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A New Wet-proof Technique of Gas-diffusion Electrodes

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The development of an electrode having a completely wet-proofed gas-permeable network was achieved by the introduction of carbon support covered with a thin hydrophobic film of directly fluorinated polyethylene. Its promising property as a long life electrode was demonstrated and the electrode structure was proposed.

Poly-tetrafluoroethylene (PTFE) has been used as a hydrophobic binder in gas-diffusion electrodes, consisting of a framework of carbon black.$^{1-5)}$ Excess flooding of the network with electrolyte is still a serious problem, reducing the life time of phosphoric acid fuel cells (PAFC) in addition to sintering of catalyst clusters. The cell performance shows a large decay over time, resulting from restricted gas diffusion to the catalyst clusters due to drawing with electrolyte. It is thought that the carbon surface is not covered with PTFE, due to the large size of conventional PTFE particles, shown schematically in Fig. 1(A), so that the hydrophobic property of the electrode is not maintained for a long time. So, the development of the completely wet-proofed gas network with good gas permeability is essential for PAFC.

We have solved this problem by covering the carbon surface with a very thin hydrophobic film of directly fluorinated polyethylene (FPE). This is shown schematically in Fig. 1(B). A FPE-treated carbon black is denoted as FPE-CB in this paper. Since the discovery of the use of fluorine gas to fluorination reactions, the direct fluorination of carbon has been carried out.$^{6,7)}$ The fluorination of bulky polyethylene (PE) surface under the presence of a small amount of oxygen has been found to provide a hydrophilic property to its surface,$^{8)}$ but there have been no studies of a hydrophobic film of FPE having a property similar to PTFE. This has

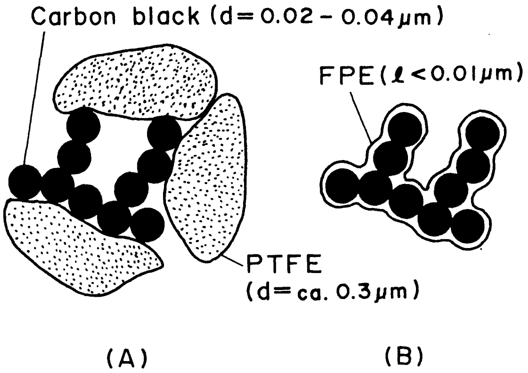

Fig. 1. Schematic structures of carbon blacks wet-proofed by (A); conventional PTFE particles and (B); fluorinated polyethylene film. Symbols d and l stand for a particle size and a film thickness, respectively.

been accomplished in the present study by the following method: mixtures of carbon black (Denka Black: Denki Kagaku Kogyo) and PE (Ultzex: Mitsui Sekiyu Kagaku Kogyo) dissolved in hexane were heat-treated at 170 °C for 30 min in nitrogen gas to obtain a smooth PE coating. The coated film was fluorinated with 5 vol% fluorine gas diluted with nitrogen at 60 °C for various reaction times from 0.5 to 4 hrs, depending on the thickness of PE film. Gravimetrically determined conversion of the film to FPE was more than 90%. The more details of this preparation will be published elsewhere.

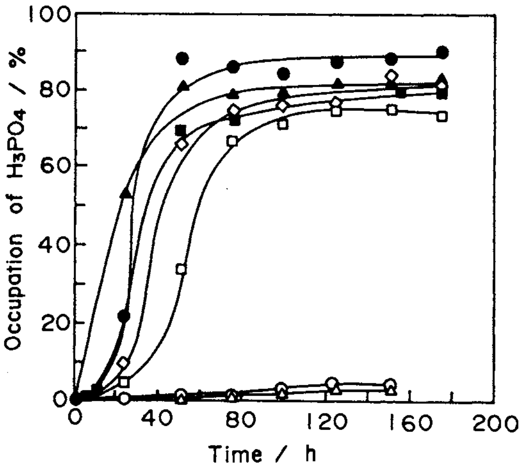

Fig. 2. The change of pore occupation by H_3PO_4 with time at 190 °C in gas-diffusion layers wet-proofed by FPE. FPE content (▲; 5%, ■;10%, ◇; 20%, △; 30%, ○; 40%, ●; 0%(PTFE=0%), □; 0%(PTFE=40%)). FPE-CB was bound with an additional 20 wt% PTFE.

The FPE-CB was applied to gas-diffusion layers by using 20 wt% PTFE dispersion (D1: Daikin Kogyo) as the binder. Figure 2 shows the filling behavior of hot phosphoric acid into the layers with time, measured by gravimetric technique, which were contacted with a porous carbon paper impregnated phosphoric acid. The electrolyte absorption increased with time and exhibited a maximum steady value. The hydrophobic properties of the layers are improved by increasing FPE content, and almost a completely hydrophobic property is achieved at 30 to 40 wt% FPE contents, i.e. only a few % of the pore volume is occupied by the electrolyte with the remainder operating as the gas supplying network. Superior property of the FPE becomes more clear, compared with a sample containing no FPE but with 40 wt% PTFE and an additional 20 wt% PTFE as the binder, indicated by (□) in the figure.

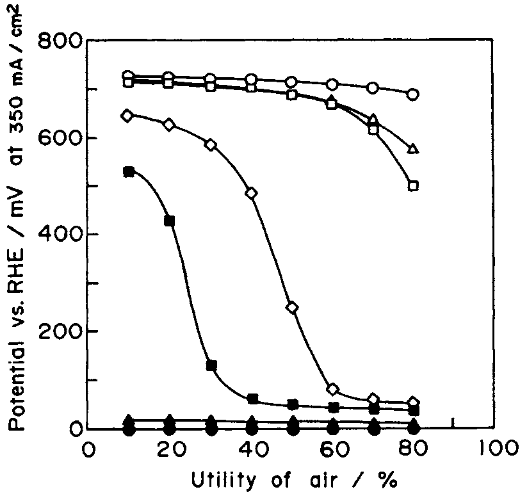

Fig. 3. Dependence of the IR free electrode performances of air cathodes, attached FPE wet-proofed gas-diffusion layers, upon the utilization of air at 350 mA/cm^2, 190°C in 100% H_3PO_4. The FPE contents correspond to the same symbols as those indicated in the caption of Fig. 3.

These layers were applied to PAFC electrodes by attaching to a conventional catalyst layer by hot-pressing. The latter consisting of a mixture of catalyzed carbon black (CBPt) loaded with 10 wt% Pt and PTFE dispersion of 40 wt% relative to the carbon black.$^{4)}$ Steady half-cell performances for the reduction of oxygen in air were measured on the electrodes at 190 °C in 100% phosphoric acid under a potentiostatic condition. Figure 3 shows the effect of FPE content on the air utilization property, where the electrode potentials at a constant current density of 350 mA/cm^2 were plotted against the utilization of air. A high electrode potential could be kept up to a high air utilization by increasing the FPE content due to the improved gas permeability, and no noticeable decrease of the electrode potential was found until 80% utilization of air was achieved at 40 wt% FPE coating. In this way, it was demonstrated that good enough gas-permeability can be achieved without the sacrifice of the hydrophobic property of the catalyst layers.

Figure 4 shows schematic structures, comparing reaction layers of gas-diffusion electrodes based on the conventional concepts (a) and on the present one (b) which is an expansion from that we have proposed previously.$^{5)}$ In the former, CBPt is mixed uniformly with PTFE, and that part not in contact with PTFE forms the electrolyte network, and the other part coated with PTFE forms the gas network. In such structure, however, the improvement of catalyst utilization and the gas permeability are in antithetical relationship. Consequently, there is an essential limitation for the improvement of the electrode performance by conventional structures through optimization of the mixing conditions. On the other hand, the functions of the electrolyte network and the gas network are allotted to the two different types of particles in the present catalyst layer shown in Fig. 4(b). We have demonstrated in a prototype structure of Fig. 4(b) that the functions can be successfully separated, resulting in 100% utilization of the catalyst clusters without the gas-diffusion polarization.$^{5)}$ The only problem was flooding of the wet-proofed carbon blacks for the gas network with time, due to the large size of PTFE as indicated in Fig. 1(a).

In order to demonstrate the superiority of the FPE-CB as the gas-pore network material, a series of FPE-CB were fabricated into catalyst layers (refer Fig. 4(b)) by hot-pressing mixtures (3/7) of the FPE-CB and the CBPt with 40 wt% PTFE as the binder, which is approximately the same PTFE content level as the conventional catalyst layer.$^{5)}$ The filling behavior with hot phosphoric acid was measured in the same manner as that for Fig. 2, and is shown in Fig. 5. The electrolyte occupation with phosphoric acid into the catalyst layer wet-proofed only with PTFE increases with time and approaches ca. 70% after 150 hours, i.e. about 30% of total pore volume remains as the gas permeable network.

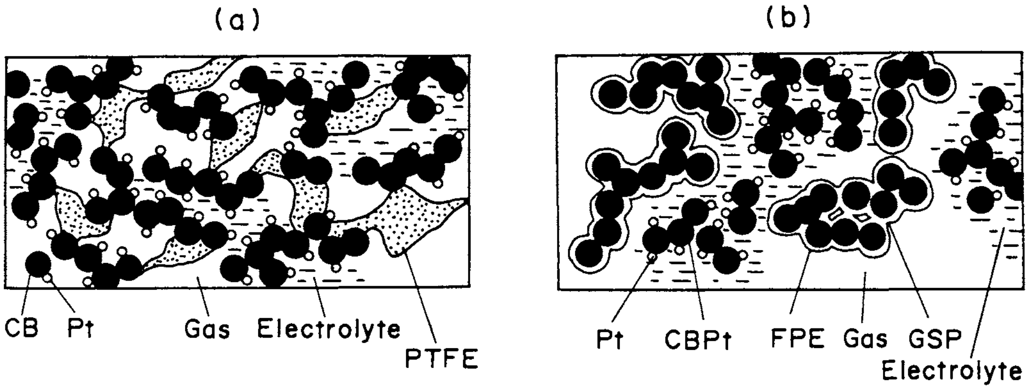

Fig. 4. Comparison of the reaction layer structures of gas-diffusion electrodes. (a) a conventional concept using PTFE, (b) a modern concept using FPE. CBPt; Catalyzed carbon black, GSP ; gas-supplying carbon powder.

The catalyst layers containing 30 or 40 wt% FPE-CB reach a similar acid occupation to that of only PTFE treatment; although they show relatively a higher hydrophobic property at the initial stages. The layer containing FPE-CB at more than 50 wt% exhibits a steady acid occupation of about 50%. It was estimated that the pore volume of the FPE-treated portion in the catalyst layers was occupied with electrolyte only to ca. 20%; although that of the PTFE treated portion achieved about 70%. The pores free from the electrolyte may be expected to act as complete gas network, extending the life of PAFC.

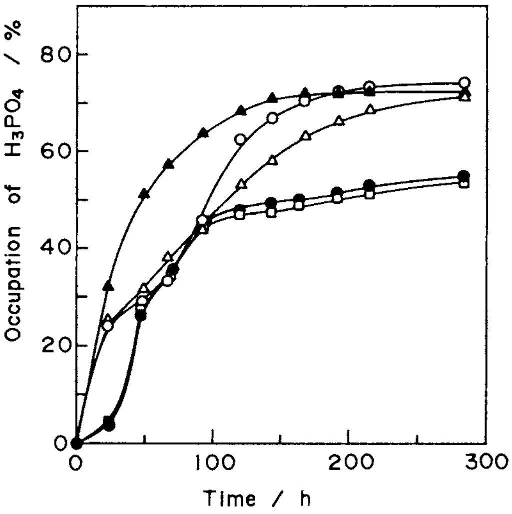

Fig. 5. The change of pore occupation by H_3PO_4 with time in the catalyst layer proposed in Fig. 4(b). FPE contents (○; 30%, △; 40%, □; 50%, ●;60%, ▲; 0%(PTFE=40%))

Problems still remaining are: the FPE-CB has relatively high electric resistivity and loses the weight at the temperatures higher than 160 °C, probably because of the insufficient PE fluorination. The former problem may be covered by the combination of the FPE-CB and the electric-conductive CBPt in the manner as shown in Fig. 4 (b). The latter must be examined by spectroscopic analyses. It was found that this proposed wet-proofing technique for carbon materials may promise longer life for fuel cells using the high hydrophobic property and the good gas-permeability in the catalyst layers. The details of electrode construction and electrode performances will be published elsewhere.

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