Influence of PTFE dispersion in the catalyst layer of porous gas-diffusion electrodes for phosphoric acid fuel cells

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Abstract

Polytetrafluoroethylene (PTFE) dispersion in the catalyst layer can be monitored and measured using an X-ray diffraction technique. The effect of PTFE dispersion is investigated at various baking temperatures and with different PTFE contents in the electrode. The results reveal that the relative dispersion efficiency increases both as the baking temperature increases from 320 to 360 °C, and as the PTFE content increases from 20 to 60%.

Introduction

Oxygen reduction on platinum electrodes in phosphoric acid fuel cells (PAFCs) has been studied extensively [1–4]. One of the chief challenges in recent PAFC development is the partial internal wetting of the porous gas-diffusion electrode. The performance of the electrode is related to the intrinsic activity of the platinum catalyst and to the wettability of the electrode. The effects of the crystalline size of the platinum catalyst on the electrode performance have also been well studied [5–7].

Many theoretical models have been developed to simulate the performance of porous gas-diffusion electrodes used in PAFCs [8–11]. Electrodes prepared with electrolyte and reactant gas networks for high performance have also been developed [12–15]. Kunz and Gruver [16] observed double Tafel slopes when oxygen diffusion was significantly hindered in a porous gas-diffusion electrode. The factor of oxygen gain was proposed to characterize the transport hindrance in the electrode [17–19]. It is generally recognized that the major concern in developing an efficient electrode is to reduce the diffusion path of oxygen to the active site of platinum in the catalyst layer by either changing the platinum content [16, 20, 21] or the wettability of electrode. As it is not feasible to vary the platinum content out of cost considerations, improvement of wettability seems more practical.

The effect of wettability of a porous gas-diffusion electrode on its performance has also been extensively studied [12–15,22–28]. The results indicate that low wettability of the catalyst layer leads to poor performance as the liquid diffusivity, ionic conductivity and platinum utilization are affected adversely. On the other hand, very high wettability may result in poor performance as the electrical conductivity and gas diffusivity become low. Hence, the electrolyte quantity in the catalyst layer of the electrode must be optimized to provide good ionic and electric conductivity, high gas and liquid phase transport of reactants, and high platinum utilization. It has been recommended [28] that the polytetrafluoroethylene (PTFE) content in the catalyst layer should be controlled at about 30 to 50 wt.% and the baking temperature of electrode at 330 to 350 °C.

The wetting characteristics of the electrode has been studied either by cyclic voltammetry [13–15, 21, 26, 29, 30] or by measuring the acid absorption of the catalyst layer [27, 28]. Maoka [26] observed that a 5 wt.% PTFE electrode has higher peaks of oxidation current than a 50 wt.% PTFE electrode. It has also been observed that the acid absorption decreases as the PTFE content in the catalyst layer increases or as the baking temperature increases [13–15, 27, 28]. By contrast, the properties of the PTFE crystallinity in the catalyst layer have received less attention. In this work, we study the change of PTFE crystallinity and its effect on the acid absorption, electric conductivity, the radius of the largest flooded pores, the agglomerate radius, and the performance of electrode. We also analyse the factors that affect the crystallinity of the PTFE, in particular the PTFE content in the catalyst layer and the baking temperature of electrode.

Experimental

A porous gas-diffusion electrode was prepared with two layers, namely, a carbon paper and a catalyst layer. The carbon paper was first made hydrophobic by impregnation in a 15% PTFE solution for 3 min. It was then dried at 80 °C to remove the solvent (water) and baked at 340 °C for 18 min. The catalyst layer was produced in the following manner. First, 3 g of carbon powder with 10 wt.% platinum loading (Vulcan XC-72), 60 cm^3 distilled water and 25 cm^3 isopropyl alcohol were mixed with PTFE solution (60 wt.% solid PTFE) to a desired weight ratio. This mixture was blended for 24 h in a low-speed blender. The mixture was spread on the carbon paper. Then, the electrode was pressed and air dried at 80 °C to remove solvent (water and isopropyl alcohol). Finally, the electrode was dried at 300 °C for 1 h in an oven to remove the residual surfactant in the catalyst layer and then baked at a temperature that ranged from 320 to 360 °C for 18 min. The oxygen reduction response was measured by potentiostatic measurement.

The electrode was tested in a Pyrex glass half-cell apparatus as shown in Fig. 1. A major component of the apparatus is the electrode holder made of PTFE, where a test electrode was mounted and exposed to phosphoric electrolyte. The carbon paper
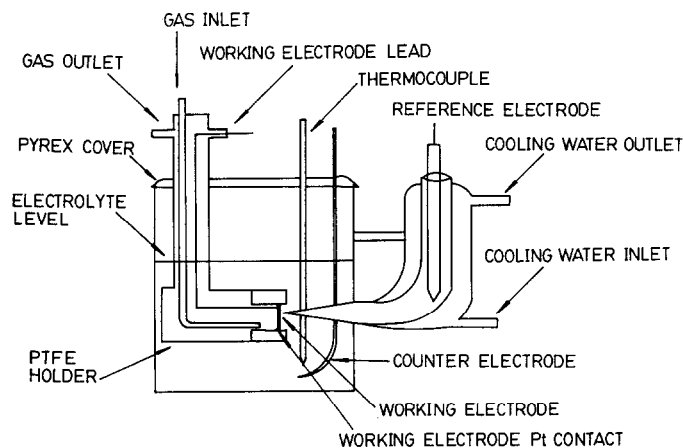

Fig. 1. Half-cell apparatus.

faced toward the reactant. The latter was supplied at a flow rate of 50 cm³/min. The reactant gas was introduced from the gas chamber into the electrode from a top hole and released from a side hole. The edge of the carbon paper of the electrode was connected to a circular platinum wire. The oxygen was then introduced into the holder. The electrode was kept in contact with 98% phosphoric acid for 24 h to achieve a complete soakage. A saturated calomel electrode was used as a reference electrode in an external chamber containing 98% phosphoric acid. A platinum sheet served as a counter electrode. The potential was shifted away from the open-circuit value in the cathodic direction at a 25 mV interval for 2 min.

The acid absorption of the catalyst layer was obtained by first placing the electrode in a vessel containing 98% phosphoric acid at 180 °C for 24 h. The difference in the electrode weight before and after the acid absorption experiment was determined. This is the absorption per unit weight of catalyst layer.

The crystallinity of the electrode was measured by means of a X-ray diffractometer (XRD) with a nickel-filtered Cu Kα radiation target. The XRD pattern was recorded at a scanning rate of $2\theta = 4°$/min with silicon as an internal standard. The electric conductivity in the catalyst layer was measured by a collinear four-probe method.

Results and discussion

Crystallinity of PTFE in the catalyst layer

PTFE is a highly crystalline polymer with a regular structure. A typical XRD pattern of 40% PTFE baked at 80 or 340 °C is shown in Fig. 2. The peaks to the left are the regular structure of carbon fibre in the carbon paper, while the peaks to the right are for PTFE crystals in the catalyst layer. The results from Fig. 2 reveal that the crystalline property decreases when the baking temperature is above the melting point of PTFE (viz., 327 °C). The intensity of the XRD pattern for PTFE in the catalyst layer depends on the treatment conditions. The conditions that can affect the crystallinity of PTFE include the baking temperature and PTFE content in the catalyst layer of the electrode. The decrease of PTFE crystallinity from its original value results from the interaction between the carbon support and the PTFE during the baking process, which chiefly controls the degree of PTFE dispersion in the catalyst layer. This phenomenon has rarely been mentioned in the literature. PTFE dispersion can affect markedly the wetting characteristics in the catalyst layer. In order to assess the PTFE dispersion condition in the catalyst layer according to XRD results, the PTFE gain is defined as the difference in the peak intensity of PTFE between 80 °C and T_b. Here, T_b is the baking temperature of the process. In this study, T_b ranged from 320 to 360 °C. The peak intensity at 80 °C is used as a standard since the electrode mixture is pressed at this temperature.

We define the relative dispersion efficiency of PTFE in the catalyst layer as follows:

$$\text{relative dispersion efficiency} = \frac{\text{PTFE gain at } T_b}{\text{peak intensity of 60 wt.\% PTFE at 80 °C}} \tag{1}$$

This index offers a relative measure of the PTFE dispersion in the catalyst layer based on the peak intensity of 60 wt.% PTFE at 80 °C under a given set of mixing conditions. Data for the relative dispersion efficiency of PTFE are shown in Fig. 3. The relative dispersion efficiency of 20 to 60 wt.% PTFE in the catalyst layer has been measured with the baking temperature between 320 and 360 °C. It shows that the relative dispersion efficiency of PTFE increases as the baking temperature increases from 320
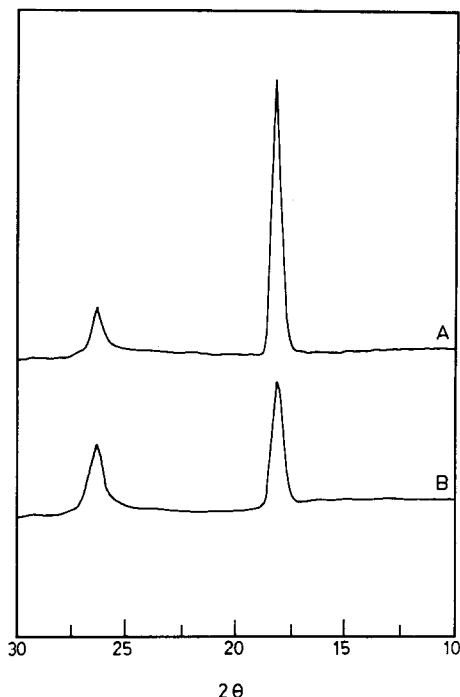
Fig. 2. The XRD patterns of 40 wt.% PTFE baked at: (A) 80 °C, and (B) 340 °C.

to 360 °C. This means that the PTFE crystallinity decreases when the baking temperature is increased. It seems that the rate of PTFE dispersion in the catalyst layer will increase with decreasing melt viscosity when the electrode is heated above the melting temperature of PTFE.

The effect of PTFE content on the relative dispersion efficiency is shown in Fig. 4. The results indicate that the relative dispersion efficiency increases sharply as the PTFE content is increased from 20 to 60 wt.%. With a high PTFE content in the electrode, the PTFE dispersion is improved due to the additional amount of PTFE. Thus, the relative dispersion efficiency of a 60 wt.% PTFE electrode is higher than that of a 20 wt.% PTFE electrode. The PTFE dispersion can be increased by raising the PTFE content in the catalyst layer.

Effect of PTFE dispersion on acid absorption

Acid absorption is an important index with respect to the wettability of the catalyst layer. Mori *et al.* [27] and Giordano *et al.* [28] found that the acid absorption decreases when the electrode is prepared at higher baking temperatures. They did not, however, investigate directly the effect of PTFE dispersion on acid absorption. A set of electrodes were therefore made to determine the acid absorption of 40 wt.% PTFE in the catalyst with a baking temperature ranging from 320 to 360 °C. The results are presented in Fig. 5. It is obvious that the acid absorption decreases as the relative dispersion efficiency increases due to the increased baking temperature. It seems that the pores fill with PTFE when the electrode is baked at high temperatures.

The change in acid absorption of the electrodes baked at 340 °C with different PTFE contents is illustrated in Fig. 6. It is seen that the acid absorption decreases
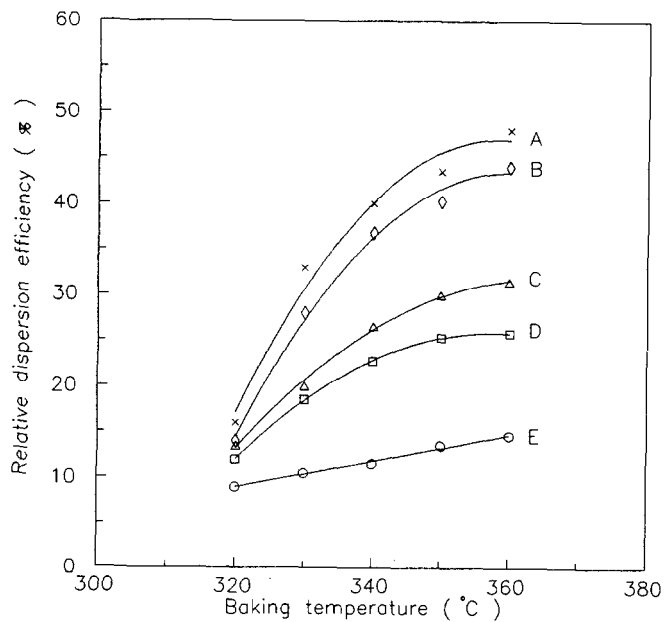
Fig. 3. Relative dispersion efficiency with a baking temperature between 320 and 360 °C. PTFE content (wt.%): (A) 60; (B) 50; (C) 40; (D) 30, and (E) 20.
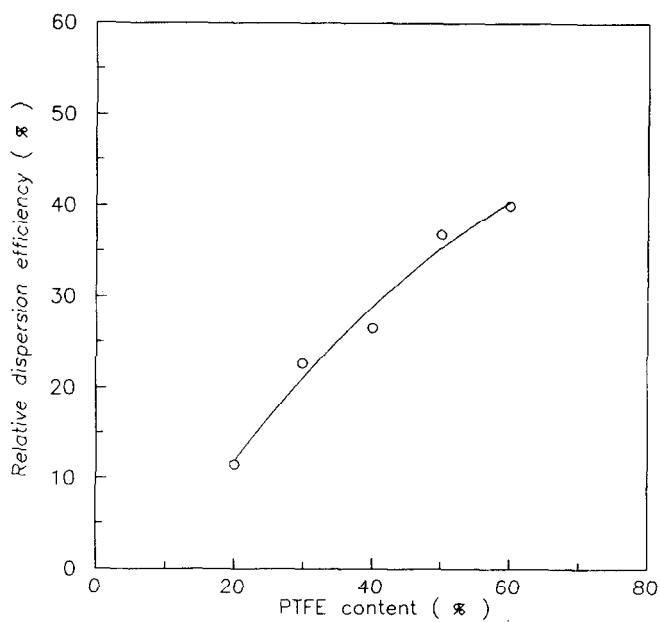
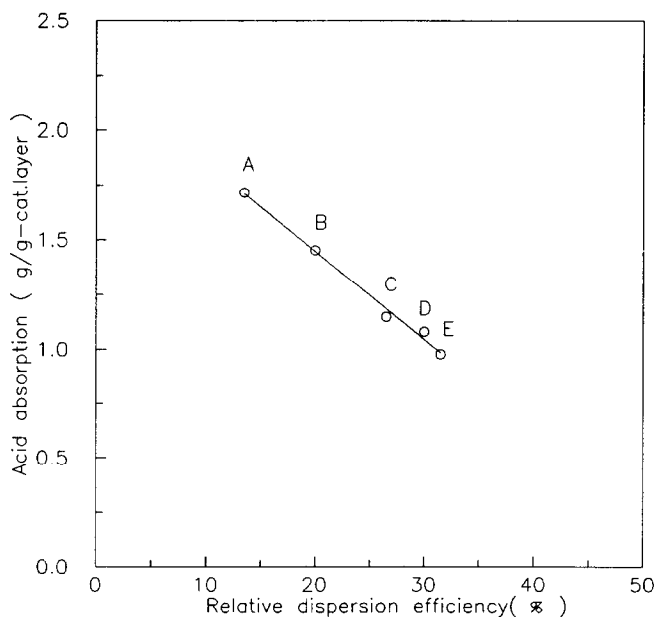Fig. 4. Relative dispersion efficiency with PTFE content in range 20 to 60 wt.% at 340 °C.

Fig. 5. Acid absorption of catalyst layer vs. relative dispersion efficiency of 40 wt.% PTFE; baking temperature (°C) as the controlling parameter: (A) 320; (B) 330; (C) 340; (D) 350, and (E) 360.

with increased relative dispersion efficiency. This is because an electrode with a high relative dispersion efficiency means higher PTFE content and higher PTFE dispersion. A high PTFE content in the electrode will promote high hydrophobicity. Our observation is that the hydrophobicity of the electrode is improved either by increasing the baking temperature or by increasing the PTFE content. It has similarly been reported by Berger [31] that the contact angle increases with increased PTFE content. The acid absorption (and, therefore, the PTFE dispersion) is regulated by changing either the amount of PTFE content in the catalyst layer or the baking temperature.

Effect of PTFE dispersion on agglomerate radius and reaction region

Giner and Hunter [8] have proposed an agglomerate model in which the catalyst particles and electrolyte are homogeneously mixed as a continuum. They suggested that the agglomerate model could suitably describe the performance characteristics of a fuel cell electrode. Kunz *et al.* [32] developed a method to calculate the size of the agglomerate radius, r_0, for a molten carbonate fuel cell. It was found that the size of the agglomerate radius was increased by raising the electrolyte quantity in the catalyst layer. The method can also be used for PAFC electrodes. When the applied pressure is larger than the liquid pressure, PV work (P dV) is done to increase the vapour–liquid interfacial free energy ($\sigma \cos \theta$ dA). The following relation is obtained:

$$P \, dV = -\sigma \cos \theta \, dA \tag{2}$$

where P is the differential pressure between the gas pressure (P_G) and electrolyte pressure (P_L); V the volume of gas, A the vapour–liquid interfacial area, σ the surface tension of the electrolyte, θ the contact angle. The differential pressure in the gas-filled pores is balanced by the surface tension of the electrolyte in the pores. The
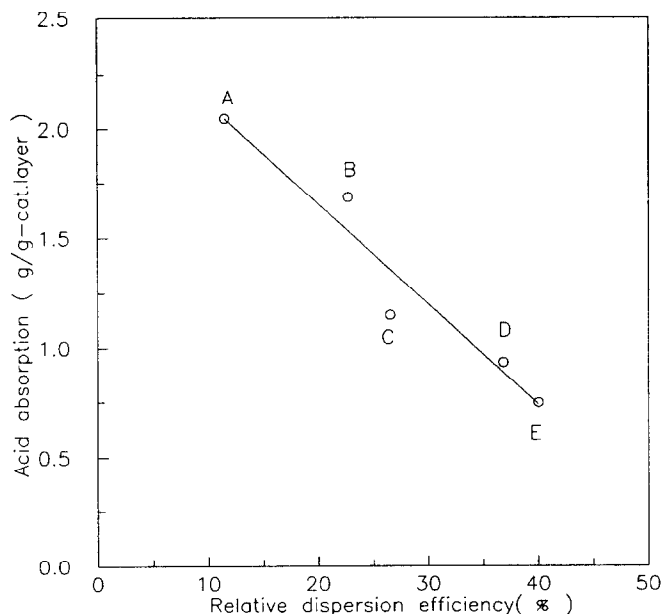
Fig. 6. Acid absorption of the catalyst layer vs. relative dispersion efficiency at 340 °C baking temperature; PTFE content (wt.%) as the controlling parameter: (A) 20; (B) 30; (C) 40; (D) 50, and (E) 60.

relation between the differential pressure $(P_G - P_L)$ and the surface tension can be written as [33, 34]:

$$P_G - P_L = \frac{2\sigma \cos \theta}{r} \tag{3}$$

where r is the pore radius obtained on the pore-size distribution graph by the mercury penetration method.

Combining eqns. (2) and (3) yields:

$$dA = \frac{2dV}{r} \tag{4}$$

Integrating eqn. (4) yields:

$$A = \int_{V_f}^{V_t} \frac{2}{r} \, dV \tag{5}$$

where V_t is the total pore volume of the catalyst layer, and V_f the pore volume wetted by electrolyte in the catalyst layer. If electrolyte and catalyst are considered to be a homogeneous continuum [8, 32], the agglomerate radius (r_0), the vapour–liquid interfacial area and the pore volume wetted by electrolyte are related as follows:

$$\frac{A}{V_f} = \frac{2N\pi r_0 \tau_e \delta}{N\pi r_0^2 \tau_e \delta} \tag{6}$$

where N is the number of agglomerates, τ_e the agglomerate tortuosity, and δ the thickness of catalyst layer. Equation (6) can be simplified further, i.e.:

$$\frac{A}{V_f} = \frac{2}{r_0} \tag{7}$$

r_0 can be obtained by eliminating A from eqns. (5) and (7):

$$r_0 = \frac{V_f}{\displaystyle\int_{V_f}^{V_t} \frac{1}{r}\, dV} \tag{8}$$

In order to express the effect of the PTFE dispersion on the size of the agglomerate radius, a plot was made of agglomerate radius versus relative dispersion efficiency of 40 wt.% PTFE with different baking temperatures (Fig. 7). The data indicate that the agglomerate radius decreases with increased relative dispersion efficiency which is to increased baking temperature. This means that the penetration of the PTFE into the pores is favoured by increasing the PTFE dispersion. The size of the agglomerate radius of the electrode baked at 340 °C with different PTFE contents is shown in Fig. 8. The results indicate that the agglomerate radius decreases with increasing PTFE content. Kunz et al. [32] reported that most pores of the catalyst layer are filled with electrolyte, and this results in a large agglomerate radius. They also indicated that the size of the agglomerate radius was small when the pores were filled with low quantity of electrolyte. This can also be predicted from eqn. (8). High PTFE dispersion will reduce the agglomerate radius so that the voltage loss due to diffusion of dissolved oxygen can be decreased. If the agglomerate radius is small, it causes the effective
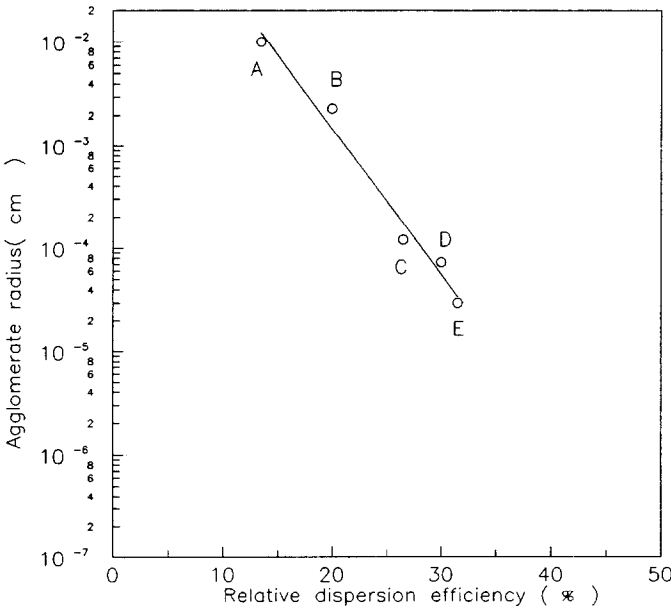

Fig. 7. Agglomerate radius of electrode vs. relative dispersion efficiency of 40 wt.% PTFE; different baking temperatures (°C): (A) 320; (B) 330; (C) 340; (D) 350, and (E) 360.
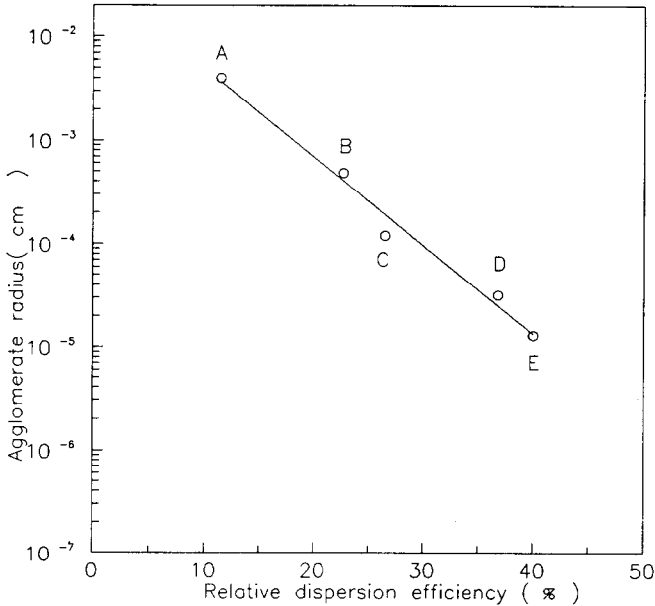
Fig. 8. Agglomerate radius of electrode vs. relative dispersion efficiency at 340 °C baking temperature with different PTFE contents (wt.%): (A) 20; (B) 30; (40) 40; (D) 50, and (E) 60.

electrolyte conductivity to decrease. The porosity of the liquid-filled pores also decreases.

Rearranging eqn. (3) gives:

$$r_f = \frac{2\gamma \cos \theta}{P_G - P_L} \tag{9}$$

where r_f is the radius of the largest flooded pores. Pores larger than r_f are filled with gas and pores smaller than r_f are flooded with electrolyte, if it is assumed that the pores can wet easily. If the pore volume filled with electrolyte and the pore-size distribution are obtained, the radius of the largest flooded pores can be calculated as follows:

$$V_t = \int_{r_*}^{r_f} dV \tag{10}$$

where r_* is the minimum radius obtained from the pore-size distribution graph. The pore volume wetted by electrolyte can be determined by integration between the minimum radius and the radius of the largest flooded pores.

Figure 9 illustrates the effect of PTFE dispersion on the radius of the largest flooded pores of 40 wt.% PTFE electrode when baked between 320 and 360 °C. Clearly, the radius of the largest flooded pores decreases as the relative dispersion efficiency increases. The radii of the largest flooded pores in the electrode baked at 340 °C with different PTFE contents are plotted in Fig. 10. The result shows that the radius of the largest flooded pores decreases with increasing relative dispersion efficiency. This means that the pores of the electrode with a high PTFE dispersion
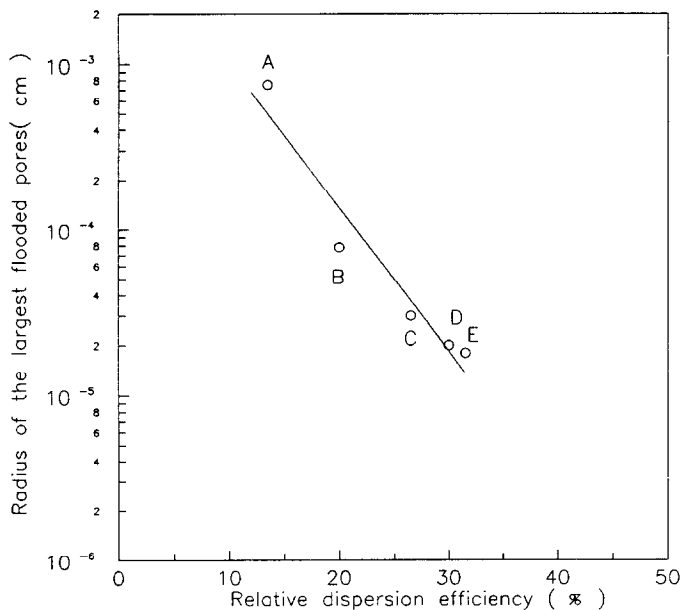
Fig. 9. Effect of relative dispersion efficiency of 40 wt.% PTFE on radius of largest flooded pores with baking temperature (°C) as the controlling parameter: (A) 320; (B) 330; (C) 340; (D) 350, and (E) 360.

are filled with gas due to the high PTFE content. All of the above results can be used for controlling the wetting region of the catalyst layer in order to improve the electrode performance.

Effect of PTFE dispersion on electric conductivity

The PTFE in the porous gas-diffusion electrode is an electric insulator. The PTFE content and its dispersion can naturally affect the electric conductivity of the electrode. The electric conductivity in the catalyst layer and its dispersion have been measured and are shown in Fig. 11. The electric conductivity decreases in response to the increased relative dispersion efficiency when the PTFE content is controlled at 40 wt.%. The electrodes in this case are controlled by PTFE dispersion due to an increased baking temperature.

The electric conductivity of the catalyst layer baked at 340 °C with various PTFE contents is shown in Fig. 12. The conductivity decreases in response to an increase in the relative dispersion efficiency by raising the PTFE content. Low PTFE content or low baking temperature leads to a high solid-phase electric conductivity and less ohmic loss. These electrodes, however, tend to have a large agglomerate radius. Electrodes with a large agglomerate radius tend to have higher diffusion resistance for the dissolved oxygen to reach the electrode surface. Kunz *et al.* [32] indicated that liquid-phase diffusion voltage loss would result from a large agglomerate radius. High PTFE dispersion will reduce the agglomerate radius so that diffusion resistance of the dissolved oxygen can be decreased. Nevertheless, the voltage loss from ionic transport would increase. Therefore, an optimized design must be obtained based on a compromise between diffusion of the dissolved oxygen and electrolytic conductivity.
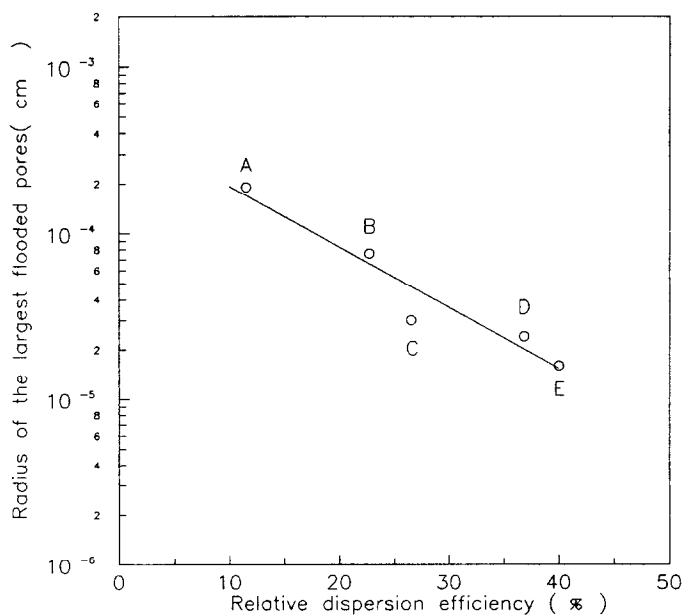
Fig. 10. Effect relative dispersion efficiency at 340 °C baking temperature on radius of largest flooded pores with PTFE content (wt.%) as controlling parameter: (A) 20; (B) 30; (C) 40; (D) 50, and (E) 60.
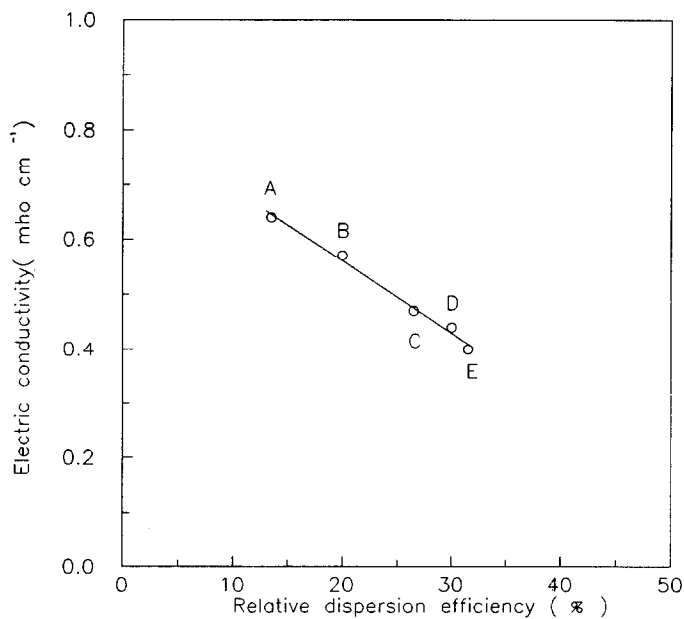

Fig. 11. Electric conductivity of catalyst layer vs. relative dispersion efficiency of 40 wt.% PTFE with different baking temperatures (°C): (A) 320; (B) 330; (C) 340; (D) 350, and (E) 360.
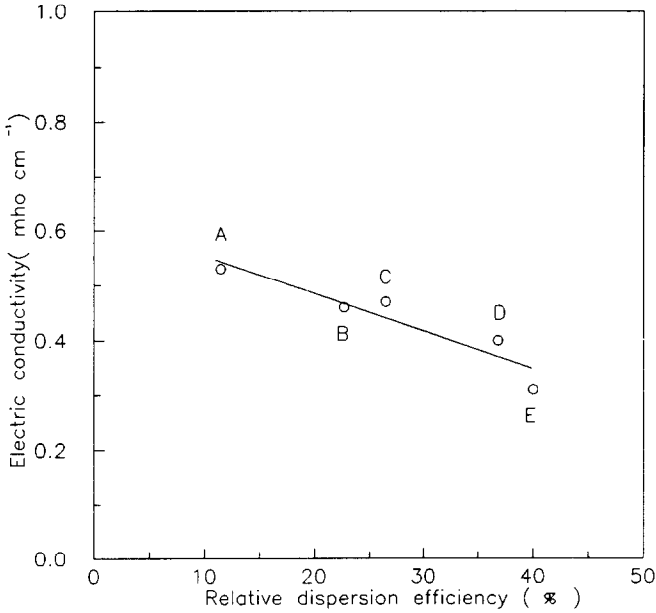
Fig. 12. Electric conductivity of catalyst layer vs. relative dispersion efficiency at 340 °C baking temperature with different PTFE contents (wt.%): (A) 20; (B) 30; (C) 40; (D) 50, and (E) 60.
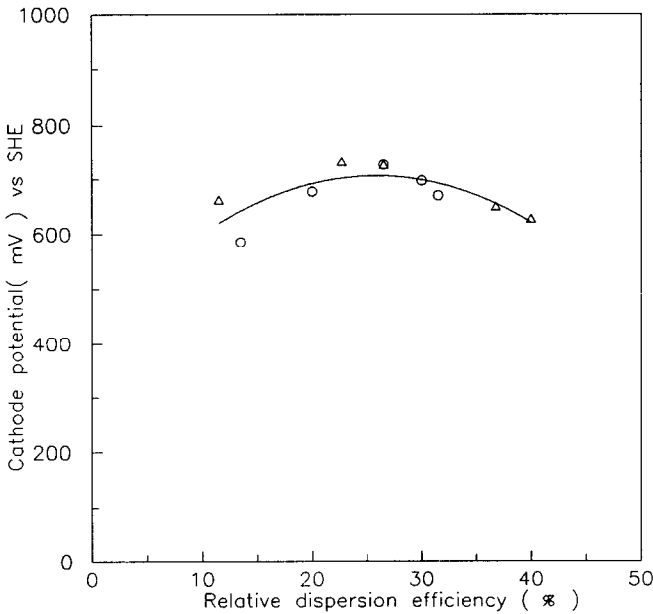

Fig. 13. Cathode potential vs. relative dispersion efficiency at 220 mA/cm² in oxygen: (O) baked at 320 to 360 °C; (△) 20 to 60 wt.% PTFE.

Effect of PTFE dispersion on electrode performance

In this three-phase reaction system, pores with optimal wettability should be formed for satisfactory performance. Figure 13 shows the cathode potential at a discharge current density of 220 mA/cm^2. Apparently, the performance has an optimal point. The performance becomes poor with low PTFE dispersion when the baking temperature is below 320 °C or the PTFE content is below 20 wt.%. The performance is also poor with high PTFE dispersion when the baking temperature is above 360 °C or the PTFE content is above 60 wt.%. Thus, the PTFE dispersion must be controlled. The information of PTFE dispersion can be used for predicting the electrode performance with two preparation parameters (baking temperature and PTFE content). In previous literature, the PTFE content and the baking temperature have only been studied individually. In the work reported here, the two parameters can be combined into a relative dispersion efficiency that becomes a critical processing parameter for fuel-cell electrodes.

Conclusions

The PTFE dispersion can affect not only the acid absorption, electric conductivity of the catalyst layer, the radius of the largest flooded pores and the agglomerate radius, but also the discharge performance of the electrode. The reaction region of oxygen reduction in a phosphoric acid fuel cell can be altered due to change in the PTFE dispersion in the catalyst layer by adjusting either the baking temperature or the PTFE content. The acid absorption, electric conductivity, the radius of the largest flooded pores and the agglomerate radius are found to decrease as the PTFE dispersion is increased. The above properties increase as the PTFE dispersion decreases. PTFE dispersion in the catalyst layer can be controlled within a desired range to prepare efficient electrodes.

Acknowledgements

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