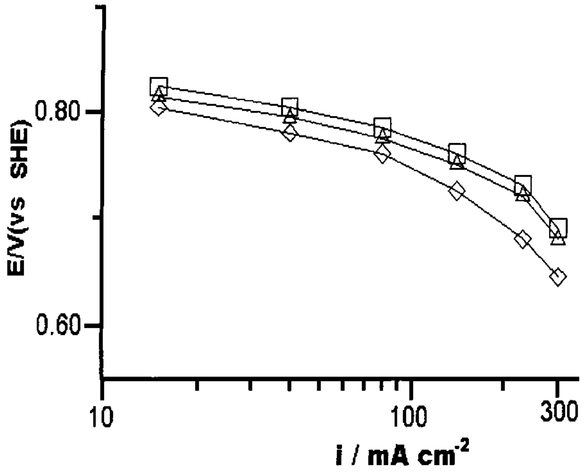

Fig. 3. Cathodic performance of electrodes at 190 °C in 105% H_3PO_4. Air was fed with 7 W electric blower and *IR* had been corrected. Key: (□) E-2, (△) E-4 and (◇) E-1.

The electrode stability was also tested according to the procedure described previously [8]. Each of the electrodes E-1, E-2, E-3 and E-4 was kept immersed in an accelerated ageing cell containing 100 ml of 105% H_3PO_4 (bubbling pure oxygen), maintained at 200 °C. A potential of 700 mV relative to a hydrogen reference electrode was applied. The surface area retention of the catalysts was measured before and after ageing according to the method of the literature [12]. The result is summarized in Table 2. It should be noted that the initial surface area of supported platinum catalyst alone was remarkably higher than that of the supported platinum alloy catalysts. However, after 5 h of accelerated ageing, the platinum alloy electrodes displayed much better surface area retention than did the supported platinum catalyst electrode. In the long run, therefore, the supported platinum alloy catalysts have much more promise for catalytic applications than dose the supported platinum alone.

4. Conclusions

Platinum–iron and/or cobalt alloy electrocatalysts have outstandingly high stability and catalytic activity. In addition, electrodes using such electrocatalysts remain stable for longer periods and have more than 20 mV to 40 mV higher output over a wide range of current densities, compared with electrodes using platinum alone as the catalysts. Because of their high catalytic activity and long service life, such electrodes may be considered to have a high practical value. The outstanding performance of such new electrocatalysts is due to the anchor effect of iron and/or cobalt to platinum on carbon. This special effect is thought to be responsible in preventing platinum on carbon from sintering and dissolving during electrode operation.

Table 2. Specific surface area of catalysts on electrodes before and after aging test

Electrode	Catalyst	Metal surface area/m^2 g^{-1}		Rate of retention /%
		Fresh	Cooked	
E-1	Pt/C*	107	48	45
E-2	$Pt_3(FeCo)/C$	68	50	73
E-3	Pt_3Fe/C	71	50	70
E-4	Pt_3Co/C	69	51	74

* Pt/C treated only at 95 °C

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