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Journal of Power Sources 62 (1996) 233–236

JOURNAL OF POWER SOURCES

Short Communication

Heat treatment of carbon-based powders carrying platinum alloy catalysts for oxygen reduction: influence on corrosion resistance and particle size

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Received 29 March 1996; accepted 9 April 1996

Abstract

The influence of heat treatment of carbon-based powders carrying platinum and platinum–iron binary alloy catalysts for oxygen reduction is investigated. The catalyst powders are subjected to heating at various temperatures for a certain time. An accelerated ageing test (AAT) is used to evaluate the corrosion resistance and sintering resistance of each catalyst. The dissolution of the catalyst in the AAT filtrate is analysed with a spectrophotometer and provides a measure of the corrosion resistance. The particle size of catalyst powders before and after AAT is determined by X-ray diffraction and indicates the sintering resistance. Transmission electron microscopy and electron diffraction techniques are also employed as supplementary testing methods. So-called 'anchor effects' are proposed to explain the enhanced effect of iron in platinum–iron binary catalysts compared with catalysts that contain platinum alone.

Keywords: Fuel cells; Platinum–iron alloy catalyst; Oxygen reduction

1. Introduction

A fuel cell is an electrochemical device for the direct conversion of a fuel and an oxidizing agent to a low-voltage direct current. The output efficiency of a fuel cell is dictated by a number of factors. Its dependency upon the activity and service life of the positive-electrode catalyst is the most important factor. With phosphoric acid fuel cells (PAFCs) operating on oxygen and hydrogen, it is well known that the activation polarization of oxygen reduction at the cathode is far larger than that of hydrogen oxidation at the anode. This is because the exchange current density for oxygen electrode is as low as 10^{-10} A cm^{-2} at room temperature whereas that for hydrogen electrode is as large as 10^{-4} A cm^{-2}. Besides, 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 operation efficiency.

To eliminate these difficulties, a wide variety of investigations have been made on carbon-based electrodes that carry platinum with various other metals, for example, platinum–vanadium, platinum–chromium, platinum–chromium–cobalt [1], platinum–iron [2], platinum–iron–cobalt [3], and platinum–palladium [4,5]. The emphasis was placed on finding optimum compositions for the alloys.

By contrasts, heat treatment was seldom given any special attention. In fact, the heat-treatment conditions were nearly the same in most of the studies. Work in the authors' laboratories has shown, however, that the heat treatment is so critical that it plays a decisive role in producing a successful platinum alloy electrocatalyst. For two kinds of alloy catalyst powder with the same composition and the same fabrication procedure, different heat treatment can produce two completely different catalysts: one may be very good, the other may be not so good or even useless.

In this communication, a platinum–iron alloy catalyst dispersed on a suitable carrier is taken as an example to demonstrate how heat treatment affects particle size and corrosion resistance, i.e., the two important characteristics of a catalyst powder.

2. Experimental

2.1. Preparation of supported platinum catalyst

27 g of CO_2-treated acetylene black (prepared as reported previously [6]) with a surface area of 104 m^2 g^{-1} were made

PII S0378-7753(96)02425-1

Table 1
Influence of heat treatment on stability and particle size of powder catalysts

Sample no.	Catalyst composition (atom %)	Temperature (°C)	Crystals detected by XRD	Dissolution of Pt in H_3PO_4 after ageing (wt.%)	Metal particle size (nm)	
					Before ageing	After ageing
1	Pt/C	95	Pt	28.7	7.5	12.2
2	Pt/C	750	Pt	2.1	35.8	36.3
3	Pt/C	900	Pt	0.2	46.7	46.7
4	67Pt33Fe/C	500	Pt	11.4	23.4	30.1
5	67Pt33Fe/C	650	Pt-Pt_3Fe	10.4	20.6	21.4
6	67Pt33Fe/C	750	Pt_3Fe	9.2	13.5	12.7
7	67Pt33Fe/C	900	Pt_3Fe	4.6	22.3	21.9

into a slurry with 200 ml de-ionized water and 200 ml isopropanol. An aqueous solution of $H_2PtCl_6 \cdot 2H_2O$ 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 de-ionized 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. *Preparation of supported platinum–iron alloy catalyst*

A 7 g sample of the supported platinum catalyst was dispersed in 50 ml distilled water and 50 ml isopropanol. The mixture was blended at high speed for 20 min. A 20 ml portion of an aqueous solution containing 0.10 g iron as ferric nitrate was added to the slurry with constant stirring. Next, very dilute hydrazine aqueous solution was added slowly until a pH of 7.0 was obtained. Under these conditions, the iron species is adsorbed completely on the supported platinum catalyst. Continuous 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 various temperatures in a flowing gas stream (7 vol.% H_2, balance N_2) for 40 min. The formation and particle size of the platinum–iron alloy was determined by X-ray diffraction (D/MAX-IIIA XRD, Rigaku, Co., Japan).

2.3. *Accelerated ageing test*

0.3 g of each catalyst (prepared as above) was immersed in 20 g 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 [7] 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 diluted with de-ionized water and filtered. The solid residue was washed thoroughly with de-ionized water, and the amount of platinum that dissolved in the filtrate was analysed with a spectrophotometer (Model 7211, Shanghai, China). Stannous chloride was used as the colour reagent [8]. The coagulation of platinum in each catalyst after such ageing was re-examined by X-ray diffraction.

3. Results and discussion

The results of accelerated ageing tests for each catalyst treated at different temperatures are summarized in Table 1. The X-ray diffraction spectra for samples 4 to 6 and shown in Figs. 1–3, respectively. It can be seen that no alloying of platinum and iron takes place when the temperature of the heat treatment is below 500 °C, and only partial alloying occurs at 650 °C. It is also found that 750 °C is the lowest temperature for the complete alloying of platinum and iron.

The transmission electron micrographs with corresponding electron diffraction patterns are presented in Figs. 4–6. The results indicate that coagulation of the catalyst crystallites progresses with increase in the temperature. The Bragg reflections of sample 7 show that additional crystal faces participate

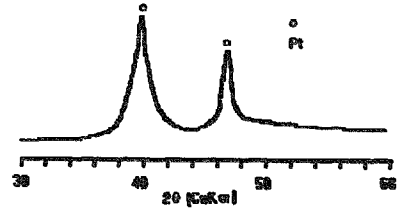

Fig. 1. X-ray diffraction spectra of sample 4.

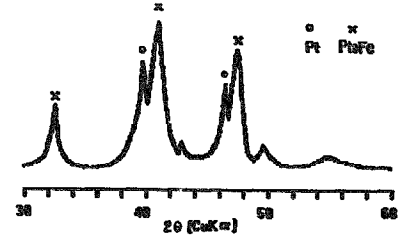

Fig. 2. X-ray diffraction spectra of sample 5.

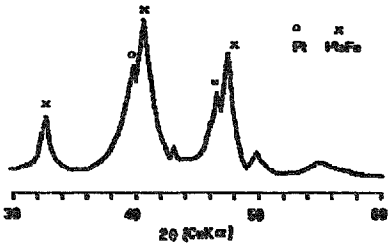

Fig. 3. X-ray diffraction spectra of sample 6.

in the electron diffraction of the catalysts treated at the higher temperatures. This bears evidence that the coagulation of small granular crystallites becomes appreciable when the temperature of heat treatment is above 750 °C.

The data presented in Table 1 also reveal that platinum–iron binary alloy catalysts exhibit a better resistance to sintering at elevated temperatures than the catalysts that contain platinum alone. This effect is ascribed to the so-called 'anchor effect' of iron to platinum on carbon substrates. The mobility of platinum atoms on carbon substrates is more difficult when iron is present. It is well known that iron has a strong tendency to alloy with carbon, the substrate material on which alloy catalysts are dispersed. Therefore, the platinum atoms are bonded more strongly to the carbon substrate through bridges of iron atoms.

In the accelerated ageing test, corrosion and sintering exist simultaneously in samples 1 and 2 that contain platinum alone, while only corrosion occurs in samples 6 and 7 that have a complete alloying of platinum and iron. Catalysts samples 4 and 5 have zero and partial alloying and display the same behaviour as samples 1 and 2. Therefore, the com-

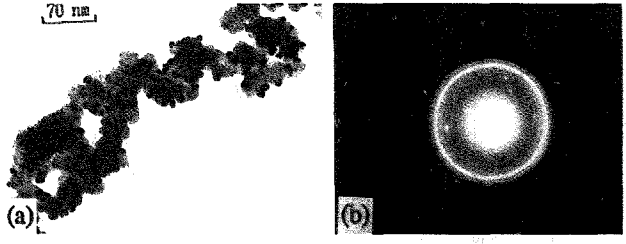

Fig. 4. (a) Transmission electron micrograph and (b) electron diffraction pattern of sample 1.

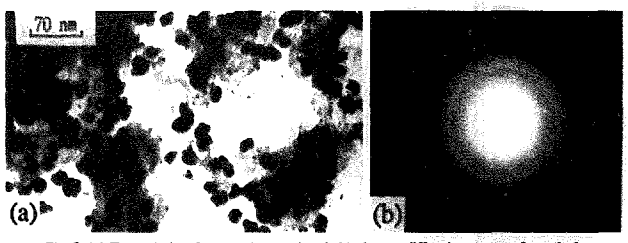

Fig. 5. (a) Transmission electron micrograph and (b) electron diffraction pattern of sample 6.

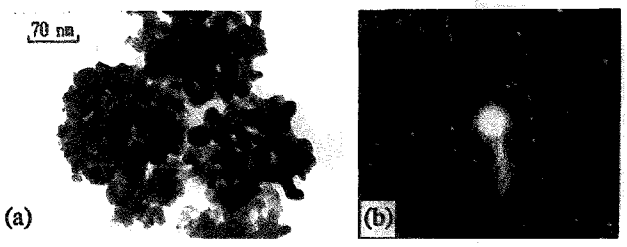

Fig. 6. (a) Transmission electron micrograph and (b) electron diffraction pattern of sample 7.

plete alloying of platinum and iron is necessary in order to obtain a catalyst with good stability. It should be noted, however, that there will a loss of effective surface area of the catalyst if the temperature of heat treatment is much higher than the temperature necessary for complete alloying.

The electrochemical properties of electrodes fabricated with the above catalyst powders have been reported elsewhere [3]. A cathodic polarization test demonstrated that the electrode made from sample 6 had the smallest polarization.

4. Conclusions

Platinum and iron alloy supported on carbon powder displays a better resistance to sintering than a platinum alone catalyst. The anchor effect of iron to platinum on carbon is thought to be responsible for preventing platinum–iron alloy catalysts from sintering during the accelerated ageing test or elevated temperature treatment. The temperature of heat treatment is a key factor for obtaining a catalyst with a proper corrosion resistance and high surface area. The optimum temperature is 750 °C.

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