

Short communication

Novel method for preparation of PEMFC electrodes by the electrospray technique

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Abstract

A novel method based on the electrospray technique has been developed for the preparation of electrodes for proton exchange membrane fuel cells (PEMFC). The material obtained was characterized by different techniques, which showed both morphological and structural improvements that contribute to a better catalyst utilization compared to conventional methods. These facts were corroborated after manufacturing several membrane electrode assemblies (MEAs) with electrodes prepared by three different methods. MEAs obtained by means of the electrospray technique exhibited three times higher power density than those prepared by the impregnation method ones and eight times higher than MEAs made with electrodes prepared by the spray technique with platinum loadings of 0.5 mg cm^{-2} . Moreover, the power density obtained was twice better than a commercial E-TEK. This technique can be scaled up and becomes a volume production method using a low-cost process.

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1. Introduction

One of the main requirements for fuel cell commercialisation is to reduce the cost of the materials used. Due to the fact that proton exchange membrane fuel cells (PEMFC) need precious metals as electrocatalyst, generally platinum and its alloys, decreasing the amount of active metal without sacrificing the performance is mandatory. For this purpose, it is important to increase the reaction sites in the catalytic layer, which are in direct contact with the membrane and the gas diffusion layer to form the membrane-electrode assembly (MEA) [1]. Moreover, in addition to the catalyst loading, there are a number of catalyst layer properties that have to be optimised to achieve a high utilization of the catalyst material: i.e. reactant diffusivity, ionic and electrical conductivities and the level of hydrophobicity, which have to be carefully balanced [2].

At the moment, there are two modes for manufacturing MEAs [3] that consist in the application of the catalyst layer to either the gas diffusion layer or the membrane. The hot-pressing procedure is then used to add the membrane or the gas diffusion layer, respectively. The first option has the advantage of preserving the membrane of chemical attacks of the solvents present in catalytic inks. It allows applying later steam or boiling water treatments, which increase the number of active sites or regions in the catalyst layers [4], or adding pore formers to the catalytic layer to create the sufficient porosity for mass transportation [5].

In order to obtain a suitable catalyst layer structure, several methods to prepare electrodes have been developed. Typical methods of manufacturing like casting [6], painting [7,8], spreading [9], spray [10–12] or catalyst powder deposition [13] do not allow a high dispersion of the catalyst and, as a consequence, the utilization of the platinum is low. So, several alternatives have been proposed to decrease the catalyst loading with adequate performance. In this way, common vacuum deposition methods that include chemical vapour

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deposition [14], physical or thermal vapour deposition [15] have been employed. Sputtering is considered as one of the best approaches to apply the catalyst to the gas diffusion layers [16,17]. However, this technique is not a volume production method and requires expensive vacuum equipment. Electrodeposition methods have been also described [18,19] and promising results were obtained.

In this work, a novel method to prepare electrodes based on the electrospray technique has been developed. To assess the quality of the materials obtained, morphological and structural characterizations have been carried out. In order to compare with other fabrication methods, electrodes prepared by impregnation and spray were obtained. Electrochemical characterization allowed measuring the performance of MEAs prepared with electrodes fabricated by different methods and quantifying the improvement of the catalyst layer structure.

2. Experimental

The preparation of the catalyst suspension ('ink') was made by mixing the catalyst (20 wt.% Pt/C supplied by E-TEK), the ionomer (Nafion, supplied by ALDRICH, 5 wt.% solution in a mixture of lower aliphatic alcohols and deionised water) and different solvents (*n*-butylacetate, ethanol and glycerol). The optimum composition was described in a previous work [20]. Once put together all components, the mixture was ultrasonicated for 30 min.

Catalytic ink was dispersed onto a carbon cloth support by means of three different methods, impregnation, spray and electrospray, to achieve a Pt loading of 0.5 mg cm^{-2} . The first method for electrodes preparation consisted in impregnating the ink directly on the diffusion layer. These electrodes will be called IM in this work. The second method consisted in spraying the catalytic mixture using commercial airbrush Vega 2000 (electrodes SP). Finally, an innovative method based on the electrospray technique [21] was developed to make electrodes (called EL in this work). It consists on applying a voltage (3300–4000 V) between a capillary tube, in which the ink is forced to flow, and the carbon cloth substrate. The effect of the high electric field, when the solution emerges, is generating a mist of highly charged droplets. During this process, the droplets are reduced in size by evaporation of the solvent and/or by "Coulomb explosion" (droplet subdivision resulting from the high charge density). In order to force the catalytic ink to pass through the capillary tube, a nitrogen pressurized tank was used. The catalytic ink was put in an ultrasonic bath to keep it in a homogeneous mixture. The carbon support was moved by means of a X–Y axes coordinated system, which was controlled by a software application.

Once fabricated the electrodes by the three methods, several characterization techniques were used to obtain information about morphology and structure of the catalytic layer. The morphology of the catalytic layer was studied by

means of a Scanning Electron Microscopy (SEM) equipment model Hitachi S-2500 with a microprobe Kevex and an image capture system RONTEC (Röntgeanalysen, Technik). The scanning electron microscope FEI QUANTA 200 with EDAX-system was used to calculate the atomic percentage of every component. The X-ray photoelectron spectroscopy (XPS) analyses were carried out with a Perkin-Elmer PHI 5400 spectrometer equipped with a Mg $K\alpha$ excitation source ($h\nu = 1253.6 \text{ eV}$) and a beam size of 1 mm diameter. Pressure in the sample chamber was $\sim 10^{-9}$ Torr. Pass energy was 89.5 eV for general spectra (0–1100 eV) and 35.75 eV for high resolution spectra. In order to take into account the charging effects on the measured binding energies, these energies were determined by referencing to the C1s, Pt4f and O1s peaks. X-ray diffraction (XRD) was carried out to assess the presence of high size crystalline agglomerates. XRD patterns were collected with a Seifert 3000P diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

The electrodes prepared by the different methods were used to obtain membrane electrode assemblies (MEA) using a hot pressing procedure. To evaluate their performance, an E-TEK commercial MEA was characterized in the same conditions and compared with them. The size of electrodes was $3 \text{ cm} \times 3 \text{ cm}$ and the membrane used was Nafion 117. Single cell tests were carried out at room temperature and atmospheric pressure.

3. Results and discussion

An electrochemical characterization of MEAs was carried out to compare electrodes obtained with the three methods. After reaching a steady state, the polarization curves were measured (Fig. 1). In order to compare the results, a normalization of voltage was proposed, where V is the voltage at different current demand and V_0 is the voltage at open circuit. As can be observed, the best results are obtained for the MEA prepared with EL electrodes. At a value of $V/V_0 = 0.5$, this MEA is able to provide an intensity more than twice better than the E-TEK MEA, nearly three times better than IM electrodes and eight times better than the value obtained using the SP ones. The same tendency was seen when the maximum power results were compared for the characterized MEAs. The ratio P/P_{max} , where P is the power at different current demand and P_{max} the maximum value obtained among all MEAs tested, is plotted in Fig. 1b. The high P_{max} value was also obtained for MEA prepared with electrodes EL. So, the reference value for this MEA is $P/P_{\text{max}} = 1$, while MEAs with electrodes E-TEK, IM and SP were 0.45, 0.36 and 0.13, respectively.

This better performance can be attributed to the higher platinum utilization and the optimisation of the catalyst layer structure. To confirm this supposition, a physicochemical characterization of the three electrodes was carried out by several techniques in order to compare the influence of the

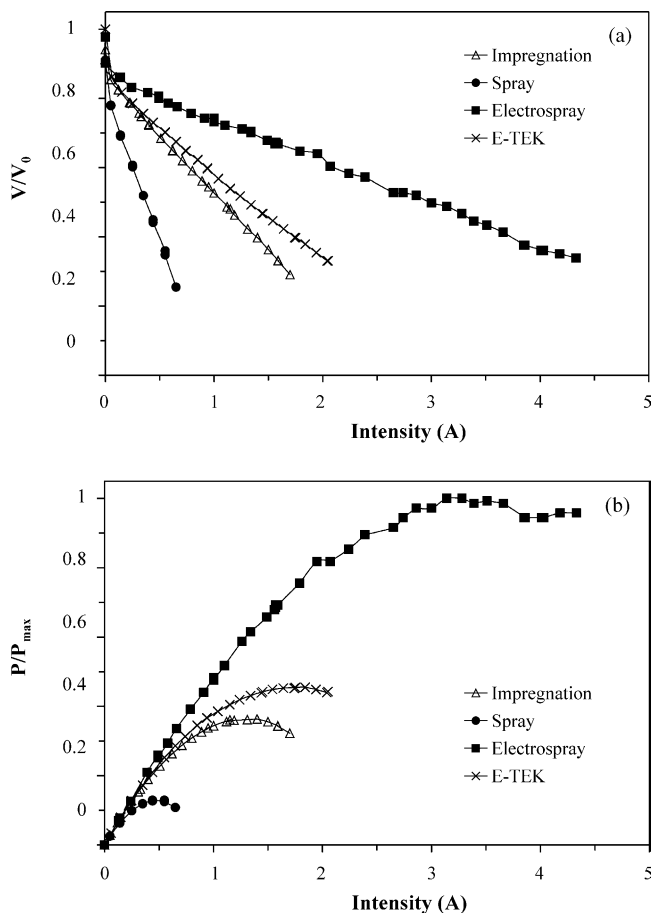


Fig. 1. Performance comparison of MEAs prepared by several methods: (a) normalized voltage curves and (b) normalized power density curves.

method of preparation in both the structure and morphology of the catalytic layers.

In Fig. 2, Scanning Electron Microscopy (SEM) was carried out on electrodes and compared with initial carbon cloth

(Fig. 2a). A great difference in the catalytic layer is detected, depending on the preparation method used, with regard to the initial structure of the gas diffusion layer. For the IM electrode (Fig. 2b), the catalytic ink was spread on the support resulting in a homogeneous layer that covers completely the fibres of the carbon cloth. By the contrary, when the spray method was used (Fig. 2c), the electrode obtained (SP) shows particles deposited on gas diffusion layer that form agglomerates among the fibres. The amount of platinum particles that takes part in the electrochemical reaction decreases. Furthermore, the diminution of space among fibres generates a decrease of the porosity and, therefore, makes the diffusion of gases and water removal worse. Finally, preparing the EL electrode by the new method of electrospray, a uniform distribution of particles along fibres is observed (Fig. 2d). This behaviour is continuous in the entire electrode surface and it makes the ionic and electronic transfer easy without altering significantly the good structure of the gas diffusion layer. Moreover, the access of reactants to the platinum particles is improved. This effect can produce a better utilization of the catalyst and, consequently, a higher performance of the electrode.

The EDAX technique allows detecting the presence of chemical elements in the catalytic layer and determining the atomic percentage of them from the intensity of their peaks. In Fig. 3, EDAX spectra for spray and electrospray methods are compared. It can be observed a higher intensity for Pt peak for the first method. In Table 1, the values obtained for the three methods of electrode preparation are shown. Data show that, in these cases, the atomic percentages of elements studied are similar but differ highly from the electrospray one. This behaviour can be due to the difference in thickness of the catalytic layers. In the EL electrode, this layer is considerably smaller and so X-ray passes through it, reaching the hydrophobic layer that covers the fibres of the gas diffusion layers and, as a consequence, the platinum value is lower on

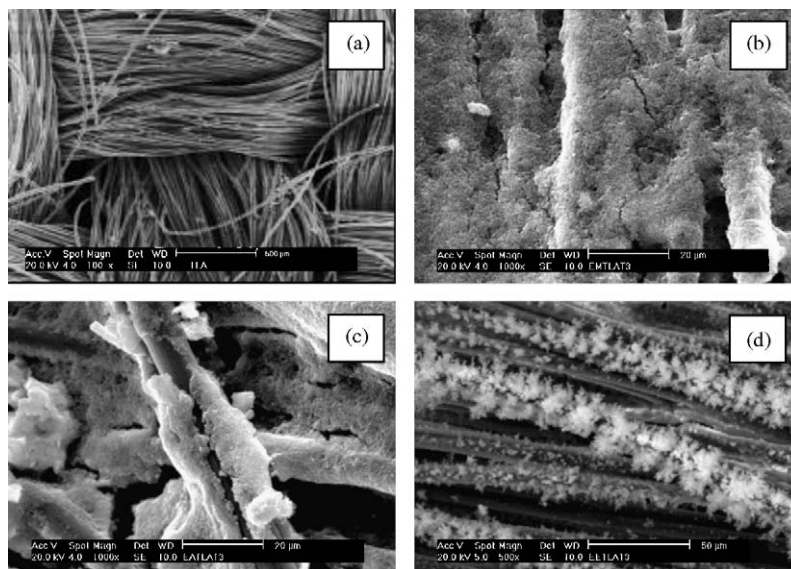


Fig. 2. SEM micrographs: (a) carbon cloth, (b) impregnation, (c) spray and (d) electrospray.

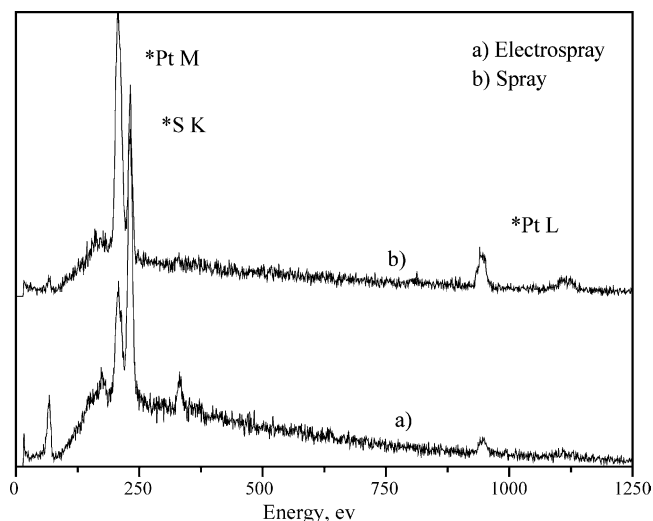


Fig. 3. EDAX spectrum: (a) electro spray and (b) spray.

Table 1

Atomic percentage of elements obtained by EDAX for the three methods of preparation

Elements	Atomic %		
	Impregnation	Spray	Electrospray
C (K)	91.91	90.64	71.52
O (K)	4.15	5.19	14.56
F (K)	1.51	1.91	10.53
S (K)	1.24	1.38	3.29
Pt (M)	1.19	0.88	0.10

average. It leads to think that the thinner active layers cause a high catalyst utilization due to minimization of transport limitations of reactants and protons in the ionomer as was reported by other authors [22,23].

Table 2

Atomic percentage of elements obtained by XPS for the three methods of preparation

Elements	Atomic %		
	Impregnation	Spray	Electrospray
F (1s)	32.2	36.2	37.2
O (1s)	13.5	16.3	11.9
C (1s)	53.1	46.5	50.1
S (2p)	0.60	0.80	0.70
Pt (4f)	0.60	0.20	0.10

The distribution of the elements on the surface was also shown by EDAX mappings of Pt, S, O and F (Fig. 4) using the electro spray method. It can be observed that platinum is present in the entire surface of the catalytic ink in the same quantity. In the case of the other elements, they are distributed along the fibres since they come from polytetrafluoroethylene (PTFE) that covers the carbon cloth and gives it hydrophobicity.

By means of the XPS technique, it was obtained information about surface element concentrations between 0.4 and 4 nm in depth. We can notice the presence of the main components: C, F, S, O and Pt. The atomic percentage of the surface atoms was calculated from the ratios of peak intensities of each element. The values obtained for each preparation method are presented in Table 2. The lower presence of platinum in the EL electrode can be attributed to a better distribution of the catalyst along the fibres as was commented in Fig. 2. This behaviour was the same that the obtained for the catalytic layer by EDAX. In the C1s spectra of the three electrodes (Fig. 5a) the signals of carbon black and of the carbon in the polymer have different binding energies: 284.1 and 291.0 eV, respectively. The carbon in the Nafion polymer is mainly in a $(CF_2)_n$ -configuration and the peak intensity varies

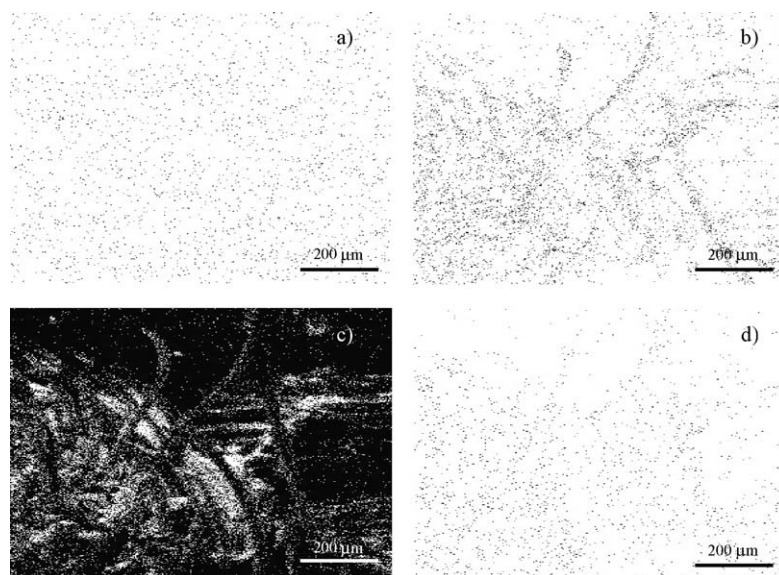


Fig. 4. EDAX mappings of electrodes prepared by the electro spray method for the elements: (a) platinum, (b) sulphur, (c) oxygen and (d) fluorine.

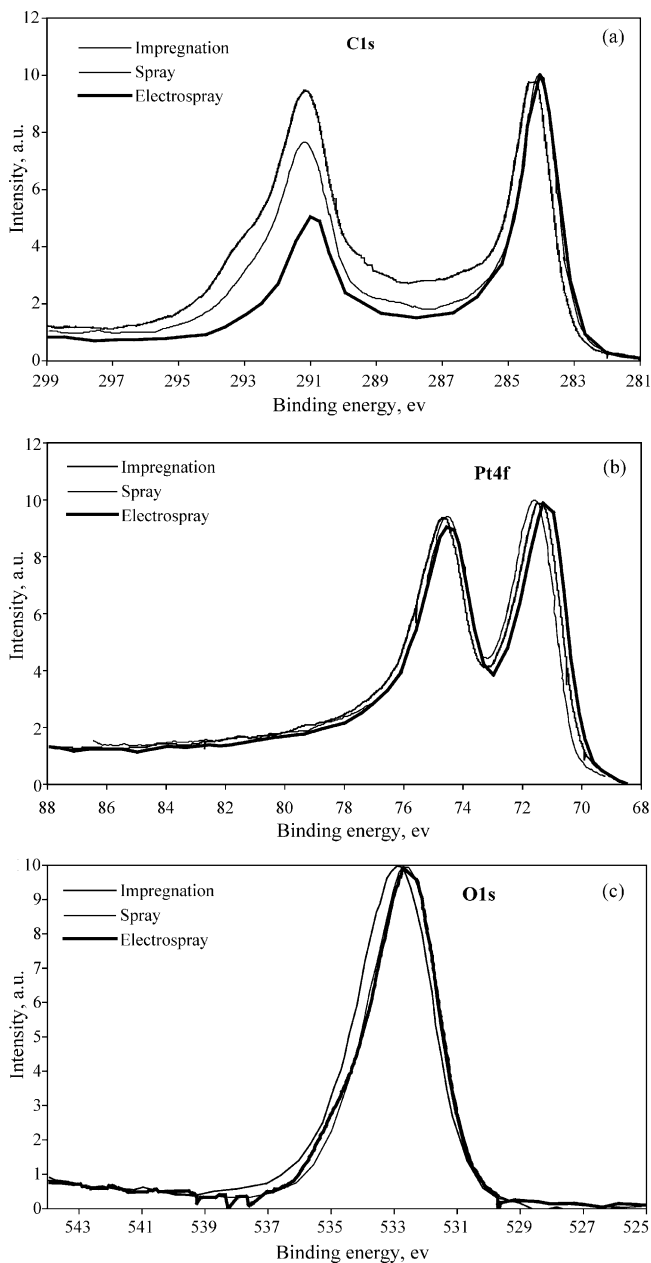


Fig. 5. XPS spectra of electrodes prepared by different methods: (a) C1s, (b) Pt4f and (c) O1s.

depending of the preparing method. For the electro spray, the peak at 291.0 eV is lower than the others. This behaviour may indicate, as it has been commented above, a better distribution of the ionomer along the surface of the electrode. However, this effect is slighter for Pt 4f (Fig. 5b) and O1s (Fig. 5c) due to the low quantity of these species on the surface.

XRD patterns are presented in Fig. 6. The electrodes obtained by the three preparation methods were compared with the commercial Pt/C catalyst used as raw material. So, the peak correspondent to platinum ($2\theta = 40$) is detected for IM electrode but it is not perceptible for SP and EL ones. It can be due to a better distribution on the surface. However, particle agglomerates are lower for the electro spray method

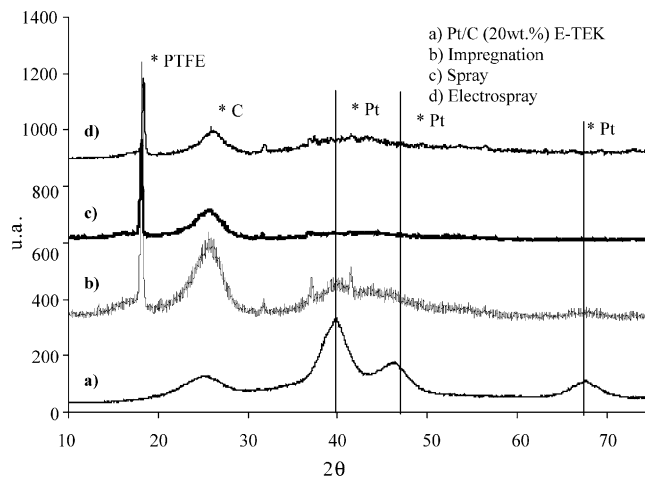


Fig. 6. XRD patterns for (a) commercial Pt/C catalyst and electrodes prepared by: (b) impregnation, (c) spray and (d) electro spray.

electrode than for the spray one as was seen in the SEM micrographs.

4. Conclusions

A novel method for electrode preparation using the electro spray technique allows improving the catalytic distribution on the electrode surface. The morphology and structure of electrodes, characterized by several techniques: SEM, EDAX, XPS and XRD, give information about the catalyst layer and the results can be compared with electrodes obtained by other conventional methods. The SEM micrographs show a different structure where the gas diffusion layer characteristics are nearly altered. The structural differences of the catalyst layer are corroborated by the X-ray characterization techniques where platinum appears better distributed. The polarization curves show the best performance for electro spray electrodes. It leads us to think that the novel method developed to prepare electrodes can contribute to a higher platinum utilization and, as consequence, a better performance for a same amount of active metal in the catalytic layer.

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