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Studies of gas diffusion electrodes for polymer electrolyte fuel cells: effect of polytetrafluoroethylene content on the microstructure of the diffusion layer.

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ABSTRACT

The following conclusions can be drawn with respect to the influence of the PTFE content on the microstructure in PTFE/C films:

- i) Two distinctive pore distributions with boundary of about 0.35 μm were detected.
- ii) The overall porosity of samples decreased with increasing PTFE content of the layer.
- iii) The microporosity of the samples was only attributable to the intra-agglomerate space of carbon particle.
- iv) The porosity of carbon agglomerates was independent of PTFE amount of the layer.
- v) From 10 to 20 wt% PTFE the polymer coated the pores with size higher than 2 μm , from 20 to 40 wt% PTFE the polymer filled the pores in the range 1 to 2 μm , above 40 wt% PTFE the only effect of the polymer was to increase the thickness of the layer.

1.- INTRODUCTION

Electrode structures in polymer electrolyte fuel cells (PEFC) have evolved from two layer structure to three layer structure. Dual-layer electrodes were constituted by a hydrophobic support layer and a porous electrocatalyst layer formed by Pt on carbon (Pt/C) as a catalyst agent, polytetrafluoroethylene (PTFE) and polyperfluorosulphonic acid (Nafion). Three layer electrodes were made by a porous support layer, a diffusion layer consisting of carbon particles and PTFE and a catalyst layer formed by Pt/C and Nafion. The performances of the electrodes depend on many parameters: 1) type of support (carbon paper or carbon cloth) and his characteristics (porosity and thickness); 2) type of catalyst (Pt alone, Pt with other metals, macrocycles, Pt amount, Pt size, type of carbon as the support); 3) PTFE amount; 4) Nafion amount; 5) thermal treatment; 6) thickness of diffusion and catalytic layers; 7) fabrication process. The fabrication process of both diffusion and catalyst layer can be carry out by different techniques as screen-printing, rolling, brushing, filtering and spraying.

The incorporation of PTFE into the diffusion or catalyst layer serves two functions: binding the high surface carbon particles into a cohesive layer, and imparting some hydrophobic character to the layer. In this report the effect of PTFE amount on the morphological characteristics of the electrode is reported.

Three layer low catalyst loading gas diffusion electrodes were prepared, using the spray technique for the deposition of both diffusion and catalyst layers.

2.- ELECTRODE PREPARATION

The electrodes were prepared by a spray technique using platinum-on-carbon (20% Pt/C) catalyst (Electrochem. Inc.), carbon powder (Vulcan XC-72, Cabot), a carbon paper

substrate (Toray TGPB-090), a polytetrafluoroethylene (PTFE) dispersion (35 wt% PTFE aqueous dispersion, Hostaflon 5033 Hoechst), a Nafion solution (5 wt% Nafion 1100 EW solution, Solution Technology Inc.) and glycerol. The carbon loading in the diffusion layer was 2 mg/cm^2 ; the platinum loading in the catalyst layer was 0.1 mg/cm^2 .

2.1- Preparation of the diffusion layer

The slurry was prepared by mixing and stirring in an ultrasonic bath at room temperature for 25 min a water/isopropanol suspension of carbon and an appropriate amount of PTFE dispersion. The suspension was sprayed onto the carbon paper. The layer was dried in a controlled air atmosphere at 120°C for 1 h, then at 280°C for 30 min to remove the dispersion agent contained in PTFE, and finally sintered at 350°C for 30 min.

2.2- Preparation of the catalyst layer

To prepare the catalyst layer, a homogeneous suspension was formed from the desired amounts of the Pt/C catalyst, the glycerol and the Nafion solution with ethanol as solvent. The resulting ink was mixed under continuous stirring in an ultrasonic bath at room temperature for 30 min. Then, the ink was spray deposited onto the diffusion layer to form the gas diffusion electrode.

3.- MORPHOLOGICAL CHARACTERIZATION

Morphological analysis of the diffusion layer was performed before the deposition of the catalyst layer, by using mercury-porosimetry and Scanning Electron Microscopy (SEM).

The diffusion layer had two distinctive pore distributions with boundary about $0.35 \mu\text{m}$. To identify these different regions, we will call micropores the pores with size lower than $0.35 \mu\text{m}$ and macropores the pores having size higher than $0.35 \mu\text{m}$.

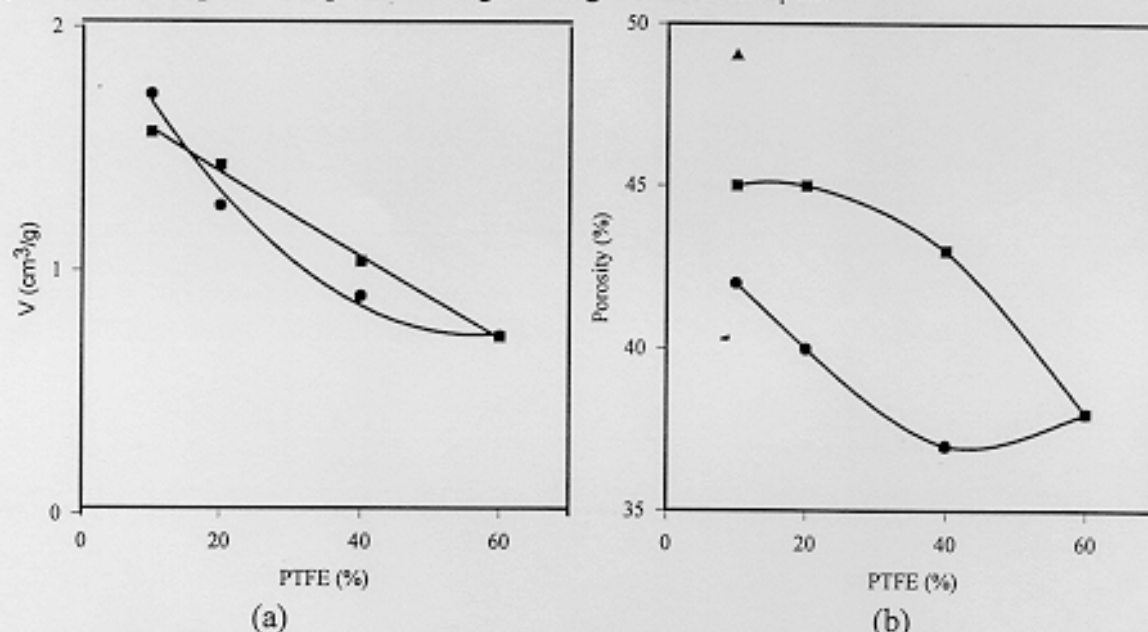


Fig.1 (a) Specific micropore volume V_{lm} (■) and macropore volume V_{ls} (●), and (b) microporosity (■) and macroporosity (▲) Layer + carbon paper, (●) layer, as a function of PTFE content of the layer.

Fig.1 shows the dependence of specific micropore volume V_{lm} and macropore volume V_{ls} (a), and microporosity and macroporosity (b) on PTFE content of the layer. The relationship between the specific pore volume V_{lf} and PTFE amount of the film is the following:

$$V_{if} = V_{Cf} + (V_{Cf} - V_{Pf}) x_P \quad (1)$$

where V_{Cf} is the specific carbon pore volume, V_{Pf} is the specific PTFE pore volume and x_P is the mass fraction of PTFE in the layer.

As shown in Fig.1a, the specific micropore volume of the layer V_{im} linearly depends on PTFE content: this means that the specific carbon micropore volume V_{Cm} and the specific PTFE micropore volume V_{Pm} are constant. By extrapolating to 0 wt % PTFE we obtain $V_{Cm} = 1.740 \text{ cm}^3/\text{g}$ and $V_{im} = 0.067 \text{ cm}^3/\text{g}$. Then, being negligible V_{Pm} en respect to V_{Cm} , the smaller pores were indentified with the space in and between the carbon particles in the agglomerates. Specific macropore volume V_{ls} , instead, do not depend linearly on fluoropolymer amount in the layer (Figs2). This means that total specific carbon pore volume V_{Ct} is a function of x_P ; then, the decrease of the specific macropore volume with increasing PTFE is not only attributable to lower PTFE porosity than that of the carbon, but to the filling the carbon interagglomerates voids by the polymer, giving rise to the decrease of the specific carbon pore volume V_{cs} .

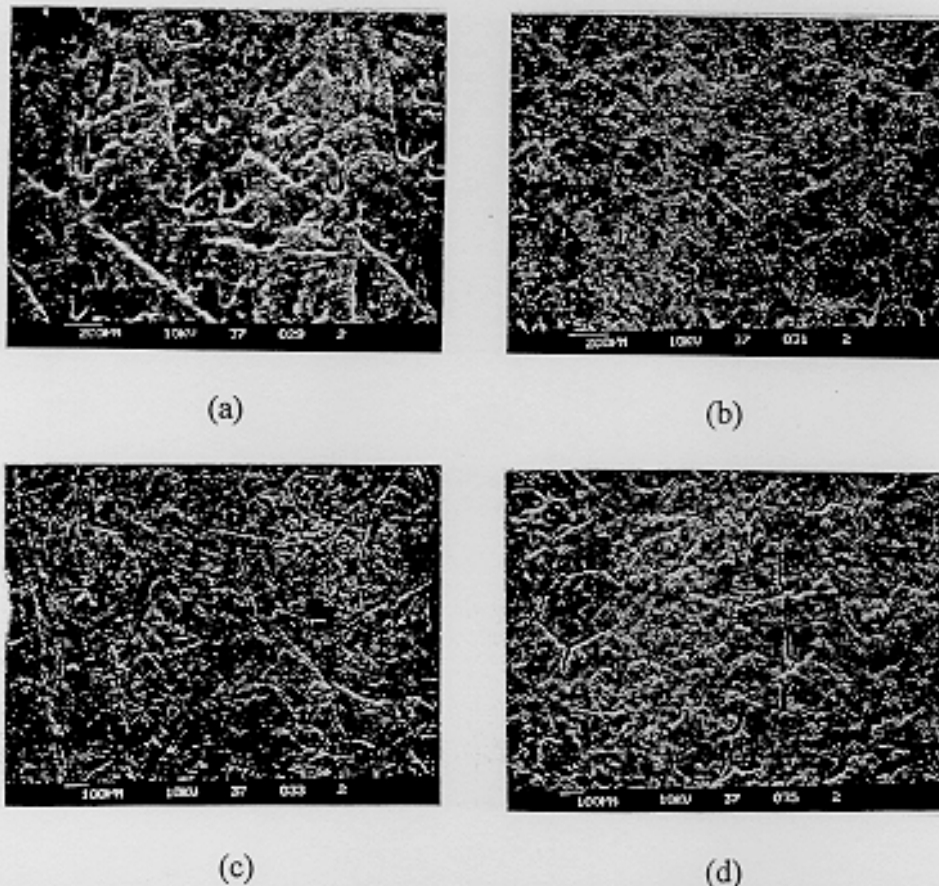


Fig.2 Scanning electron micrographs of the surface of C/PTFE diffusion layer-carbon paper system with (a) 10 wt % PTFE, (b) 20 wt % PTFE, (c) 40 wt % PTFE and (d) 60 wt % PTFE.

Fig.2 a-d shows SEM micrographs of the diffusion layer on the carbon substrate after sintering at 350°C: a clear distinction of carbon particles and polymer is not possible. In Fig.2a both macropores and the fibers of the carbon paper are visible; macroporosity is related both to C/PTFE film and to the substrate. At higher contents of PTFE, as shown in Fig.2 b-d, it seems that the polymer covers all the surface of the layer; the presence of

cracks, increasing with PTFE content, is also revealed.

The average thickness of the films can be calculated from porosimetric and gravimetric measurements, as the following relationship (neglecting the fraction of polymer which enters the porosity of the substrate):

$$Z = [V_{it} + (1 - x_p)/\rho_C + x_p/\rho_P]W_I \quad (2)$$

where Z is the average thickness of the film, ρ_C and ρ_P are the densities of carbon (2.0 g/cm^3) and PTFE (2.2 g/cm^3), respectively. As the relation (2), the thickness of the samples slightly increases up to 40 wt% PTFE, while a very high increase is denoted going from 40 to 60 wt% of fluoropolymer.

From porosimetric and gravimetric data, we have evaluate total porosity, microporosity and macroporosity of the layer, as:

$$P_f = V_{if} W_f / Z \quad (3)$$

Where P_f is the porosity of the film (when $f = t$ total porosity, $f = m$ microporosity, $f = s$ macroporosity). Fig.1b shows the dependence of microporosity and macroporosity on PTFE: the microporosity decreases with increasing PTFE, by the decrease of the amount of carbon in the samples. The macroporosity, instead, seems to go through a minimum. To analyse this behaviour, we have divided the macroporosity into three parts, the first from 2 to 50 μm , the second from 1 to 2 μm , and the third from 0.35 to 1 μm .

Going from 10 wt% to 20 wt% PTFE, besides coating carbon paper porosity, the polymer coats carbon interagglomerate pores with size $> 2 \mu\text{m}$; the increase of porosity with pore size $> 2 \mu\text{m}$ above 20 wt% PTFE is attributable to the formation of cracks (see Fig.2 b-d) during thermal treatment of the samples.

The polymer fills the pores in the range 1 to 2 μm (carbon inter-agglomerate pores) going from 20 to 40 wt% PTFE, binding the agglomerates of carbon particles.

The pores in the range 0.35 to 1 μm show the same dependence on fluoropolymer as that of microporosity; being these pores related to carbon porosity, their decrease going from 40 to 60 wt% PTFE is due to the decrease of carbon amount in the layer.

A.c. Impedance Spectroscopy measurements were performed on electrodes having the C/PTFE film as the diffusion layer. Generally the impedance spectra for SPEFC cathode include two arc, a higher frequency arc reflecting the combination of an effective charge transfer resistance and a double-layer capacitance within the catalyst layer, and a lower frequency arc reflecting mass-transport limitations in the gas phase within the diffusion layer. Such an increase in effective charge-transfer resistance at the higher cell current densities occurs when the O_2 concentration drops within catalyst layer as a result of oxygen transport limitations. The feature of the lower frequency loop is affected by both porosity and thickness (as higher are porosity and thickness as higher is low frequency resistance) of the diffusion layer. When PTFE fills the pores, as the diffusivity of oxygen in PTFE is very low, the O_2 partial pressure is lowered at the diffusion/catalyst layer interface. The monotonous increase of resistance from low frequency impedance measurements with increasing PTFE content of the film is in agreement with the decrease of total porosity with increasing PTFE.