Short communication

A high-performance phosphoric acid fuel cell

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Abstract

Although, phosphoric acid fuel cell technology is now nearly commercially mature, it is mandatory to make it cost competitive with existing power technologies. Since, the cost and power density of fuel cells are linked to each other, attempts are being made to enhance the power density of phosphoric acid fuel cells. This study demonstrates that phosphoric acid fuel cells with power density values as high as 560 mW cm^{-2} are realizable by employing a combination of SiC and ZrSiO$_4$ as an electrolyte matrix, and Pt-Co/C as a cathode catalyst. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Phosphoric acid fuel cell technology has now reached a level of maturity where developers are focusing their resources to produce commercial capacity, multi-unit demonstrations, and pre-prototype installations. The technology is still too costly, however, to be economic in comparison with alternative power-generating systems except perhaps in niche, premium power applications. There is a need to increase the power density of the cell and to reduce costs, both of which are inextricably linked [1]. Attempts to enhance the performance of phosphoric acid fuel cells (PAFCs) have mainly been directed to electrodes, electrocatalysts and system engineering [2–5]. It is only recently that Gonzalez et al. [6] demonstrated that the use of a proper electrolyte matrix material could also appreciably enhance the power density of PAFCs.

In PAFCs, carbon-supported platinum is the most commonly used catalyst, both for the oxidation of hydrogen fuel at the anode and oxygen reduction at the cathode. Nevertheless, platinum dissolution and carbon corrosion become problematic at cell voltages above 0.8 V. Although, the hydrogen oxidation reaction proceeds favorably on a platinum electrode, the oxygen-reduction reaction has been found to be kinetically hindered. Many alloys of platinum with transition metals have been reported [7–9] to promote the oxygen-reduction reaction. In this communication, we report that by the proper choice of an electrolyte matrix in conjunction with a suitable

oxygen-reduction cathode catalyst, PAFCs with power density values as high as 560 mW cm^{-2} can be realized.

2. Experimental

2.1. Preparation of cathode catalysts

2.1.1. 30 wt.% Pt/C catalyst

A catalyst of 30 wt.% platinized carbon was prepared by the sulfito-complex route [10]. For this purpose, a Na$_6$[Pt(SO$_3$)$_4$] precursor was obtained from chloroplatinic acid. The acid was dissolved in distilled water and the pH was adjusted to 7 by adding Na$_2$CO$_3$. Subsequently, the pH of the solution was lowered to 3 by adding NaHSO$_3$. The solution was then gently warmed until it became colorless. The pH of the solution was then raised to 6 by adding Na$_2$CO$_3$. This resulted in a white precipitate of Na$_6$[Pt(SO$_3$)$_4$], which was filtered, washed copiously with hot distilled water, and dried in an air oven at 80°C.

To obtain a 30 wt.% Pt/Vulcan XC-72 catalyst, the required amount of Vulcan XC-72 carbon was suspended in distilled water and agitated in an ultrasonic water bath at about 80°C to form a slurry. The required amount of Na$_6$[Pt(SO$_3$)$_4$] was dissolved in 1 M H$_2$SO$_4$ and diluted with distilled water. This solution was added dropwise to the carbon slurry with constant stirring at 80°C. 30% H$_2$O$_2$ was then added dropwise with the temperature maintained at 80°C. This resulted in vigorous gas evolution; the solution was further stirred for 1 h. Subsequently, platinized carbon was obtained by reduction with 1 wt.% formic acid solution,

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which was filtered, washed copiously with hot distilled water, and dried in an air oven at 80°C for 2 h.

2.1.2. 30 wt.% Pt-Co/C binary alloy catalyst

The required amount of 30 wt.% Pt/Vulcan XC-72 carbon was prepared as described in Section 2.1.1 and dispersed in distilled water followed by ultrasonic blending for 15 min. The pH of the solution was raised to 8 with dilute ammonium hydroxide. Stirring was continued during and after the pH adjustment. The required amount of cobalt nitrate solution containing the required amount of the salt was added to this solution. This was followed by the addition of dilute HCl to the solution until a pH of 5.5 was attained. Stirring was continued for 1 h and the resultant mass was dried at 90°C in an air oven for 2 h. The product was grounded well and the powder was heat-treated at 900°C in a nitrogen atmosphere for 1 h to form the respective binary alloy catalyst. The catalyst composition was maintained at 30 wt.% Pt-Co/C.

Powder X-ray diffraction (XRD) patterns for Pt/C and Pt-Co/C cathode catalysts were obtained on a Philips X-pert 3710 X-ray diffractometer using Cu Kα radiation at a scan rate of 1° min^{-1}. The catalysts were also subjected to energy dispersive analysis by X-rays (EDAX) employing a Jeol JSM-840A scanning electron microscope to determine the composition of the constituent elements.

2.2. Electrochemical studies

PAFCs were constructed by arranging the anode, electrolyte matrix, and cathode between two high-density graphite blocks with ribbed flow fields to provide a hydrogen gas supply to the anode and an oxygen gas supply to the cathode.

The anodes for the PAFCs were supplied by Bharat Heavy Electricals, India, and essentially comprised a Teflonized (35 wt.%) carbon paper loaded with a platinized carbon (Pt/C) catalyst layer. The anode was prepared by screen-printing an ink made of Pt/C, 10 wt.% Teflon, 5 wt.% polyvinyl alcohol, and 3 wt.% t-butyl phosphate solution. The catalyst loading on anodes was 0.5 mg cm^{-2} of Pt. The cathodes for PAFCs were prepared in a similar manner with Pt/C or Pt-Co/C catalyst layers which contained 0.5 mg cm^{-2} of Pt. The catalyst ink was prepared as described above and coated on to a Teflonized (40 wt.%) carbon paper. After air-drying, the electrodes were sintered at 340°C for 3 h. The electrolyte matrix for the PAFCs were prepared either from SiC or SiC + ZrSiO$_4$ or SiC + Zr$_3$(PO$_4$)$_4$ by mixing it with 10 wt.% of Teflon solution, 5 wt.% polyvinyl alcohol and water. A layer with a thickness of about 100 μm was then applied to the cathode side of the cell. It was subsequently filled with 100% phosphoric acid and left for acid absorption for 100 h at 180°C in an air oven. Galvanostatic polarization data on PAFCs with different electrolyte matrices and cathode catalysts were collected at 180°C and at ambient gas pressures. Scanning electron micrographs of the matrices were obtained at 4000× and 19,000× magnification to examine their morphologies. In situ cyclic voltammograms for the PAFCs were recorded on an Autolab (Auto-30) galvanostat/potentiostat to determine the electrochemical surface areas (ESAs) of the cathode catalysts.

3. Results and discussion

The powder XRD patterns of the cathode catalysts are shown in Fig. 1. The diffraction peak at $2\theta \approx 25°$ observed
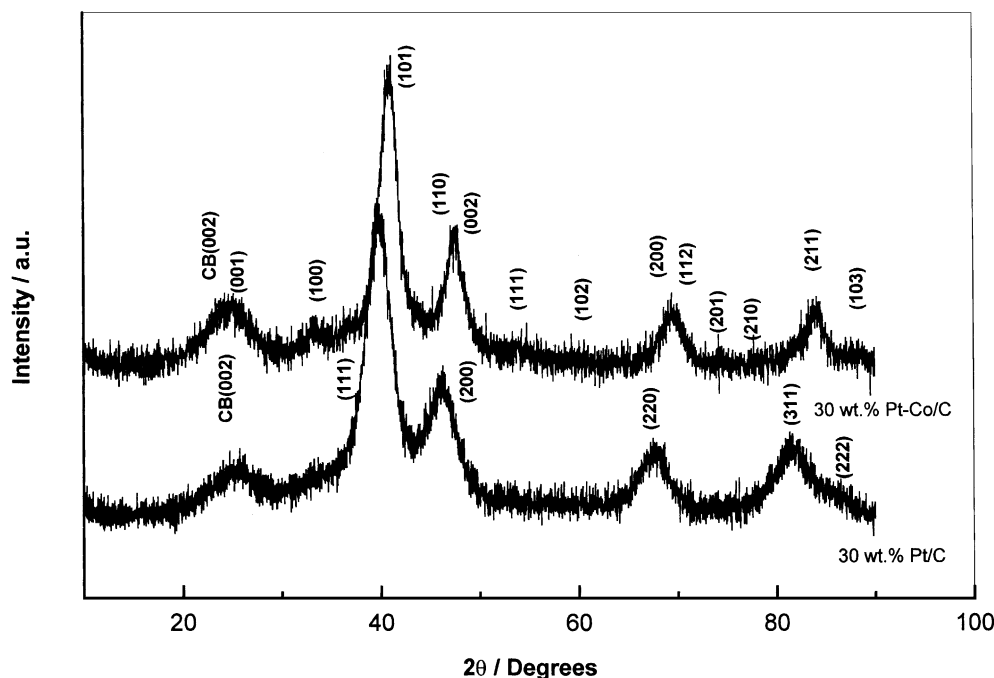

Fig. 1. Powder XRD patterns of carbon-supported Pt and Pt-Co cathode catalysts.

in the diffraction patterns of both the carbon-supported Pt and the Pt-Co alloy catalysts is due to the (0 0 2) plane of the hexagonal structure of Vulcan XC-72 carbon. While the XRD pattern of Pt/C resembles a face-centered cubic structure, the XRD pattern of the Pt-Co/C catalyst resembles the tetragonal structure of the Pt-Co alloy [11]. There is a shift in the peak positions of the Pt-Co/C electrocatalyst to higher Bragg angles. This suggests a contraction in the lattice parameter [12]. EDAX analysis of the Pt-Co/C catalyst gave an approximately (1:1) atomic ratio of Pt:Co. Scanning electron micrographs of the electrolyte matrices are given in Fig. 2. From the electron micrograph in Fig. 2(a), the average particle size of SiC particles is about 5 μm.
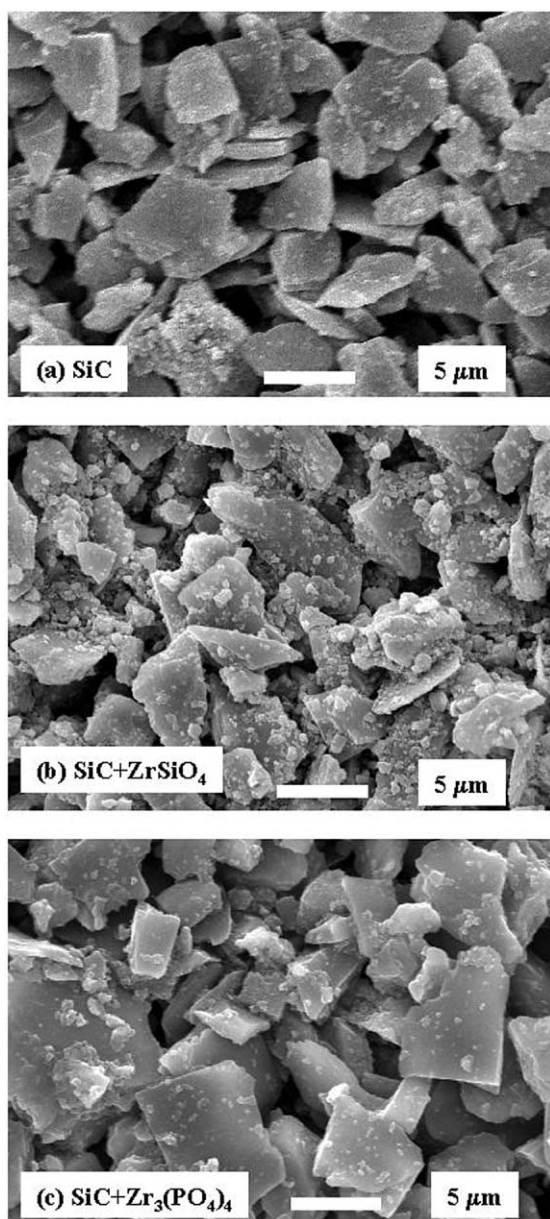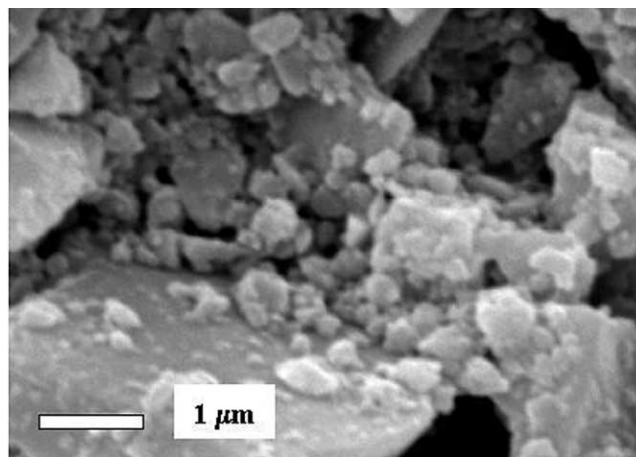

Fig. 3. Scanning electron micrograph of SiC:ZrSiO$_4$ (7:3) matrix at 19,000× magnification.

The large particles are found to be loosely packed with voids between the crystalline particles. The electron micrographs of the composite matrices of SiC + ZrSiO$_4$ and SiC + Zr$_3$(PO$_4$)$_4$ are shown in Fig. 2(b) and (c), respectively. In these electrolyte matrices, the voids contain filler components, namely ZrSiO$_4$ or Zr$_3$(PO$_4$)$_4$. This results in an appreciable decrease in the void size. The electron micrograph of the SiC + ZrSiO$_4$ matrix at a higher magnification (19,000×) is shown in Fig. 3. The micrograph shows clearly the fine pores of the composite matrix. ESAs as determined from in situ cyclic voltammograms of the Pt/C cathode catalyst with various matrices are listed in Table 1. The maximum ESA is obtained for the SiC + ZrSiO$_4$ matrix.

Galvanostatic polarization data for PAFCs obtained with different electrolyte matrices and cathode catalysts are shown in Fig. 4. The open-circuit voltage of a PAFC with a Pt/C catalyst and a SiC matrix is ∼900 mV, which is lower than the open-circuit voltage of PAFCs assembled with composite matrices and a Pt/C cathode catalyst. This could be due to reactant crossover through the voids in SiC matrix. The PAFCs with both the composite matrices of SiC + ZrSiO$_4$ or SiC + Zr$_3$(PO$_4$)$_4$ exhibit better performance over the entire range of polarization. The pores in these composite electrolyte matrices have better retention of phosphoric acid electrolyte, and the acid penetration is

Fig. 2. Scanning electron micrographs of electrolyte matrices at 4000× magnification: (a) SiC; (b) SiC:ZrSiO$_4$ (7:3); (c) SiC:Zr$_3$(PO$_4$)$_4$ (7:3).

Table 1
Electrochemical surface areas of 30 wt.% Pt/C cathode catalyst in conjunction with various electrolyte matrices[a]

Electrolyte matrix	Electrochemical surface area (m^2 g^{-1})
SiC	33.6
SiC:ZrSiO$_4$	48.3
SiC:Zr$_3$(PO$_4$)$_4$	35.9

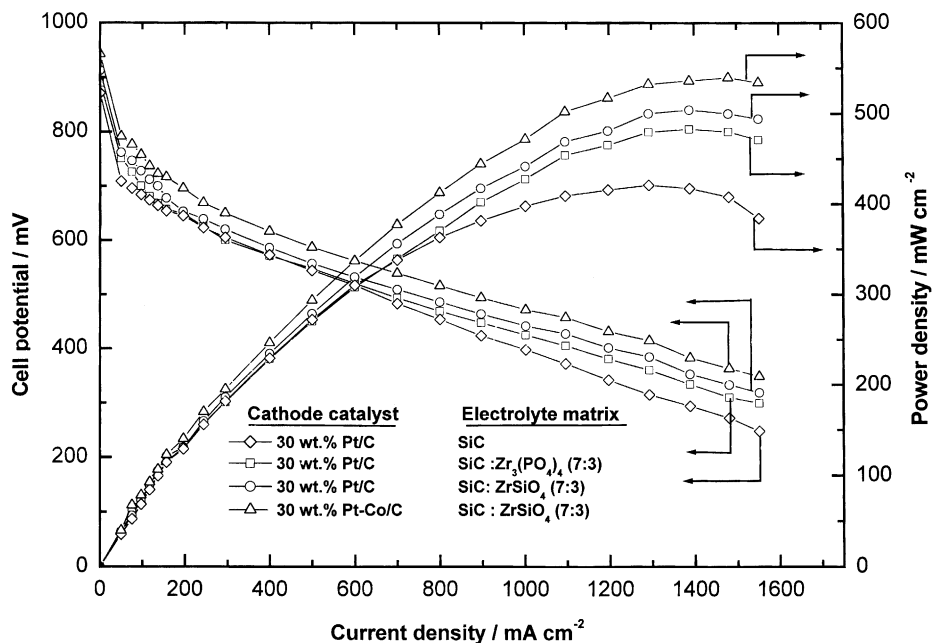[a] As determined from in situ cyclic voltammetry.

Fig. 4. Galvanostatic polarization data for PAFCs with various electrolyte matrices and cathode catalysts obtained at 180°C and ambient gas (hydrogen and oxygen) pressures.

high when the pore size is reduced with fillers. This is quite likely due to a drop in the hydrostatic pressure in the capillaries [6]. It is noteworthy that the electrolyte penetration is inversely proportional to the radius of the capillary according to the Laplace formula [13]. The reduction of oxygen on a Pt/C cathode catalyst is kinetically hindered. By contrast, alloys of Pt with transition metals, in particular a Pt-Co/C catalyst show an enhancement in the oxygen-reduction reaction [14]. Accordingly, we find an enhancement in the performance of PAFC when the Pt/C cathode is substituted with a Pt-Co/C cathode catalyst along with a $SiC + ZrSiO_4$ matrix, as shown in Fig. 4. The maximum power density obtained with a PAFC with a Pt-Co/C cathode and a $SiC + ZrSiO_4$ composite matrix is 560 mW cm^{-2}. Several factors such as changes in the morphology of catalyst [15], surface roughening [16], geometric parameters like reduction in lattice parameters [17], changes in electronic properties upon alloying [18], and Pt enrichment on the catalyst surface [19] are attributed to this enhancement in the performance of PAFCs.

4. Conclusions

Composite electrolyte matrices comprising $SiC + ZrSiO_4$ and $SiC + Zr_3(PO_4)_4$ exhibit a better uniformity and overall stability relative to SiC. Higher electrolyte retention in SiC matrix is achieved with fillers like $ZrSiO_4$ or $Zr_3(PO_4)_4$. Composite matrices show lower ohmic losses relative to SiC matrix. A Pt-Co/C catalyst promotes the reduction of oxygen on the cathode of PAFCs. It is found that by employing Pt-Co/C in conjunction with composite electrolyte matrices comprising $SiC + ZrSiO_4$ or $SiC + Zr_3(PO_4)_4$, the performance of PAFCs can be enhanced in relation to SiC and power densities of about 560 mW cm^{-2} can be achieved.

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