

Morphological characteristics of carbon/polytetrafluoroethylene films deposited on porous carbon support

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The effect of polytetrafluoroethylene (PTFE) content on morphological characteristics of carbon/PTFE films deposited on porous carbon support was investigated by mercury-porosimetry, scanning electron microscopy (SEM) and a.c. impedance spectroscopy. The microstructure of the film was affected by the content of fluoropolymer. The layer has two distinctive pore distributions with a boundary of about 0.35 μm . The polymer coated the pores with size higher than 1 μm (carbon interagglomerate pores), while the pores with size lower than 1 μm were not influenced by the presence of PTFE. Above 40 wt % PTFE, a further supply of polymer did not fill the pores, but increased the thickness of the sample. The presence of cracks, increasing in number and size with PTFE content, was also revealed.

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1. Introduction

Porous carbon/polytetrafluoroethylene (PTFE) films deposited on a carbon substrate are used as diffusion layer in polymer electrolyte fuel cell (PEFC) electrodes [1,2]. PTFE is added to high surface area carbon powder as a binder and hydrophobic agent, coating the pores between the carbon particle agglomerates [3,4]. Few works have been published on the effect of PTFE amount on the morphology of the Pt/C/PTFE layer [5,6]. No work was performed on the morphological analysis of C/PTFE films. Efforts to verify PTFE in thin Pt/C/PTFE layer by transmission electron microscopy (TEM) were unsuccessful [7,8]. Also, electron energy loss spectrometry (EELS) was utilized in an attempt to identify PTFE in thin films by the presence of fluorine. Although fluorine can be detected in very thin PTFE films by the EELS technique, the fluorine K-shell edge is very weak. This condition necessitates regions which are spatially large but still thin for edge visibility; specimens of this nature can be made from bulk PTFE, not from C/PTFE films generally used in the electrode material [8].

Mercury porosimetry, coupled to scanning electron microscopy (SEM), seems to be the best method to analyse the morphology of Pt/C/PTFE layer [5,6]. Moreover, by porosimetric measurements it is possible to evaluate the average thickness of the layer; this allows one to overcome the difficulty of the measurement of the non-uniform thickness of the layer. Finally, a.c. impedance spectroscopy measurements,

being related to the porosity of the diffusion layer of the samples [9], were also performed.

The aim of this work is to establish a relation between PTFE amount and morphology of C/PTFE films, obtained by spray deposition of a homogeneous suspension of carbon powder and fluoropolymer on a porous carbon support.

2. Experimental procedure

A homogeneous water/isopropanol suspension was prepared by mixing and stirring the carbon powder (ground Vulcan XC-72 powder, Cabot) with an appropriate amount of PTFE dispersion (35 wt % PTFE aqueous dispersion, Hostafion 5033 Hoechst) in an ultrasonic bath at room temperature for 25 min. The suspension was spray deposited on a porous support (carbon paper Toray TGPH-090). The diffusion layer was dried in air at 120 °C for 1 h, followed by thermal treatment at 280 °C for 30 min to remove the dispersion agent contained in PTFE, and finally sintered in air at 350 °C for 30 min. Sintering temperature must be higher than the PTFE melting point (around 325 °C) [10]; from the results of electrochemical measurements of a Pt/C/PTFE layer with 50 wt % PTFE [11] it can be inferred that when the sintering temperature is lower than the PTFE melting point, the polymer does not coat the pores.

To prepare the electrode for a.c. impedance analysis, a homogeneous suspension, formed from the desired amounts of the Pt/C catalyst (20 wt % Pt/C,

Electrochem. Inc.), the glycerol and the Nafion solution (5 wt % Nafion 1100 EW solution, Solution Technology Inc.) with ethanol as solvent, was spray deposited onto the diffusion layer to form the catalyst layer.

Porosimetric measurements were performed using a C. Erba Mercury Porosimeter model 2000. Micrographs were obtained with a Cambridge Stereoscan 250 mk3 scanning electron microscope. Electrochemical impedance measurements were performed by a Solartron frequency response analyser model 1260.

3. Results and discussion

The layer has 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 smaller than $0.35 \mu\text{m}$ and macropores the pores with size greater than $0.35 \mu\text{m}$.

Table I shows the experimental values obtained by porosimetric measurements (the specific pore volume of the carbon paper substrate alone and with C/PTFE film), the weight of carbon per unit area of support and the weight of the diffusion layer per unit area of support. As a side of the substrate is covered by the film, we have divided the specific pore volume of the carbon paper by two. From the data of Table I we have calculated the specific pore volume of the C/PTFE layer by the following relationship

$$V_{\text{if}} = (V_{\text{if}}W_{\text{t}} - V_{\text{sf}}W_{\text{s}})/W_{\text{l}} \quad (1)$$

where V_{if} , V_{sf} and V_{if} are the specific pore volumes of the layer, the substrate and the substrate with C/PTFE film, respectively (when $f = t$, total specific pore volume, $f = m$, specific micropore volume and $f = s$ specific macropore volume); W_{s} , W_{l} and W_{t} are the weight of the substrate, the layer and the substrate with the film, respectively.

Fig. 1a–c shows the dependence of V_{it} , V_{im} and V_{is} on PTFE content of the layer. The relationship between the specific pore volume V_{if} and PTFE amount of the film is as follows

$$V_{\text{if}} = V_{\text{Cf}} + (V_{\text{Pf}} - V_{\text{Cf}})x_{\text{P}} \quad (2)$$

where V_{Cf} is the specific carbon pore volume, V_{Pf} is the specific PTFE pore volume ($f = t$ total, $f = m$ micro,

TABLE I Total specific pore volume of the substrate with the layer (V_{it}), specific micropore volume of the substrate with the layer (V_{im}), weight of carbon per unit area of support (W_{C}), and weight of layer per unit area of support (W_{l}) at different PTFE content of the layer

PTFE (%)	V_{it} ($\text{cm}^3 \text{g}^{-1}$)	V_{im} ($\text{cm}^3 \text{g}^{-1}$)	W_{C} (mg cm^{-2})	W_{l} (mg cm^{-2})
10	0.584	0.291	1.95	2.17
20	0.531	0.289	1.92	2.40
40	0.5705	0.312	2.51	4.18
60	0.470	0.244	1.78	4.45

The specific pore volume of the substrate was $0.1225 \text{ cm}^3 \text{g}^{-1}$ (total, V_{st}), $0.0735 \text{ cm}^3 \text{g}^{-1}$ (micropore, V_{sm}) and $0.0490 \text{ cm}^3 \text{g}^{-1}$ (macropore V_{ss}); the weight of the substrate, W_{s} , was 12.72 mg cm^{-2} .

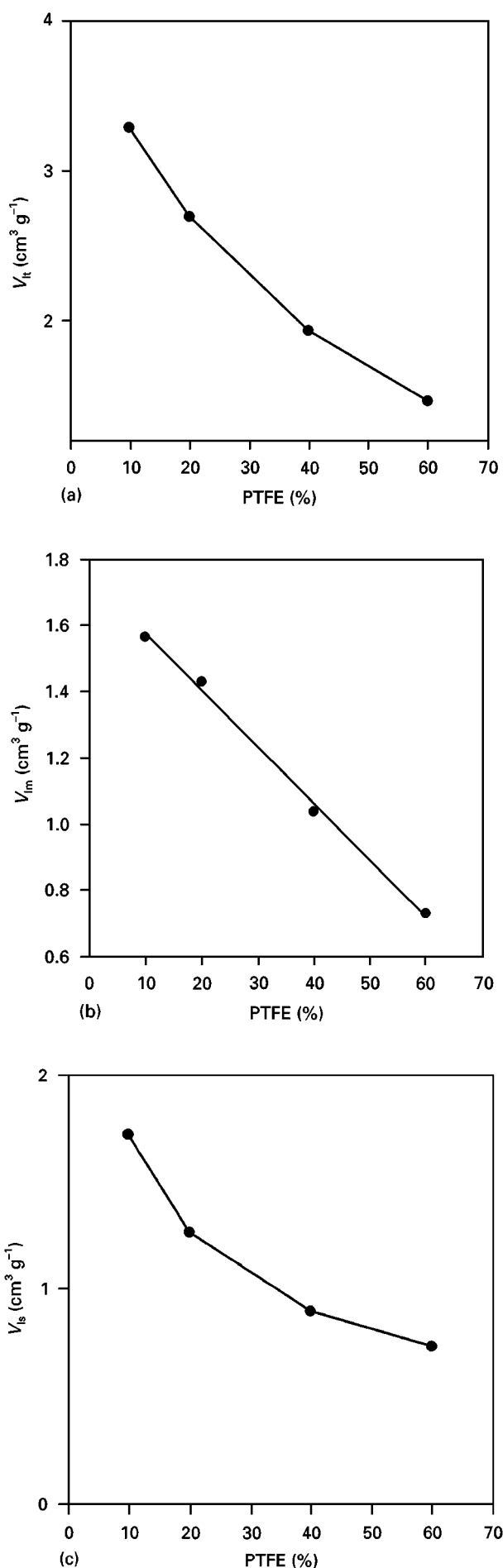


Figure 1 Total specific pore volume V_{it} (a), specific micropore volume V_{im} (b) and specific macropore volume V_{is} (c) as a function of PTFE content of the film.

$f = s$ macro) and x_p is the mass fraction of PTFE in the layer.

As shown in Fig. 1b, the specific micropore volume of the layer V_{lm} 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 $V_{Cm} = 1.740 \text{ cm}^3 \text{ g}^{-1}$ and $V_{Pm} = 0.067 \text{ cm}^3 \text{ g}^{-1}$. Then, as V_{Pm} is negligible with respect to V_{Cm} , the smaller pores were indentified with the space in and between the carbon particles in the agglomerates.

Total specific pore volume V_{lt} and specific macropore volume V_{ls} , instead, do not depend linearly on fluoropolymer amount in the layer (see Figs 1 and 3). This means that specific carbon macropore volume V_{Cs} is a function of x_p ; then, the decrease of the specific macropore volume V_{ls} with increasing PTFE is not only attributable to lower PTFE porosity than that of the carbon, but also to the filling the carbon inter-agglomerates voids by the polymer, giving rise to the decrease of the specific carbon macropore volume V_{Cs} .

Fig. 2a–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 fibres 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. 2b–d, the polymer covers all the surface of the carbon paper network; the presence of cracks, increasing in number

and size with PTFE content, is also revealed. The depth of these cracks increases with PTFE (Fig. 3a, b).

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)

$$Z = [V_{lt} + (1 - x_p)/\rho_C + x_p/\rho_P]W_1 \quad (3)$$

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.

Table II shows the average thickness of samples as Equation 3. The thickness of the sample with 10 wt % PTFE, anomalously higher than that of the sample with 20 wt % PTFE, is overvalued, as part of porosity is related to carbon paper (this is shown in the SEM micrograph (Fig. 2a)), so it cannot contribute to the thickness. For this reason, in the first approximation, in the following relations we will use for 10 wt % PTFE sample the same value of thickness as that of 20 wt % PTFE sample. The high value of thickness for sample with 40 wt % PTFE is caused by carbon loading, higher than that of other samples. To evaluate the net effect of PTFE content on thickness, we have normalized to the same carbon loading, $C = 2 \text{ mg cm}^{-2}$, as in Equation 4

$$Z_n = ZW_{C2}/W_C \quad (4)$$

where Z_n is the normalized average thickness, W_C and W_{C2} are the actual and normalized carbon loading,

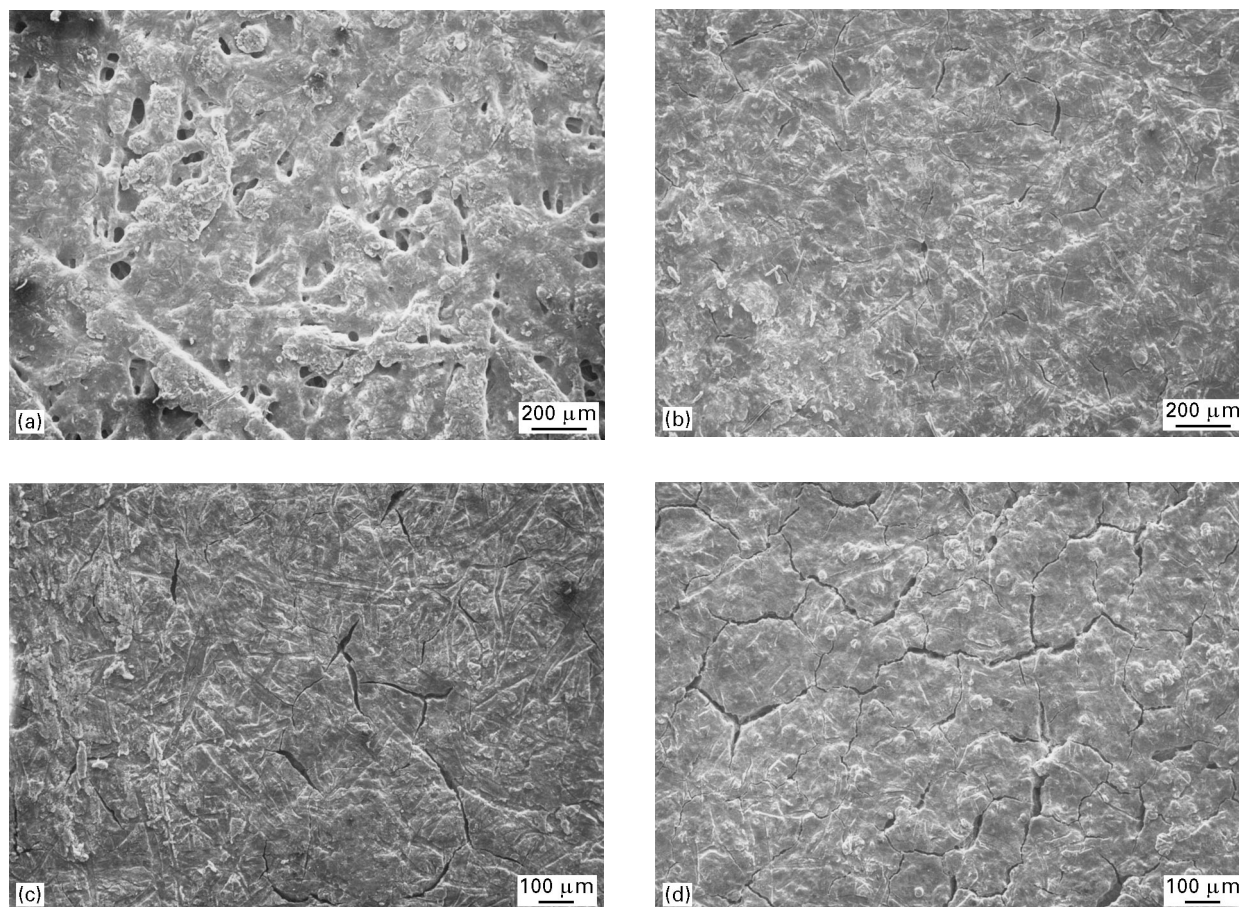


Figure 2 Scanning electron micrographs at magnification $50\times$ of the surface of C/PTFE film-carbon paper system with (a) 10 wt % PTFE, (b) 20 wt % PTFE, (c) 40 wt % PTFE and (d) 60 wt % PTFE.

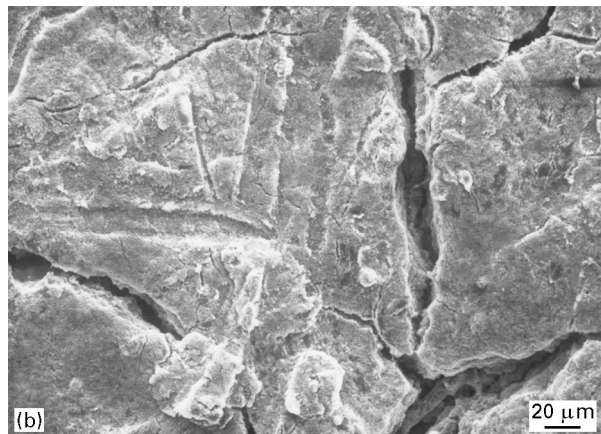
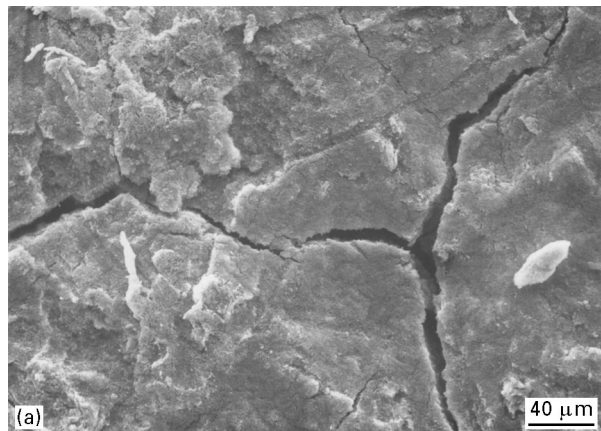


Figure 3 Scanning electron micrographs at magnification $300\times$ of the surface of C/PTFE films with (a) 20 wt % PTFE and (b) 60 wt % PTFE.

TABLE II Sample thicknesses at various PTFE content of the film as in Equation 3

PTFE (%)	Z (μm)
10	82
20	76
40	101
60	86

respectively. As shown in Fig. 4, where Z_n is plotted as a function of PTFE, the thickness of the samples slightly increases up to 40 wt % PTFE, while a very high increase is noted going from 40 to 60 wt % of fluoropolymer.

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

$$P_f = V_{if} / [V_{it} + (1 - x_P) / \rho_C + x_P / \rho_P] = V_{if} W_i / Z \quad (5)$$

where P_f is the porosity of the film (when $f = t$ the total porosity, $f = m$, microporosity, $f = s$ macroporosity).

As shown in Fig. 5, total porosity of the samples decreases with increasing PTFE content of the layer. As previously denoted, all the micropore volume resides within the agglomerates of carbon particles and

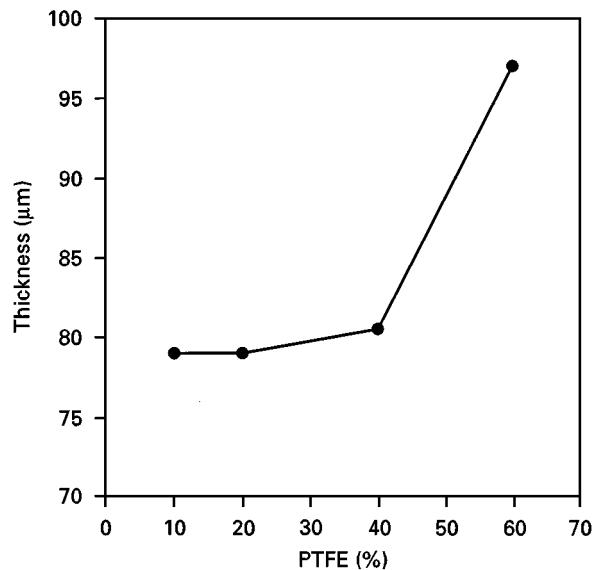


Figure 4 Normalized film thicknesses versus PTFE content.

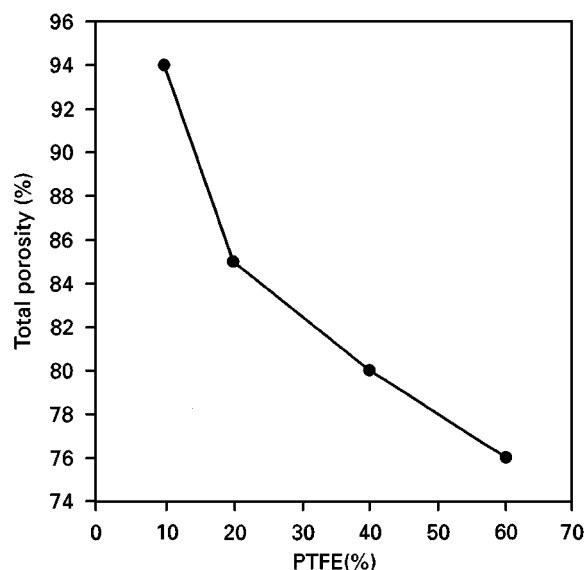


Figure 5 Dependence of total porosity on PTFE amount of the layer.

PTFE is not present within carbon agglomerates, on this basis we can calculate the carbon intraagglomerate porosity as

$$P_{Cm} = P_m / (1 - P_s - \phi_P) \quad (6)$$

$$\phi_P = x_P W_i / Z \rho_P \quad (7)$$

where P_s is the macroporosity and ϕ_P is the volume fraction of PTFE in the layer. As shown in Fig. 6, the microporosity (pore size in the range $0.0038\text{--}0.35\ \mu\text{m}$) decreases with increasing PTFE, by the decrease of carbon amount in the samples. Instead, as indicated in Table III, the value of carbon agglomerate porosity P_{Cm} is about 0.78 for all the samples, independent of PTFE content of the film. Only the sample containing 10 wt % PTFE shows an anomalously high value; this result can be explained, as in the case of the thickness, by considering that the macroporosity P_s of 10 wt % PTFE sample is attributable both to the carbon paper

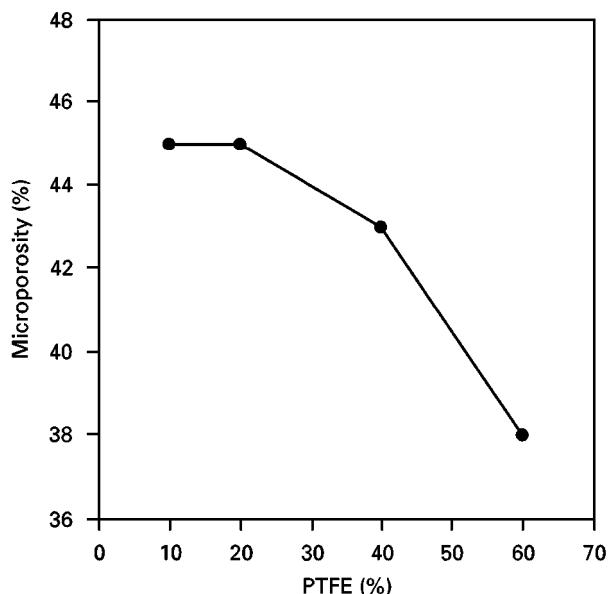


Figure 6 Dependence of microporosity on PTFE amount of the layer.

TABLE III Carbon intraagglomerate porosity P_{Cm} at various PTFE content of the film as in Equation 6

PTFE (%)	P_{Cm} (%)
10	89
20	79
40	77
60	78

porosity and to the layer porosity. Giving $P_s = 0.42$ instead of the resulting value from Equation 5, 0.49, we obtain $P_{Cm} = 0.78$: this means that 0.07 of the macroporosity is related to the carbon paper. On this basis, in Figs 7 and 8 for the composition with 10 wt % PTFE we have taken the porosity of the substrate from total macroporosity. Fig. 7 shows the dependence of macroporosity on PTFE content of the layer; it 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 (Fig. 8), the second from 1 to 2 μm (Fig. 9), and the third from 0.35 to 1 μm (Fig. 10). As can be seen in Fig. 8, going from 10 wt % to 20 wt % PTFE, besides coating carbon paper porosity, the polymer coats carbon inter-agglomerate pores with size $> 2 \mu\text{m}$; the increase of porosity above 20 wt % PTFE is attributable to the formation of cracks (see Fig. 2b–d) during drying of the samples. Going from 20 to 40 wt % PTFE, the polymer fills the pores in the range 1 to 2 μm (carbon interagglomerate pores), binding the agglomerates of carbon particles (see Fig. 9). As shown in Fig. 10, the pores in the range 0.35 to 1 μm show the same dependence on fluoropolymer as that of microporosity; these pores being related to carbon porosity, their decrease going from 40 to 60 wt % PTFE is because of the decrease of carbon amount in the layer.

A.c. impedance spectroscopy measurements were performed on electrodes having the C/PTFE film as

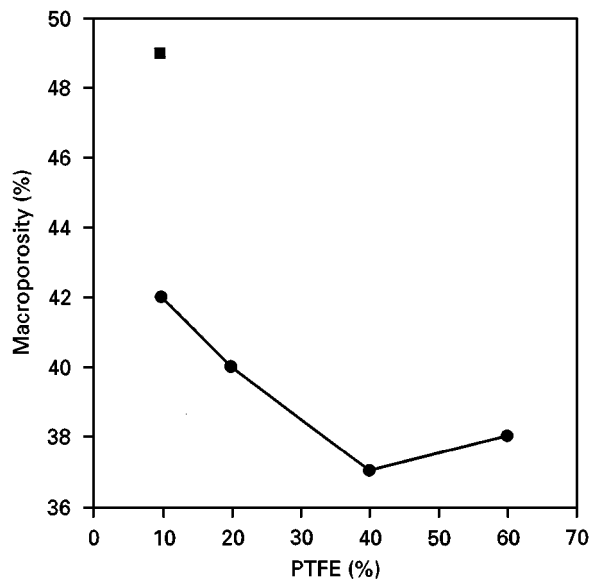


Figure 7 Dependence of macroporosity on PTFE amount of the layer. (■) Layer + carbon paper, (●) layer.

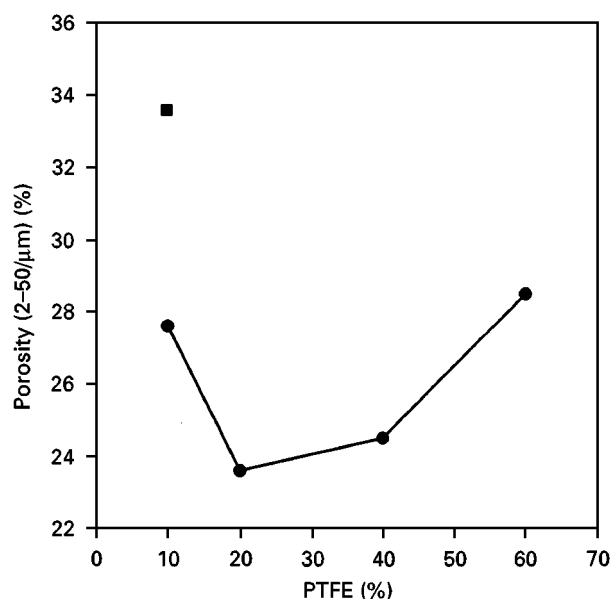


Figure 8 Dependence of porosity with pore size in the range 2 to 50 μm on PTFE amount of the film. (■) Layer + carbon paper, (●) layer.

the diffusion layer. Generally the impedance spectra for PEFC cathode include two arcs, 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 the diameter of the arc and the low frequency resistance) of the diffusion layer. When PTFE fills the pores, as the diffusivity of oxygen in PTFE is very low

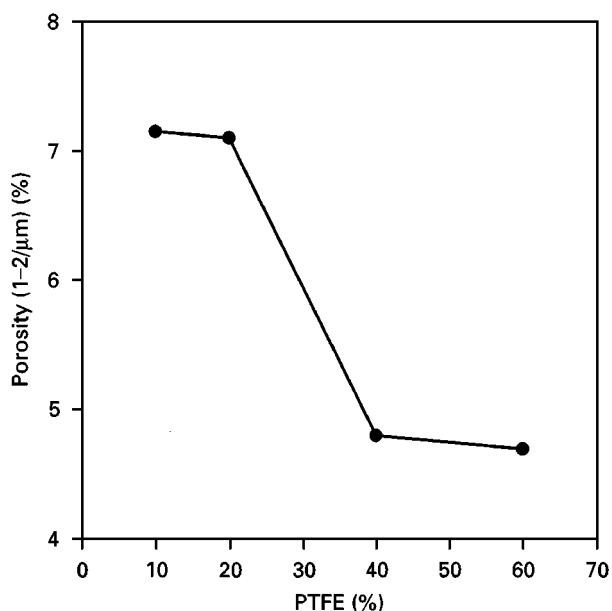


Figure 9 Dependence of 1 to 2 μm porosity on PTFE content.

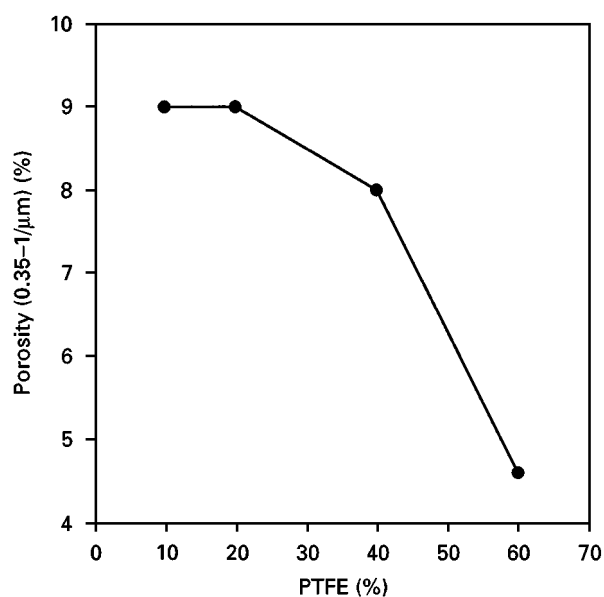


Figure 10 Dependence of 0.35 to 1 μm porosity on PTFE content.

[12], the O_2 partial pressure is lowered at the diffusion/catalyst layer interface. While the values of thickness of the samples go through a maximum (see Table II), the monotonous increase of low frequency resistance from impedance measurements with increasing PTFE content of the film, as shown in Fig. 11, is in agreement with the decrease of total porosity with increasing PTFE.

Summarizing, from porosimetric and electron diffraction measurements it can be inferred that going from 10 to 20 wt % PTFE, the polymer coats both the pores of the substrate and the pores of the film with pore size higher than 2 μm. From 20 to 40 wt % PTFE, the polymer coats the macropores with size in the range 1 to 2 μm. Above 40 wt % PTFE, a further supply of polymer does not fill the pores, but increases

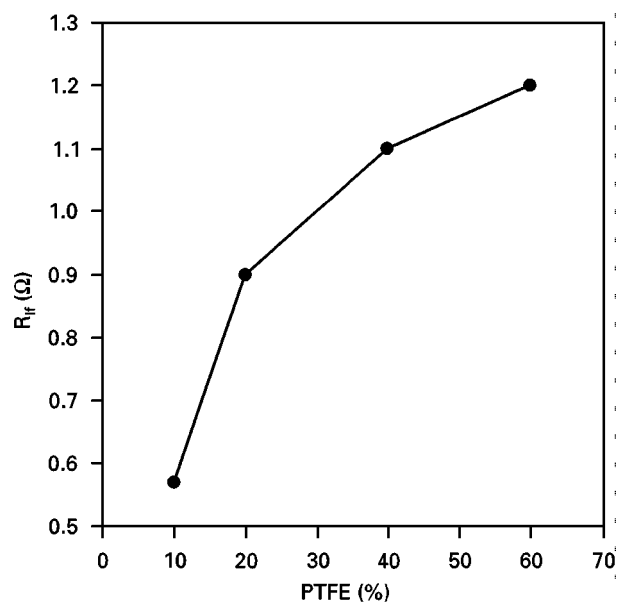


Figure 11 Low frequency resistance R_{lf} as a function of PTFE content of the layer.

the thickness of the film. On this basis, the binding effect of the polymer is completed at 40 wt % PTFE. The formation of cracks, increasing in number and size with increasing PTFE content of the layer, is revealed starting from 20 wt % PTFE.

4. Conclusions

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

1. Two distinctive pore distributions with boundary of about 0.35 μm were detected.
2. The overall porosity of samples decreased with increasing PTFE content of the film.
3. The microporosity of the samples was only attributable to the intraagglomerate space of carbon particle.
4. The porosity of carbon agglomerates was independent of PTFE amount of the layer.
5. 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.

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