

Morphological variation of platinum catalysts in phosphotungstic acid fuel cell

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Abstract

Morphological modifications occurring on platinum catalysts during operation in a phosphotungstic acid fuel cell were investigated by using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy–energy dispersive atomic X-ray (SEM–EDAX) analyses. An increase of platinum particle size was observed on both anodes and cathodes with the time of operation in fuel cell. This phenomenon was significantly larger on the cathode. The uptake of electrolyte by the catalyst layers increased during cell operation. Concurrently, an increase of cell performance was recorded. On the basis of physicochemical characterizations, the growth mechanism of platinum particles was attributed to a dissolution–redeposition phenomenon involving smaller crystallites. Whereas, the increase of cell performance during the first period of operation is likely due to an increase of the three-phase reaction zone at the electrode–electrolyte interface whose positive contribution to the cell polarization prevails over the effects of platinum crystallite growth. © 1998 Elsevier Science S.A.

Keywords: Fuel cells; Phosphotungstic acid; Platinum electrocatalyst; Physicochemical characterizations

1. Introduction

A new low-temperature phosphotungstic acid-based fuel cell (PWAFC) has been recently investigated [1–7]. The main advantages of this device over polymer electrolyte fuel cells (PEMFCs) concern a significantly lower cost of the electrolyte and a high performance at room temperature and atmospheric pressure. These characteristics of operation allow a rapid start-up of the device which could be advantageously utilized in those fields where portable power generators are requested. The high power density output of PWA fuel cell at room temperature was mainly attributed to the promoting effect of the PWA electrolyte toward the oxygen reduction reaction (ORR) [1,6]. The exchange current density for oxygen reduction on platinum and the oxygen solubility in the PWA electrolyte at low temperature conditions are comparable to those obtained in perfluorosulfonic acid electrolytes and larger than those observed in 85 wt.% H₃PO₄ solution [1]. The PWA electrolyte also showed higher specific proton conductivity with respect to Nafion 117 (DuPont Product) usually em-

ployed in polymeric membrane fuel cells [2]. In the last years we have addressed our investigation towards some technological aspects of the PWA fuel cell such as cell design [3], hydrophobic properties of the gas diffusion electrodes [4], chemical cross-over [5], and life-time experiments, including start-up and shut-down cycles [6].

A variation of electrochemical behaviour observed during the lifetime experiments [6] has prompted us to concentrate our efforts towards a more complete comprehension of the phenomena occurring on the electrodes during cell operation. In the experiments carried out on hydrophobic (40 wt.% polytetrafluoroethylene loading) gas-diffusion electrodes we have observed an increase of electrochemical performance during the initial time of operation. Such a phenomenon was tentatively interpreted as due to the uptake of the electrolyte by the catalyst layer in the electrodes. The observed cell behaviour was dependent on the content of hydrophobising agent (PTFE) into the layer [6]. Besides, modification of physicochemical properties of platinum on carbon (Pt/C) catalyst could have occurred during the period of fuel cell operation. Morphological modifications of carbon-supported platinum catalysts have been extensively studied in the literature, especially with

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regard to the ageing effect in phosphoric acid fuel cells (PAFC). In PAFC systems, operating at about 200°C, sintering of platinum particles with the time was experimentally observed. Different interpretations were given by various authors on the influence of the electrode potential on the agglomeration process; Honji et al. [8] affirmed that such agglomeration was significantly affected by electrode potential whereas Bett et al. [9] and Gruver et al. [10] showed that the surface area loss of platinum was not dependent on the potential. Blurton et al. [11] found that the particle growth mechanism in PAFC occurred by crystalline migration; this phenomenon was also invoked by Wilson et al. [12] to explain the loss of platinum surface area in PEMFC.

The present paper deals with an *ex situ* investigation of gas diffusion electrodes after operation in PWA fuel cell under electrochemical load conditions. Chemical, structural and morphological properties are studied by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy–energy dispersive atomic X-ray (SEM–EDAX) analyses. Electrochemical polarization experiments carried out with electrodes which had operated for different times are also reported. The role played by the electrolyte flooding and by the platinum particle size on the fuel cell performance is discussed at the light of the results obtained by the solid-state investigation.

2. Experimental

2.1. Preparation of electrodes

Gas-diffusion electrodes (anode and cathode) utilized in single cell experiments consisted of a catalyst layer and a diffusion layer. The catalyst layer was prepared by the doctor-blade technique. A paste containing catalyst, PTFE and water was spread over the surface of a carbon paper (diffusion layer) previously wetproofed with fluoroethylene–propylene polymer (FEP). The catalyst paste was prepared by mixing under ultrasonic waves a catalysed carbon powder (20 wt.% Pt/C), a PTFE dispersion and water at 55°C. The suspension was allowed to flocculate by addition of isopropyl alcohol. The flocculate was then separated from the upper liquid and stratified over the carbon paper. The electrode was successively pressed and thermally sintered at 350°C. The catalyst was purchased from ElectroChem (Woburn, MA), the PTFE and the FEP dispersions were from Du Pont de Nemours, the carbon paper was TGP 090 produced by Toray. Anodes and cathodes, utilized in single cell tests, had the same composition and thickness. They contained 40 wt.% of PTFE and 0.5 mg cm⁻² of dispersed platinum in the catalyst layer and 30 wt.% of FEP in the diffusion layer. The thickness of catalytic layer was 0.010 cm. The thickness of the total electrode was 0.040 cm.

2.2. Characterization of electrodes

To study electrode modifications during single cell testing, a series of analyses was carried out on electrode samples discharged from the single cell which were electrochemically tested for different periods. XRD, TEM, SEM–EDAX analyses were carried out on raw electrodes and after operation for 6 and 73 h. Before the analyses, the samples used in the single cell tests were washed with boiling water for 1 h to eliminate the excess of electrolyte crystallized over the electrode surface and in the macropores.

XRD analysis was carried out on electrodes, Pt/C catalyst, hydrophobised carbon paper and PTFE powder, with a Philips X-Pert diffractometer using a Cu-K α radiation and operating at 40 kV and 30 mA. The diffractometer consisted of a PW1830 HT-generator and a PW3710 control unit which was controlled by a PC computer equipped with Philips PC-APD software. Continuous scans were collected by using a Bragg–Brentano para-focusing optical system. The X-ray diffraction patterns were collected with a scan rate of 0.5° min⁻¹. The spectral contribution from Cu-K α_2 was subtracted by a software correction algorithm. Peak profiles were obtained by a non-linear least square fitting of the raw data by using the Marquardt algorithm. Instrumental broadening was determined by a standard Pt sample under the same analysis conditions.

TEM analysis was performed with a Philips CM12 apparatus, equipped with super-twin objective lens, working at an accelerating voltage of 120 kV. The ultimate spatial resolution of the instrument was 2 Å. The specimens for TEM analysis were prepared removing small fractions of catalytic layer from the surface of electrodes, and transferring these in a test tube containing isopropyl alcohol kept under ultrasonic mixing. A drop of the obtained dispersion was transferred to a standard Cu grid covered with carbon film for TEM observations.

The morphology of the electrodes was investigated using a Philips XL20 scanning electron microscope, equipped with a LaB₆ filament, working at an accelerating voltage of 20 kV. Chemical composition was determined using an EDAX microanalyser unit equipped with an ultrathin Be window. Concentrations of various elements were determined by the ZAF intensity correction algorithm. Micrographs and chemical profile measurements were taken on cross-sections of the electrochemically tested electrodes.

2.3. Single cell experiments

To evaluate the electrochemical performance of PWA fuel cell, a single cell having 40 cm² geometrical area was employed. Before electrochemical testing, the cell components (anode, matrix and cathode) were assembled under slight pressure (10 atm) at room temperature and inserted between two ribbed graphite end-plates. The end-plates

had the double function of current collectors and gas distributors. The reagent gases, H_2 and O_2 , were fed at atmospheric pressure and the cell was operated at room temperature. It should be noted that before the start-up cell temperature was $19^\circ C$, but during operation at 400 mA cm^{-2} the cell reached the steady-state temperature of $40^\circ C$ due to the heat dissipated from the electrochemical reaction. A 60 wt.% aqueous phosphotungstic acid solution was used as electrolyte. It was slowly circulated through the cell ($F = 0.5 \text{ cm}^3 \text{ min}^{-1}$) to avoid excessive dilution by the water formed at the cathode during the electrochemical process. The electrolyte flew through a porous matrix of glass microfiber paper, having a thickness of 0.024 cm, located between the electrodes. The diluted electrolyte going out of the cell was reconcentrated to the proper value and recirculated through the cell. The cell was connected to a HP 6060B electronic load. Two particular single cell runs, named run A and B, characterized by different times of operation, were considered. The A and B runs were performed at constant current density of 400 mA cm^{-2} for 6 and 73 h, respectively. The run A was interrupted after 6 h of continuous operation. The run B was conducted in a discontinuous way: the cell operated 7–8 h per day and was shut-down for the night, the cycle was then repeated every day until the test was intentionally interrupted. In the shut-down period, the gas compartments of the cell were filled with inert gas and the electrolyte pumping was stopped. A polarization curve was obtained

every day to evaluate the electrochemical performance in the whole range of currents allowed by the PWA fuel cell.

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction analyses were carried out on the electrodes before and after the electrochemical experiment to investigate the platinum modification occurring during cell operation. Since the electrodes were composed of different materials, the first analysis was devoted to qualitative attribution of the reflection peaks and to the investigation of possible chemical interaction occurring among these compounds. Fig. 1 shows XRD patterns of final electrode, and electrode components, i.e., Pt/C catalyst, PTFE and FEP/carbon paper. The XRD pattern of the electrode contains both the reflection peaks of FEP/carbon paper and PTFE together with those of the Pt/C catalyst. Due to the large penetration of X-rays through the amorphous carbon matrix of the Pt/C catalyst and the small thickness of the catalyst layer (0.010 cm), the diffraction peaks of FEP/carbon paper substrate are largely prevailing in the electrode pattern. Yet, the peaks due to the substrate interfere only with the (002) reflection of carbon black in the catalyst allowing an accurate analysis of platinum reflections. Similar evidences were found for the PTFE compound. The catalyst mixing with PTFE (40%) appears

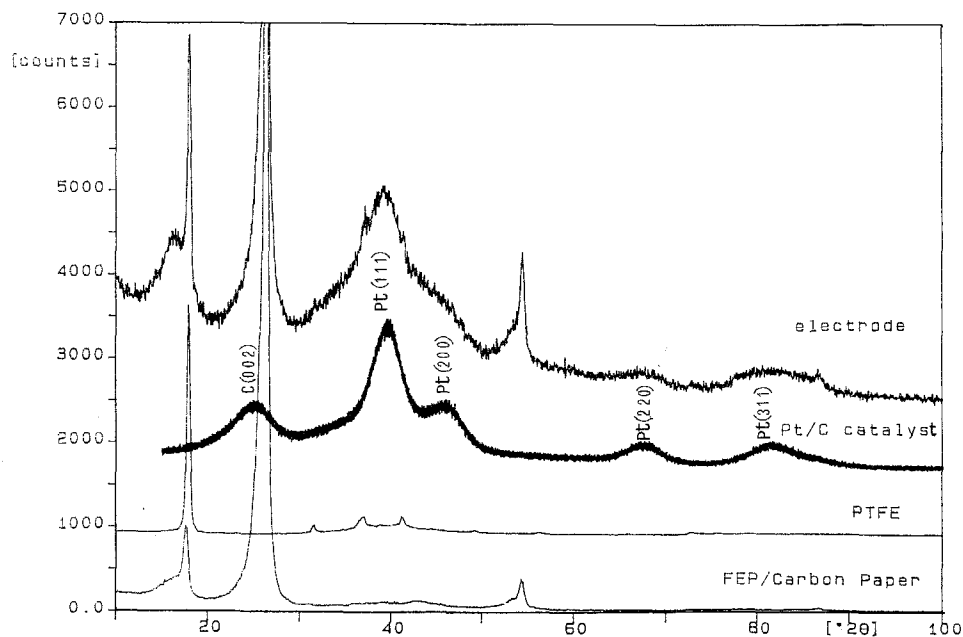


Fig. 1. X-ray diffraction patterns of FEP/carbon paper, PTFE, Pt/C catalyst and electrode.

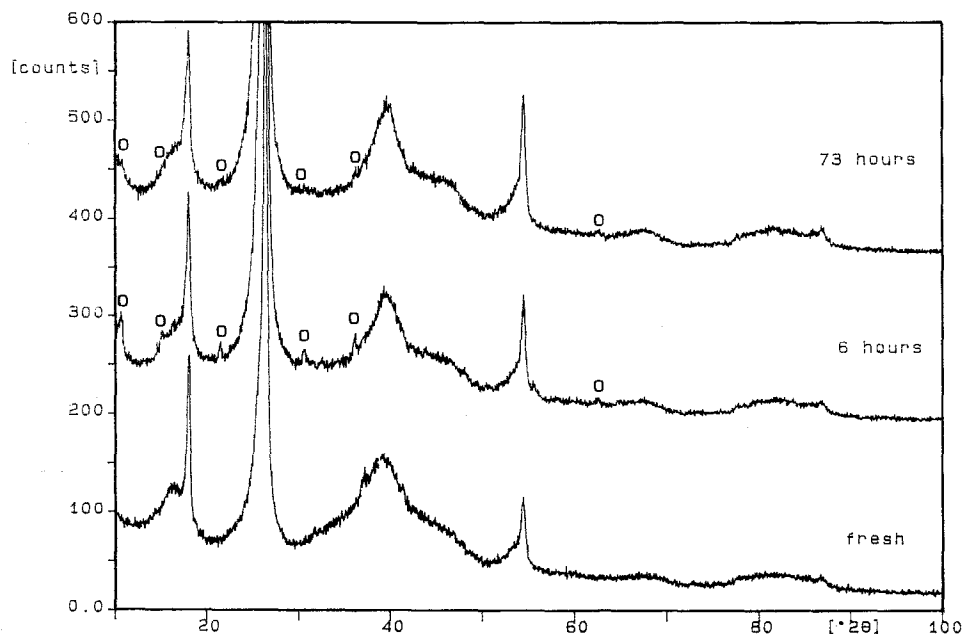


Fig. 2. X-ray diffraction patterns of raw electrode and 6 and 73 h tested anodes. The (○) symbol marks the $H_3PW_{12}O_{40} \cdot 6H_2O$ peaks.

to affect the reflection lines coming from inner Pt particles since these appear less defined in the electrode with respect to the raw catalyst. Such a modification could be also due to the small thickness of the catalyst layer or to the electrode preparation procedure including ultrasonic and thermal treatment of the catalyst. The platinum peaks (111) and (200) are less affected from interferences from other compounds and they have been utilized to investigate the particle size modifications of the platinum crystallites.

Figs. 2 and 3 show a comparison of the XRD spectra for the untested and electrochemically tested (run A and B) anodes and cathodes, respectively. At a first glance, the Pt reflection peaks appear more sharpened after the electrochemical operation of the electrodes in fuel cell whereas PTFE and FEP/carbon paper peaks are relatively unaffected. Furthermore, the comparison of the relative intensities of Pt(111) reflection at $2\theta = 40^\circ$ with PTFE or FEP/carbon paper peaks at about $2\theta = 18^\circ$ and 54° , re-

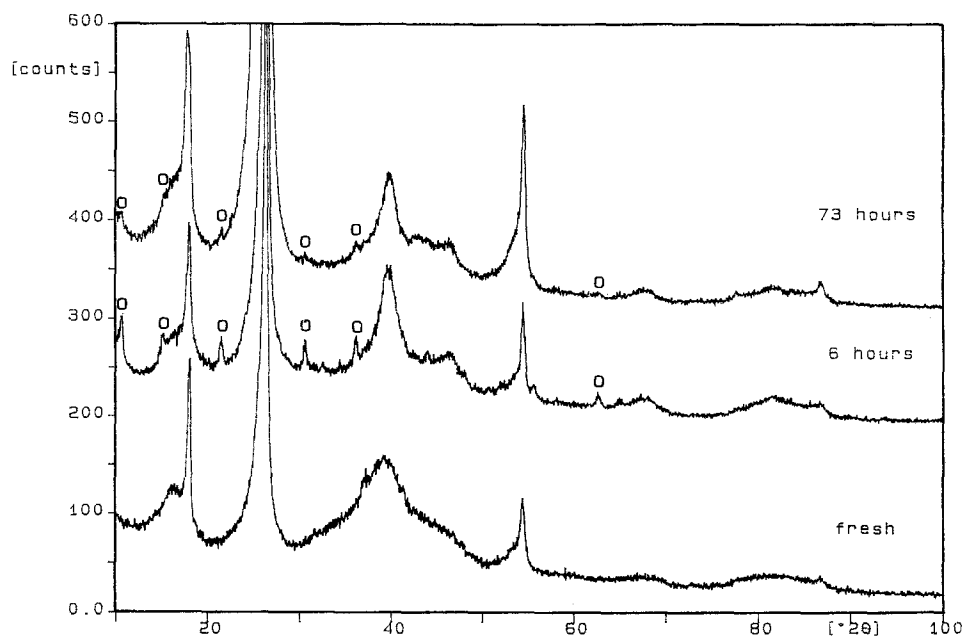


Fig. 3. X-ray diffraction patterns of raw electrode and 6 and 73 h tested cathodes. The (○) symbol marks the $H_3PW_{12}O_{40} \cdot 6H_2O$ peaks.

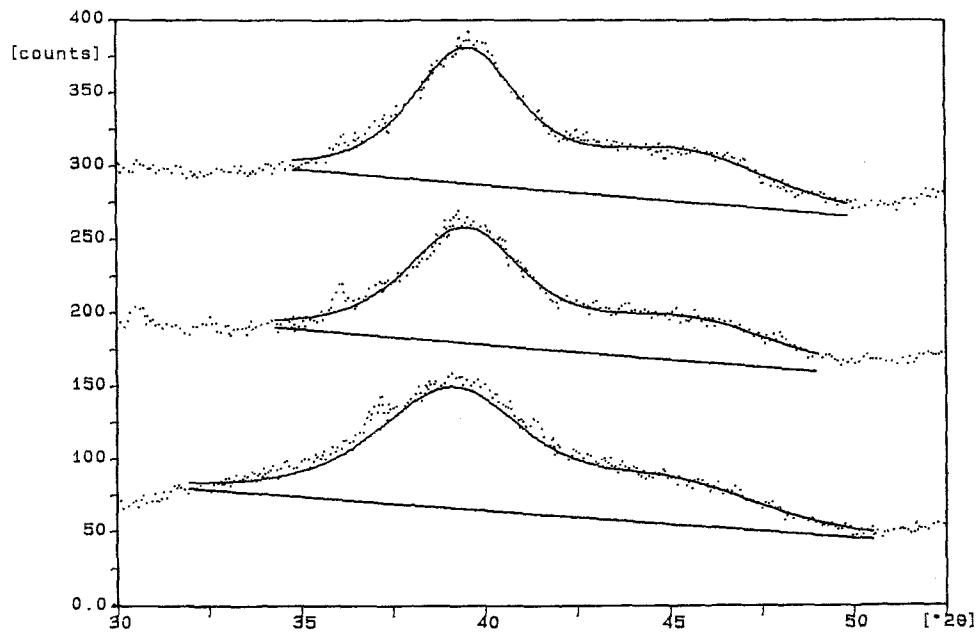


Fig. 4. Peak profile fittings for the (111) and (200) reflection of the Pt structure in the raw electrode and in the 6 and 73 h tested anodes.

spectively, shows a progressive decrease of the Pt signal (especially in the cathodes) with the operation time of electrodes in the fuel cell. Yet, modifications of shape and intensity of Pt reflections were practically observed in the first period of fuel cell run since the spectrum recorded for an electrode tested up to 400 h was not significantly different from that of electrodes tested for 73 h.

Although the electrodes were repeatedly washed in boiling water there is some evidence of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$

reflection peaks in the XRD patterns of electrochemically tested electrodes (Figs. 2 and 3). This indicates a strong interaction of the electrolyte with the porous catalyst. SEM observation of these electrodes revealed that such peaks could derive from some localized PWA crystallization on the outer electrode surface that was not removed by extensive washings. For a quantitative evaluation of the platinum modifications, the Pt(111) and (200) peak profiles were determined by nonlinear least squares fitting using

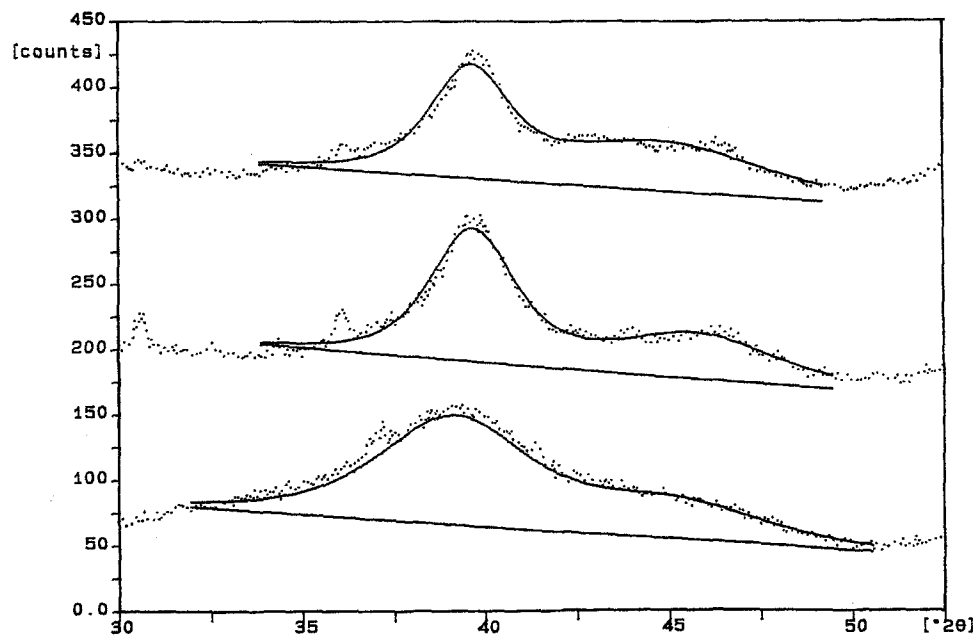


Fig. 5. Peak profile fittings for the (111) and (200) reflection of the Pt structure in the raw electrode and in the 6 and 73 h tested cathodes.

Table 1
Platinum particle size in untested and 6 and 73 h tested electrodes obtained by mathematical method applied at XRD spectra

Electrodes	Test time (h)	Pt particle size (Å)
Untested	0	23
Anode	6	25
Anode	73	28
Cathode	6	37
Cathode	73	41

the Marquardt algorithm (Figs. 4 and 5). The sharpening of the platinum peaks at 6 and 73 h in the anodes and cathodes (Figs. 4 and 5) is quite evident in this analysis and denotes a significant increase of crystallite average dimension. Such phenomenon has been generally attributed in fuel cell literature to the dissolution or the migration [8–13] of the smaller particles of platinum, which are relatively more amorphous, and to the subsequent recrystallization or agglomeration as bigger particles, which are characterized by a relatively more crystalline form.

The average particle size in the electrodes was determined from the broadening of the (111) reflection of the Pt fcc lattice (Figs. 4 and 5) by using the Debye–Scherrer equation. The fitting profiles shown in Figs. 4 and 5 are derived from a calculation using Pt(111) and Pt(200) contributions to the scattered X-ray intensity. The data obtained by the mathematical fitting are reported in Table 1. They confirm the increase of the average particle size of platinum with electrode testing time in fuel cell. There is an evidence that this effect is more pronounced in the cathodes in respect to the anodes. In particular the average particle size of platinum in cathodes changes from 23 Å of the untested electrode to 37 and 41 Å in those samples which have been worked for 6 and 73 h, respectively. The variation for the corresponding anodes is from 23 to 25 and 28 Å.

3.2. Transmission electron microscopy analysis

The variation of morphological properties of platinum crystallites in the electrodes were further investigated by TEM analysis. Figs. 6–8, shows the TEM micrographs of

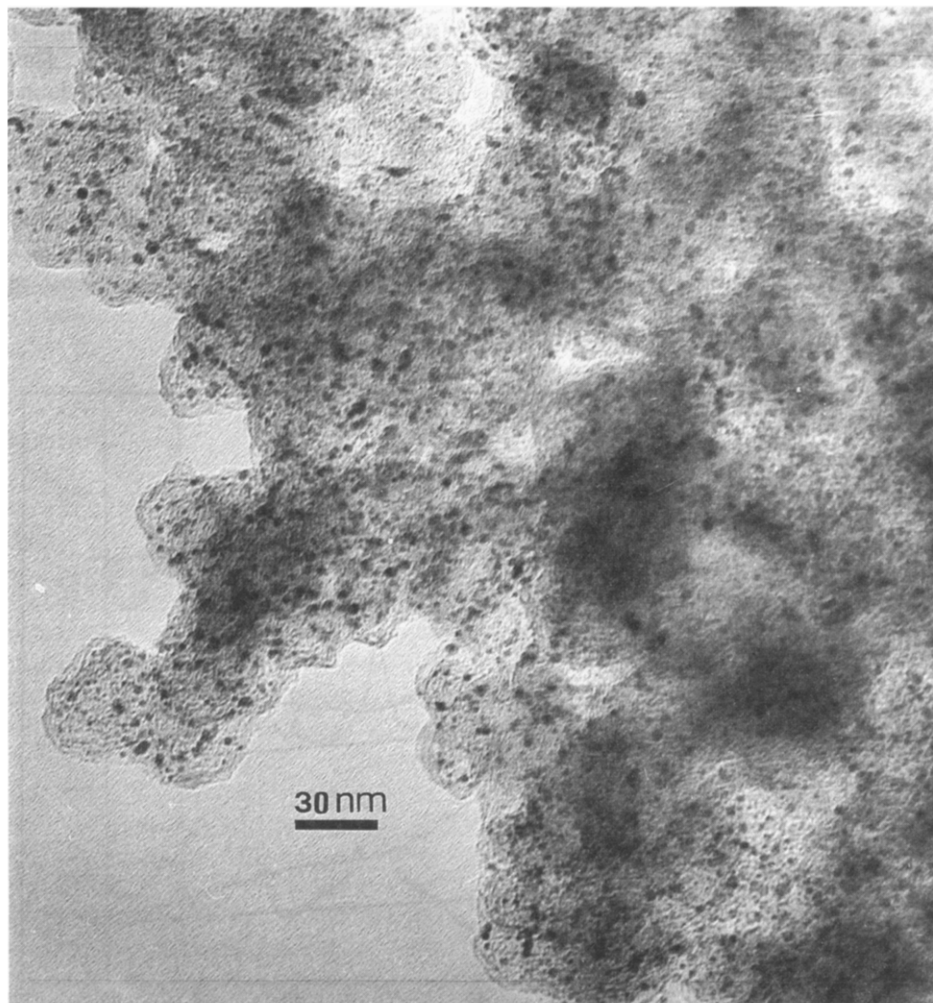


Fig. 6. Bright field TEM micrograph of catalyst layer of raw electrode.

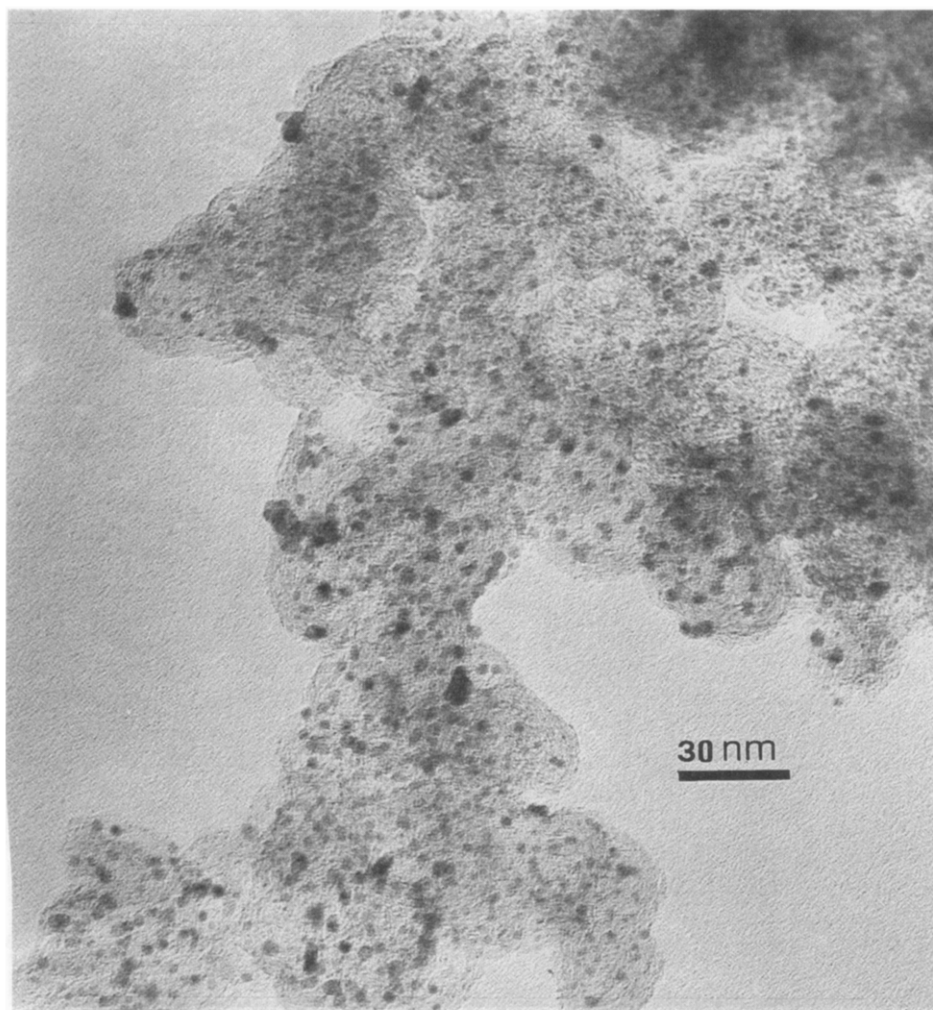


Fig. 7. Bright field TEM micrograph of catalyst layer of cathode tested for 6 h.

the cathode catalyst layers of fresh and tested electrodes for 6 and 73 h, respectively. The untested electrode shows a homogeneous dispersion of Pt particles on carbon black with particle size ranging from 19 to 38 Å. The average particle size estimated by the micrograph is about 25 Å which is in good agreement with XRD results. A slight increase of particle dimensions is observed after electrochemical operation for 6 h (particle size ranging from 20 to 54 Å) although the crystallite shows no significant agglomeration at this stage. After 73 h of operation a further increase of Pt crystallites dimension and a significant particle agglomeration are observed (particle size from 20 to 115 Å). The estimated average particle size is about 50 Å, a value higher than that determined by XRD analysis. The difference can be explained by considering that TEM analysis is mainly carried out on the outer surface of the catalyst layer while the XRD analysis take into account the whole layer. The Pt crystallites appear slightly more localized on the outer surface of carbon agglomerates. The main features observed in Figs. 7 and 8 are the presence of some big platinum particles that are not

observed in the untested sample (Fig. 6) and, the decrease of the density of smaller platinum particles. It is well-known that dissolution is mainly concerning smaller Pt particles. Since the electrolyte is continuously recirculated through the cell in a close loop, from which only water goes out, it is argued that the Pt dissolved in the electrolyte is likely redeposited from the solution to larger particles. Such a phenomenon could involve only a small fraction of Pt crystallites and essentially those having smaller dimensions [8]. The final results is an evident growth of crystallites. The relative intensity of Pt peaks compared to PTFE by XRD decreases after prolonged operation. This would mean that the redeposition of Pt does not occur completely. The anodes show less increase of platinum particle size after testing in single cell (not shown). These results are in well agreement with XRD analysis. Thus, the platinum particle size increases more significantly at the cathode with respect to the anode. This fact led us to the conclusion that the electrode potential influences the dissolution–redeposition process more significantly than the operation time. Thus, the recrystallization phenomena of Pt

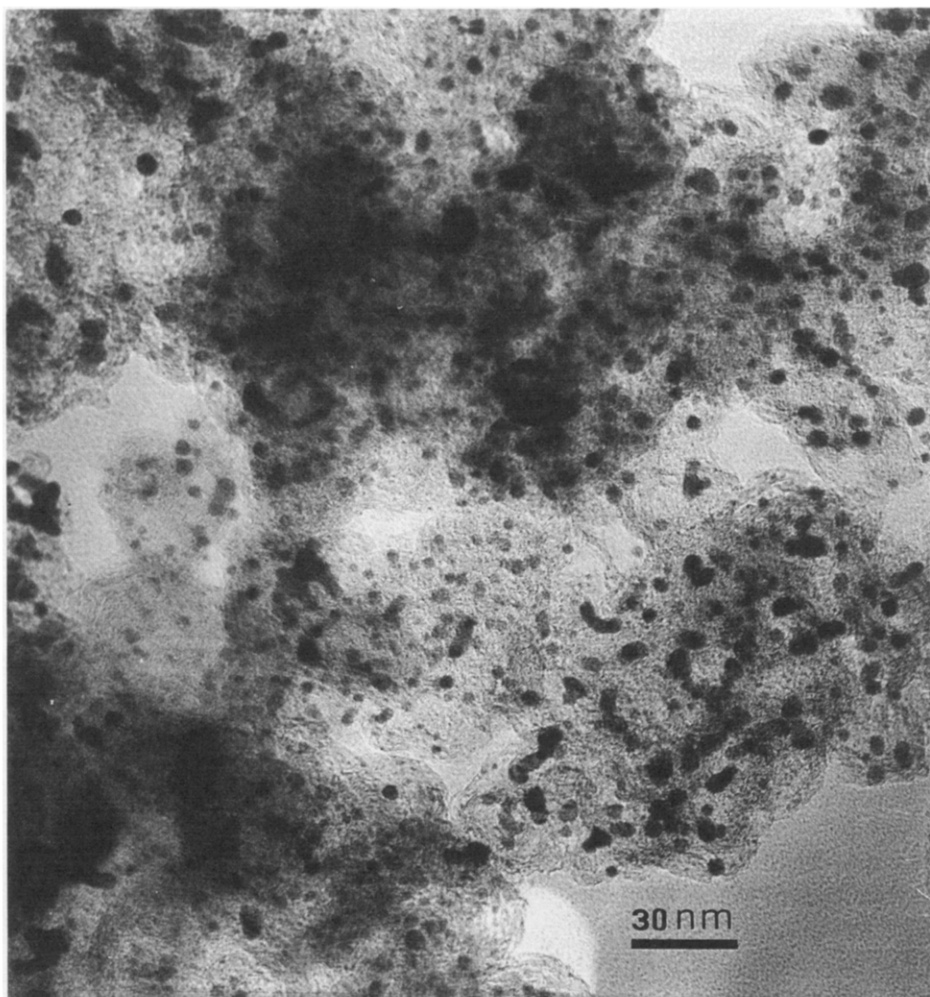


Fig. 8. Bright field TEM micrograph of catalyst layer of cathode tested for 73 h.

occurring in the PWA fuel cells are mainly electrochemical in nature.

3.3. EDAX and SEM analyses

EDAX analyses have been carried out to obtain information on the variation of platinum content and electrolyte uptake by the catalyst layer after different periods of operation (Fig. 9). The PTFE in the electrodes is chemically very stable in the cell operation conditions, thus the fluorine signal related to this compound in the EDAX spectra is chosen as the internal standard for quantitative evaluations. The platinum and tungsten contents were obtained by EDAX analyses carried out at low magnification on various parts of the catalyst layer. Pt-M α and W-M α peaks were normalized with respect to the F-K α signal (Fig. 9; Table 2). The obtained results suggest a decrease of Pt content in the anode tested for longer time. The platinum signal recorded from the anode tested for 73 h is about 17% lower than that coming from the electrodes tested for 6 h. The normalized data for tungsten show similar uptake of electrolyte in the anodes after different

operation periods. A little decrease observed for the 73 h tested sample with respect to 6 h electrode is within the limit of instrumental precision, which is about 5% under the analysis conditions. Concerning the cathode, a significant amount of Pt is dissolved in the electrolyte during the first period of operation. Yet, an increase of about 11% in the Pt content is observed on the cathode tested for 73 h with respect to that tested for 6 h. Determination of the electrolyte uptake by electrodes after different period of operation was not possible due to the crystallization of electrolyte on the front surface. Thus, a washing treatment in boiling water was carried out in the same conditions for all electrochemically tested samples. In order to get information on the electrode flooding by electrolyte at different times, cross-sections of the gas diffusion electrodes were analysed by scanning electron microscopy (Fig. 10) and quantitative analysis of tungsten was made by focusing the electron microprobe inside the electrode, just at 50 μm distance from the front surface. This procedure is needed since the chemical profile shows that tungsten is distributed along the electrode cross-section (Fig. 10) in both 6 and 73 h tested electrodes. In our opinion, the diffusion

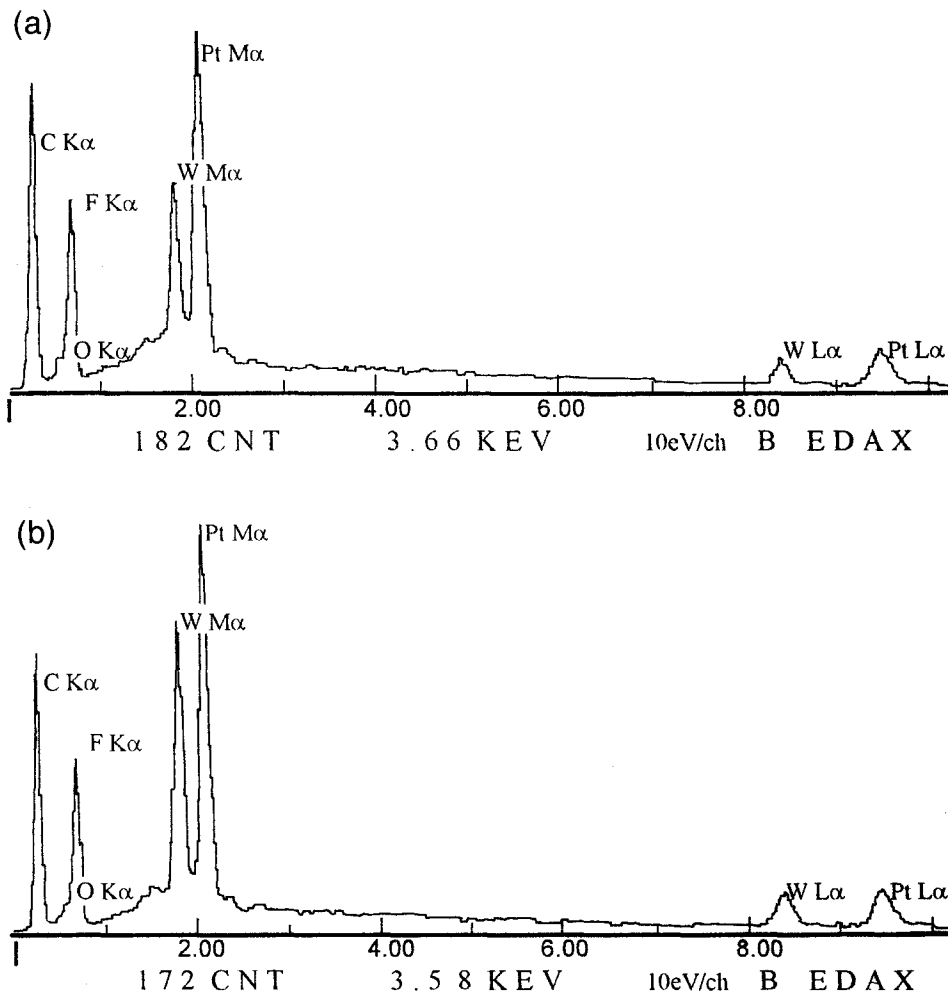


Fig. 9. EDAX spectra of cathodes tested for 6 h (top) and 73 h (bottom) in PWA single cell.

of PWA electrolyte in the electrode macropores rapidly occurs during the first time of operation of the fuel cell. On the other hand mass transport inside catalyst micropores requires a longer time. Accordingly, the tungsten signal is significantly higher (51% increase) in the electrode tested for a more prolonged time. Taking into account that the electrode samples were washed in boiling water before EDAX analysis, the significant increase of W is relative to the electrolyte blocked in the micropores, or bonded to the carbon black support through an acid–base interaction, or precipitated as insoluble compound into the layer.

Table 2
Data of EDAX analysis normalized with respect to fluorine peak area

Electrodes	Test time (h)	Pt/F	W/F
Anode	6	1.85	1.41
Anode	73	1.53	1.34
Cathode	6	1.90	1.19
Cathode	73	2.12	1.80

3.4. Single cell results

Fig. 11 shows the polarization curves obtained, after various cell operation times at constant current density of 400 mA cm^{-2} . There is a progressive increase of cell performance during the first 73 h of operation. The cell reached the steady-state behaviour after 100 h of operation [6]. It is thought that due to the hydrophobic character of the electrode only the outer surface of the catalyst layer is in contact with the electrolyte during the first hours of operation. Afterwards electrolyte diffusion inside catalyst pores increases the extension of the three-phase reaction zone at electrode–electrolyte interface. This phenomenon was already investigated by De Sena et al. [14] for phosphoric acid fuel cells. Fig. 11 also shows that a significantly higher electrochemical performance is obtained by the cell after 73 h of operation, with respect to the initial polarization. With the support of the previous analyses, we can interpret the increase of electrochemical performance during cell operation, as principally due to the modifications occurring on the cathodes that appears to be strong

time dependent. Although a slight increase of platinum loading in the cathode after 73 h with respect to 6 h is observed as a consequence of redeposition from the electrolyte, the increase in electrochemical performance is likely due to the major penetration of electrolyte into the catalyst pores. On the other hand it appears that little influence on the cell performance is noticed by the decrease of platinum loading in the anode with the operation time.

It is known that the rate of the overall electrochemical process occurring in the acid electrolyte-based fuel cells is mainly due to the oxygen reduction reaction at the cathode and this depends on the active surface area of platinum in contact with the electrolyte as well as on the reagent gas access to catalyst sites. The increase of platinum particle size, drawn from XRD and TEM analyses, is apparently in contrast with the improvement of cell performance, because a decrease of the specific platinum surface area is detrimental for the electrochemical processes. Nevertheless, our data show that the positive effect on performance, due to the increase of the extension of the three-phase

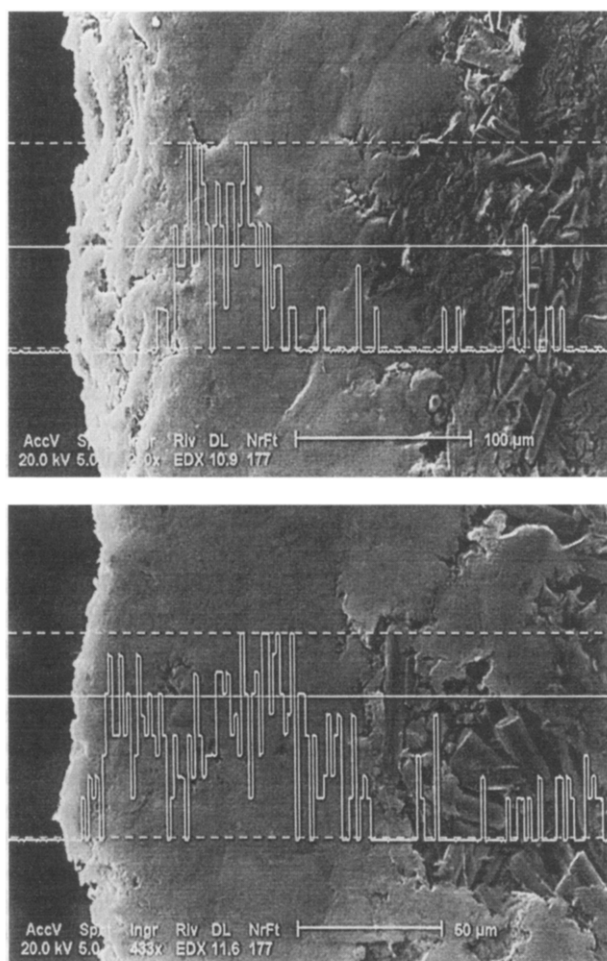


Fig. 10. SEM micrographs of cross-sections of the electrodes tested for 6 h (top) and 73 h (bottom) in PWA single cell. The chemical profile of W along the electrode cross-section is displayed.

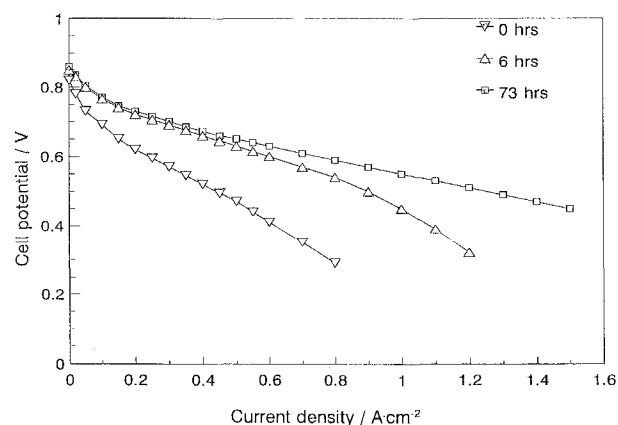


Fig. 11. Polarization curves obtained at different time of cell operation.

reaction zone due to the electrolyte penetration into the cathode catalyst pores, prevails over the negative effect of particle size growth. Furthermore, since the access of PWA electrolyte to smaller catalyst micropores is hindered by its molecular dimensions (20 Å including the secondary structure due to solvation sphere, i.e., 29 H₂O molecules) [15], there is a significant fraction of small platinum crystallites inside electrode micropores that are not in close contact with the electrolyte. Dissolution of these small Pt particles upon operation in fuel cell and recrystallization on the outer surface of catalyst pores in slightly bigger particles likely produces catalytic sites which are readily accessible by reagent gas thus producing a higher utilization of platinum.

4. Conclusions

An increase of the average particle size of Pt crystallites during operation in a PWA fuel cell was observed by XRD and TEM analyses in both the anode and the cathode. SEM–EDAX analyses indicated that the growth mechanism was mainly due to a dissolution–redeposition process. The dissolution process concerns the smaller platinum particles and occurs quite significantly at both the anode and the cathode during the first hours of operation. The platinum redeposition process from the solution occurs over larger particles of the active metal and is favoured on the cathode.

A pronounced increase of platinum particle size was observed in the cathode after 6 and 73 h. In the anode, the increase of average Pt particle size with time was slower and it was likely not due to a significant increase of the particle size but to the dissolution of very fine particles.

A slight increase of platinum loading at the cathode from 6 to 73 h of operation was obtained due to the Pt redeposition from electrolyte. At the same time the electrolyte diffusion increased more significantly.

The PWA fuel cell performance after 73 h of operation significantly increased with respect to that obtained after 6 h. This likely derives from the larger extension of the three-phase reaction zone of the electrode–electrolyte interface which increases with the penetration of the electrolyte into the catalyst pores.

After about 100 h of operation no significant increase of Pt crystallite dimension and electrolyte uptake was recorded. Concurrently, the cell performance reached a steady-state behaviour.

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