

Study of membrane electrode assemblies for PEMFC, with cathodes prepared by the electrospray method

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Available online 30 January 2007

Abstract

The electrospray deposition of platinum supported on carbon (Pt/C) particles has been used for the preparation of electrodes for proton exchange membrane fuel cells (PEMFCs). The departing suspensions contain the Pt/C electrocatalyst together with an ionomer (Nafion[®]) and a solvent. Two types of solvent have been used, isopropanol and a mixture of butylacetate, ethanol and glycerol (BEG). The microscopic characterisation of electrosprayed films shows the electrospray deposited Pt/C films with a dendritic morphology. XPS analysis of the films reflects changes in the ionomer component after electrospray deposition. A decrease in the signal corresponding to backbone chain (CF₂) is observed on the films deposited with the low evaporation temperature solvent (isopropanol), indicating some disruption of ionomer chains during the electrospray process. With high evaporation temperature solvent (BEG), the disruption effect seems less acute. Membrane electrode assemblies were prepared with the electrosprayed electrodes as cathodes. Good general performance is encountered, comparable with standard commercial cathodes. Electrosprayed electrodes prepared from high evaporation temperature solvent (BEG) show a higher surface specific area. The internal resistance is something higher for MEAs with electrosprayed cathodes. The long term stability test shows a performance loss of about 10 $\mu\text{V h}^{-1}$ over 700 h continuous testing. © 2007 Elsevier B.V. All rights reserved.

Keywords: Electrocatalyst; Electrospray deposition; Cathode; PEMFC

1. Introduction

One of the main objectives for future generations of polymer electrolyte fuel cells is cost reduction, which largely relies on a decrease of the platinum loading of the electrodes. This objective may be attained by different routes, like improved electrode preparation methods with higher control for platinum particle deposition, the search for high temperature tolerant membranes to promote electrocatalysis and hence reduce electrocatalyst requirements, or the search for new electrocatalyst materials other than platinum. Among novel electrode preparation methods, most interesting are those attaining thin films with high platinum dispersion and high surface area. In addition, the methods should be able to allocate platinum particles in a close proximity to the membrane surface to optimize the activity [1].

One interesting electrocatalyst deposition method is based on the electrospray effect. The electrospray effect consists of the transfer of a material (a liquid or suspension) to an aerosol phase (mist) under the action of an electric field [2]. From the aerosol phase, the material can be transferred to a substrate (electrospray deposition). Metal and compound nanoparticles have been deposited by electrospray and electrospray–pyrolysis with variable film morphology [3–6]. Localised deposition of organic and inorganic materials is possible with micrometric lateral resolution [7]. The electrospray effect is also applied for sample inlet in mass spectrometry [8] and for micro and nano-sized encapsulation [9].

Among the interesting properties of this technique, are the relatively simple experimental set up, which does not require special conditions in terms of temperature or vacuum, and the possibility to grow films with high uniformity and variable morphology. The electrostatic interaction between the charged particles and the surface substrate during electrospray deposition will prevent formation of agglomerates and favor the adhesion to the substrate. Surface morphology may be changed, depending on experimental parameters, such as substrate temperature,

Presented at Second National Congress on Fuel Cells, CONAPPICE 2006.

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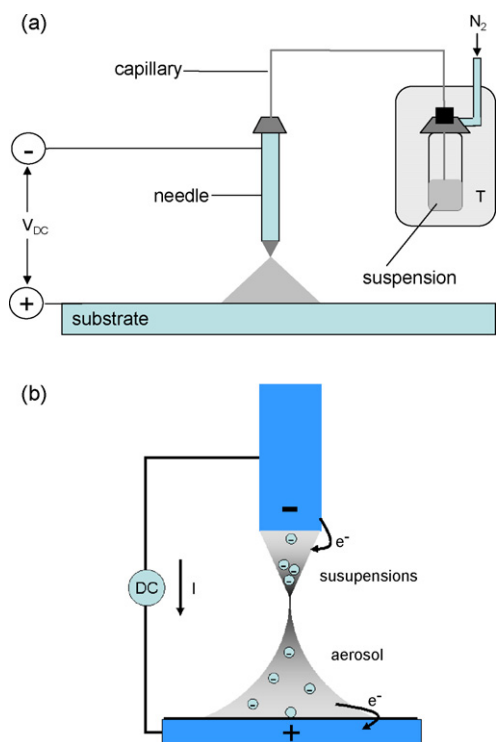


Fig. 1. (a) Scheme of the set up for electro spray deposition of Pt/C suspensions. (b) Detail of the electro spray process in the needle to substrate space.

liquid flow rate, dc voltage and tip-to-substrate distance, which control solvent evaporation and droplet size [6]. In addition, there is the possibility to use multiple electro spray jets [10,11] to increase the growth rates.

Electro spray deposition has already been used for the preparation of electrodes for PEMFC with good initial performance (1 A cm^{-2} at 700 mV , 80°C and 300 kPa , using Nafion® 112 membrane and 0.36 mg cm^{-2} Pt loading), but significant mass transport losses [12]. In our laboratories, the electro spray deposition has been recently set up for the preparation of PEMFC electrodes [13], and studies about electrocatalysis for oxygen reduction have been performed on electro sprayed films with the rotating disk electrode [14].

Electrodes for PEMFC are usually prepared from a suspension containing the Pt/C catalyst together with a proton conductor (ionomer) in a solvent. The suspension is deposited onto the electrode substrate (carbon cloth, carbon paper) leaving, after solvent evaporation, a film ('active film') of the catalyst and ionomer, which exhibits both electronic and proton conductivity. Electro spray deposition of Pt/C films departs from the same type

of suspension. During the electro spray process, the suspension is forced through a silica capillary to a metallic tip, where the liquid meniscus acquires a typical inverted cone shape (Fig. 1a). Here, a high concentration of ionised species (ions, molecules, particles) is created by electron transfer from the tip (Fig. 1b). The ionised droplets will reduce in size by evaporation of the solvent, and 'Coulomb explosion' occurs when the charge density on the drops overcomes surface tension forces, giving rise to an aerosol of very small and uniform ionised particles that are deposited and discharged on the substrate. The electro spray flux closes an electric circuit where a dc current flows, proportional to the deposition rate (Fig. 1b). For more details of the electro spray method we refer the reader to the specialised literature [3–11].

The electro spray process is very dependent on the presence of dissolved ions and surface charges on colloids and particles. Therefore properties like the dielectric constant of the solvent are of high importance. Other important properties are the density, viscosity and surface tension, which will control droplets size and flux rate.

In this work, electrodes for PEMFC have been prepared by the electro spray deposition method. For the preparation of starting suspensions, two liquids have been used, isopropanol and a mixture of butyl acetate, glycerol and ethanol (BEG). Membrane electrode assemblies (MEA) have been prepared using the electro sprayed electrodes as cathode, together with commercial electrodes as anode and Nafion 112 membrane. Results of the characterization in fuel cells are compared with those of MEAs prepared with commercial components.

2. Experimental

Suspensions of Pt/C powder (E-TEK, 20 wt%) were prepared using two different solvents, isopropanol and a mixture of butylacetate, ethanol and glycerol (BEG). Nafion® solution (Aldrich, 5% in aliphatic alcohols) was added to the suspension in 33 wt% of solids. Properties of the liquids alone and with the Nafion® solution added are given in Table 1. Viscosity (μ) was measured with a rotational viscosimeter (ST-DIGIT L); dielectric constant (ϵ) determined with a Liquid Dielectric Constant Meter (Bi-870); density (ρ) with a Gay-Lussac picnometer (Álamo); ionic conductivity (σ) with a conductivity cell (Beckman) and evaporation temperature (T_{evap}) from thermogravimetric analysis (Mettler Toledo).

The electro spray deposition was carried out on uncatalysed carbon cloth covered with gas diffusion layer (ELAT ETEK) over 29.2 cm^2 area, by imposing a dc voltage between 3300 and 4000 V (Bertran, Model 205B-10R), between a metallic needle

Table 1
Viscosity (μ), dielectric constant (ϵ), density (ρ), ionic conductivity (σ) and evaporation temperature (T_{evap}) of the solvent and mixtures used in this work for the preparation of Pt/C suspension, measured at 25°C

Liquid medium/solvent	μ (cP)	ϵ	ρ (g cm^{-3})	σ ($\mu\text{S cm}^{-1}$)	T_{evap} ($^\circ\text{C}$)
BEG (45:50:5)	1.67	14.5	0.869	0.92	180
BEG + Nafion (33%)	1.78	14.8	0.874	0.63	–
Isopropanol	1.91	18.3	0.793	1.59	82.4
Isopropanol + Nafion (33%)	2.04	22.4	0.804	1.07	–

BEG, butylacetate/ethanol/glycerol (45/50/5).

(ejector) and the substrate (carbon cloth), with the substrate connected to the positive pole. During deposition a dc current of 100–500 nA is measured using 1 M Ohm resistance, due to the electro spray flux. The suspension is placed in a beaker connected with the needle by a silica capillary (100 μm internal diameter). The beaker is submitted to ultrasonic stirring to maintain particles in suspension, and pressurized with N_2 (1–2 bar) to force the flow of the suspension through the silica capillary to the metallic needle. The substrate is heated at 60 $^\circ\text{C}$ ($\pm 5^\circ\text{C}$) with an infrared lamp, and placed on a computerised X–Y stage (Physik Instrumente) for deposition in successive sweeps. A scheme of the set up is shown in Fig. 1a.

For XPS characterisation, the Pt/C + Nafion[®] (33%) films were deposited onto a Si substrate, previously etched in an aqueous HF 10% solution (2 min, 50 $^\circ\text{C}$). The films were deposited onto the etched Si substrate by electro spray and by pulverization method, for comparison, using an airbrush (Vega System) and the same suspension composition. A Perkin Elmer PHI 5400 spectrometer was used, with Mg K α radiation ($h\nu = 1253.6 \text{ eV}$), 300 W source strength and 25 mm \times 25 mm beam size, under 10^{-9} Torr pressure in the sample chamber. Parameters of the XPS signals (binding energy, width and intensity) were measured with the equipment software, by fitting to a symmetric Gaussian-Lorentzian (0.8–0.2) sum functions after subtracting the background by the Shirley method. SEM images were obtained with a Hitachi-S-2500 equipment.

Membrane electrode assembly preparation was carried out by hot-pressing (120 $^\circ\text{C}$, 55 kN, 180 s), using electro sprayed electrodes on the cathode side, commercial ETEK on the anode side and a Nafion 112 membrane. Single cells were built with graphite flow field plates with a three-fold serpentine for gas flow, and stainless steel end plates.

Characterisation in single cells was carried out in a test bench, under thermostatic control for the cell, the gas humidifiers and the gas conduits. An electronic load (Hewlett Packard) was used for current demand. Gas flow rates were controlled with mass flow controllers. CO stripping voltammetries were carried out on MEAs to determine cathode surface area at 10 mV s^{-1} , 80 $^\circ\text{C}$, with H_2/N_2 on anode and cathode, after passing 1% CO + 99% N_2 gas on the cathode side during 15 min at 80 $^\circ\text{C}$ and 125 mV polarisation. Internal resistance measurements were carried out by the current pulses method, submitting the cell to short current demand pulses (5 A, 10 μs) and measuring the voltage change with an oscilloscope [15].

3. Results

3.1. Characterisation of electro sprayed films

The morphology of the film deposited by electro spray is shown in Fig. 2. The surface of the substrate (Fig. 2a) shows micrometric cracks crossing the carbon gas diffusion layer. The deposited Pt/C layer shows a dendritic morphology (Fig. 2b), covering the entire substrate. Such a morphology is observed with both solvent types used in this work (see properties in Table 1), and is typical for a deposition process limited by the slow flux of material. Particles arrive at the substrate at a slow

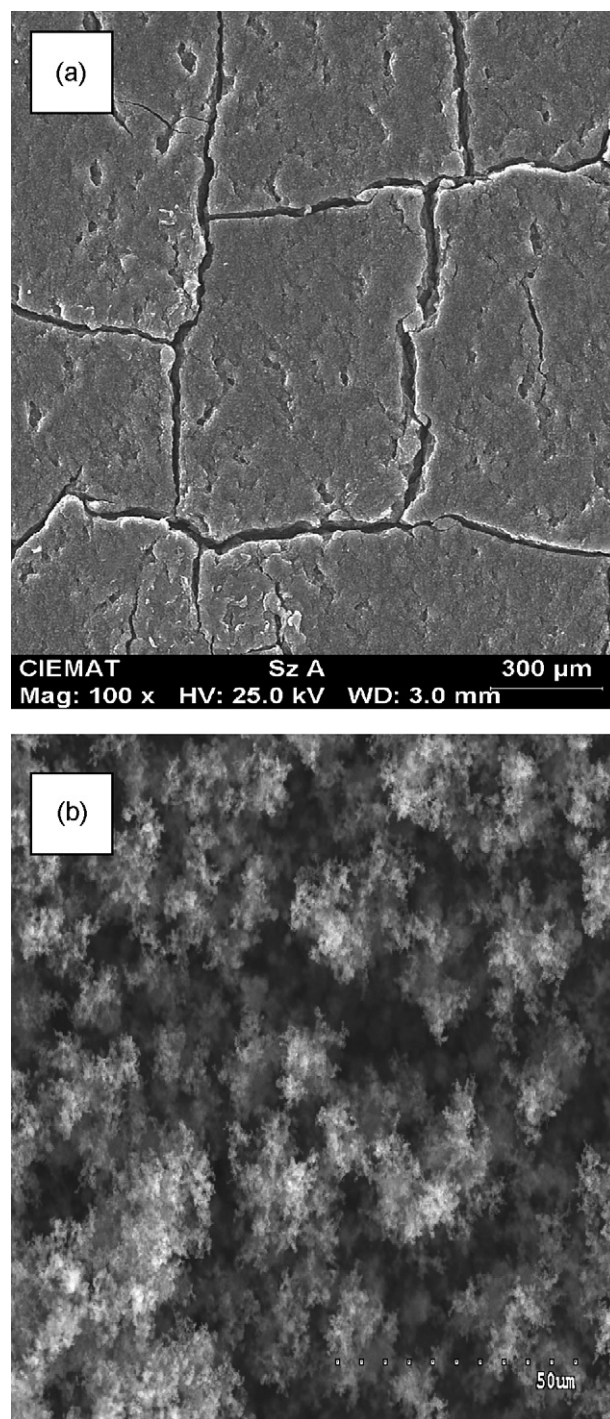


Fig. 2. SEM images of uncatalysed gas diffusion layer substrate (a) and electro sprayed deposited Pt/C-Nafion[®] (33 wt%) suspension.

flow rate (0.2 to 1 ml h^{-1}), and deposit almost free of solvent [11,16,17]. Each arriving particle allocates on lowest resistance (needle to substrate), energetically most favorable, sites.

TEM images of the Pt/C electrocatalyst before (a) and after (b) electro spray deposition are shown in Fig. 3. Particles of less than 5 nm diameter can be seen in both images, maintaining apparently a similar distribution as the starting material, except for some increase in mean particle size after electro spray deposition, probably because of the formation of some agglomerates

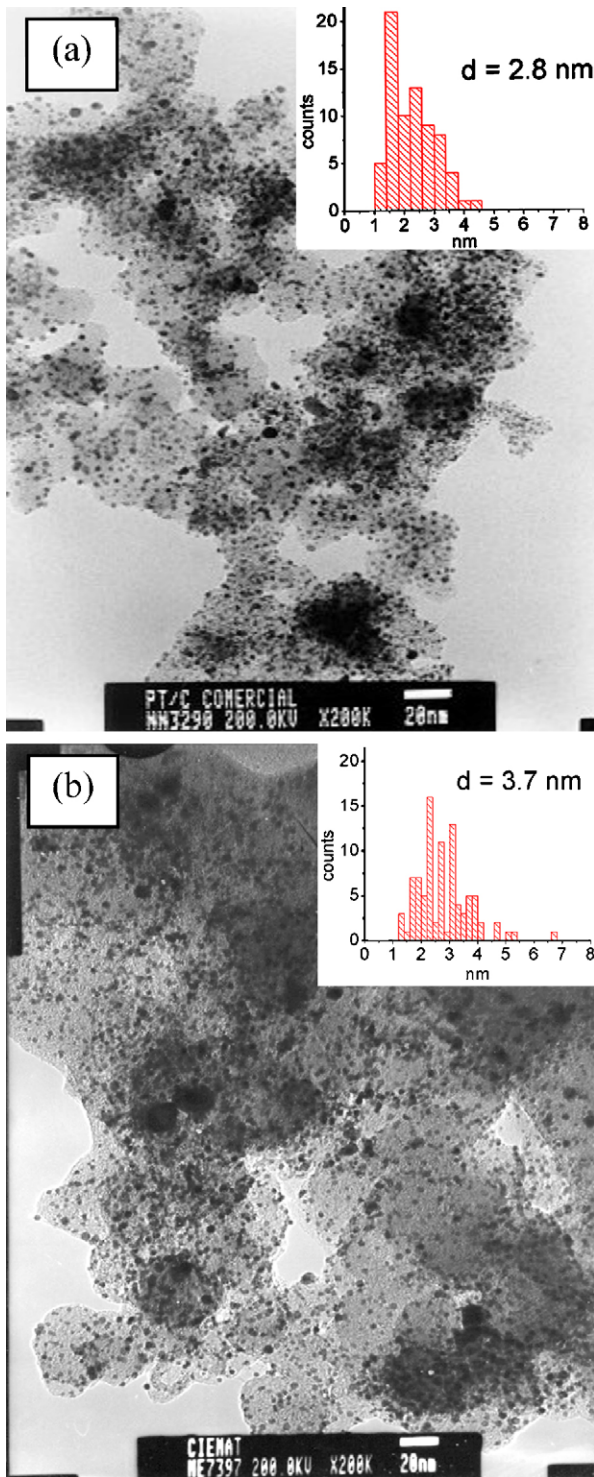


Fig. 3. TEM images of the Pt/C electrocatalyst powder (Etek, 20 wt% Pt) (a) and of a Pt/C-Nafion[®] (33 wt%) powder, after electro spray deposition.

(Fig. 3b). It may be concluded from these images that the electro spray process does not alter significantly electrocatalyst conditions to a nanometer scale, except for some agglomerate formation.

Surface chemical analysis of the Pt/C films deposited on Si substrate was carried out with the XPS technique. The Pt 4f signal (Fig. 4) shows metallic platinum with almost identical

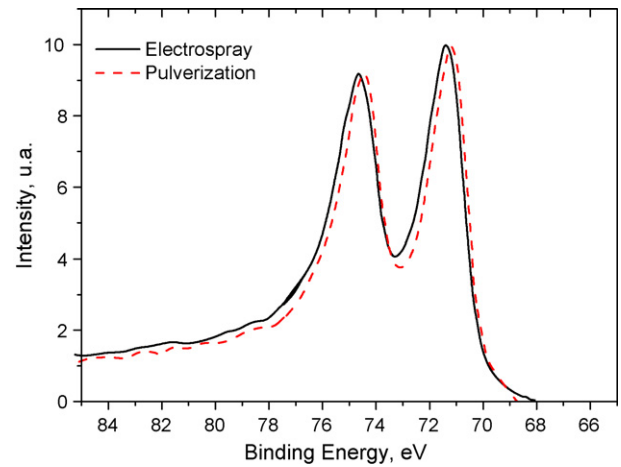


Fig. 4. Pt 4f XPS signal corresponding to two Pt/C-Nafion (33 wt%) films deposited by electro spray and by pulverization with airbrush, in isopropanol solvent.

characteristics for electro sprayed films ($E_B = 71.3$ eV) and films deposited with an airbrush ($E_B = 71.2$ eV). However, the C 1s signals show differences due to the solvent and deposition method (Fig. 5). The analysis of this signal shows five contributions (Table 2): two main components at $E_B = 284.5$

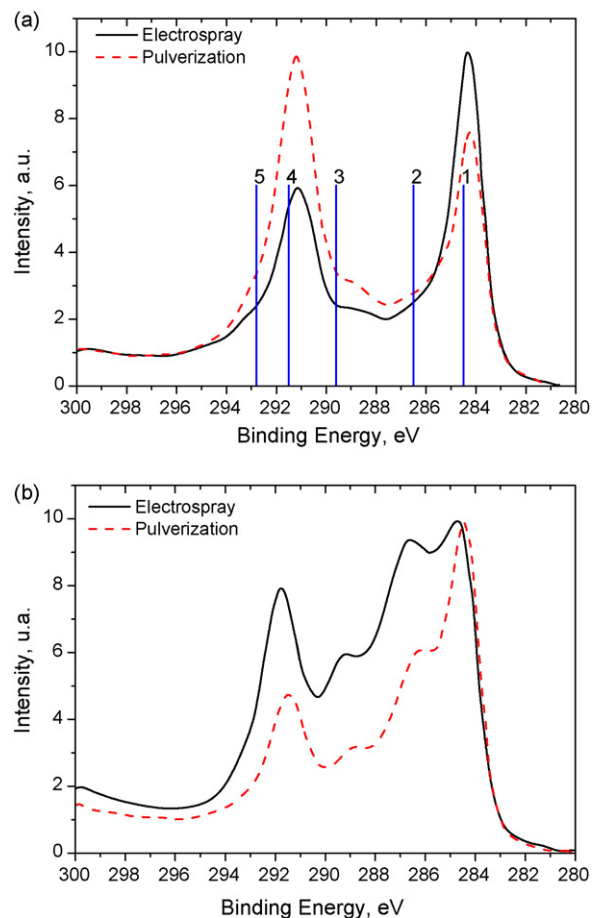


Fig. 5. C 1s XPS signal corresponding to Pt/C-Nafion (33 wt%) films deposited by electro spray and by pulverization with airbrush, using: (a) isopropanol and (b) BEG, as dispersants for the suspensions.

Table 2

Binding energy (E_B), species identification and Pt/C suspension component, corresponding to the C 1s XPS signal of Pt/C films electro-spray deposited on Si substrate

n	E_B (eV)	Chemical species	Component of the suspension
1	284.5	CH ₂ , C–C	Isopropanol, BEG, C-support
2	286.5	C–OH	Isopropanol, BEG
3	289.6	COOH, CF (b)	BEG, Nafion
4	291.5	CF ₂ (b,s), OCF (s), OCF ₂ (s)	Nafion
5	292.8	CF ₃ (b,s)	Nafion

(b) Backbone and (s) side chain.

and 291.5 eV attributed to C–C species of the carbon support, and CF₂, OCF and OCF₂ groups of the Nafion[®], respectively [18]. This second signal can be considered as a backbone signal of the Nafion[®] polymer, which for each molecular formula (EW = 1000) contains 11 CF₂, 2 OCF₂ and 1 OCF [19]. Other contributions appear at $E_B = 286.5$ eV, due to C–OH, and $E_B = 289.6$ eV due to COOH and CF. The identification of the signals is summarized in Table 2.

Pt/C films prepared with BEG solvent (Fig. 5b) show more intense COOH and COH signals, as compared to those prepared with isopropanol (Fig. 5a). This result indicates incomplete elimination of BEG solvent from the films after deposition. A difference in C 1s signals can also be observed in Fig. 5, due to the deposition method. On films deposited with airbrush, Pt/C shows a more intense Nafion[®] backbone signal (291.5 eV), when using isopropanol rather than using BEG solvent. This trend is reversed with the electro-spray method.

3.2. Membrane electrode assembly characterisation

For MEAs preparation, electro-sprayed electrodes (0.3 mg cm⁻²) were used as cathodes, and commercial electrodes (E-TEK, 0.6 mg_{Pt} cm⁻²) as anode. The characterisation of MEAs in single cells was carried out after 200 h running under a constant current demand (500 mA cm⁻²). The Pt roughness coefficient, i.e. the quotient of the total platinum area and the electrode geometric area and mass specific area (area of platinum per gram) were measured from CO stripping voltammetry experiments (Fig. 6). Resulting values are given in Table 3, showing significant differences among the electrodes. The samples prepared by the electro-spray method using BEG solvent show the highest mass specific surface area (101 m² g_{Pt}⁻¹) and a roughness coefficient $r = 289$, as compared to electro-sprayed

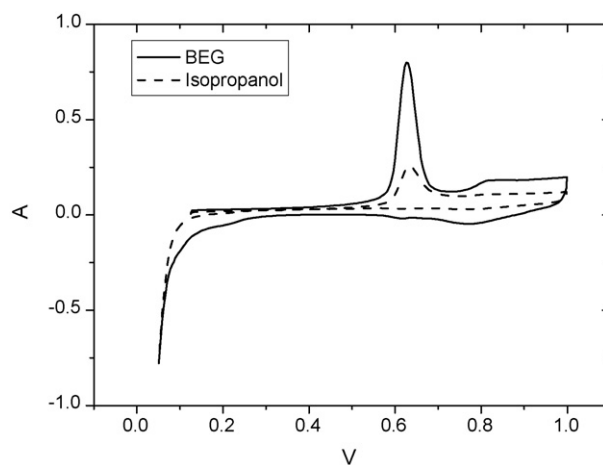


Fig. 6. CO-stripping voltammetry on electro-sprayed cathodes prepared from BEG and isopropanol suspensions.

electrodes using isopropanol solvent and commercial ETEK cathodes.

The internal resistance of the MEAs was measured by the current pulses method (Table 3). The values show some higher resistance for MEAs prepared with electro-sprayed cathodes (72–77 mΩ cm²) than with commercial cathodes (62–65 mΩ cm²).

Polarisation curves using H₂ and O₂ with stoichiometry factors 1.5 and 9.5 for anode and cathode, respectively, are shown in Fig. 7a, for the electro-sprayed cathodes prepared with BEG and isopropanol as solvents, and for two commercial ETEK electrodes (Table 3). The behaviour at low current densities is shown in the inset, reflecting a better performance at these potentials for electro-sprayed electrodes with BEG solvent. Tafel slopes (b) were obtained from the linear portion in the 0.9–0.8 V potential interval (Table 3). Values measured are similar for all of them, in the range from 66 to 78 mV dec⁻¹. In Fig. 7b, the polarisation curves are displayed normalised to the respective electrode surface area, whereas in Fig. 7c the same curves are normalised to their platinum content. The surface area normalised plot shows differences preferentially in the high current regime, above 1 mA cm²_{Pt}, whereas the plot normalized to the platinum content exhibits major differences among the MEAs in the low current regime.

Polarisation curves taken with different gas composition in the cathode feed are compared in Fig. 8. Curves are shown for H₂/O₂ (1.5/9.5) and for H₂/air (1.5/2.0) gas feed. As expected,

Table 3

Information and data from MEAs studied in this work, including anode and cathode types, Pt loading for anode and cathode, cathode roughness coefficient (r), cathode mass specific surface (s), Tafel slope (b) and internal resistance (R_i)

Anode	Cathode	Pt load (mg cm ⁻²)		$r(c)$ (cm ² cm ⁻² _{Pt})	$s(C)$ (m ² g ⁻¹)	b (mV dec ⁻¹)	R_i (mΩ cm ²)
		Anode	Cathode				
E-TEK	E-TEK	0.6	0.6	190	32	77.3	65
E-TEK	E-TEK	0.5	0.5	190	38	66	62
E-TEK	ELPRAY/BEG	0.6	0.3	289	101	73.1	72
E-TEK	ELPRAY/Isop	0.6	0.3	87	29	71	77

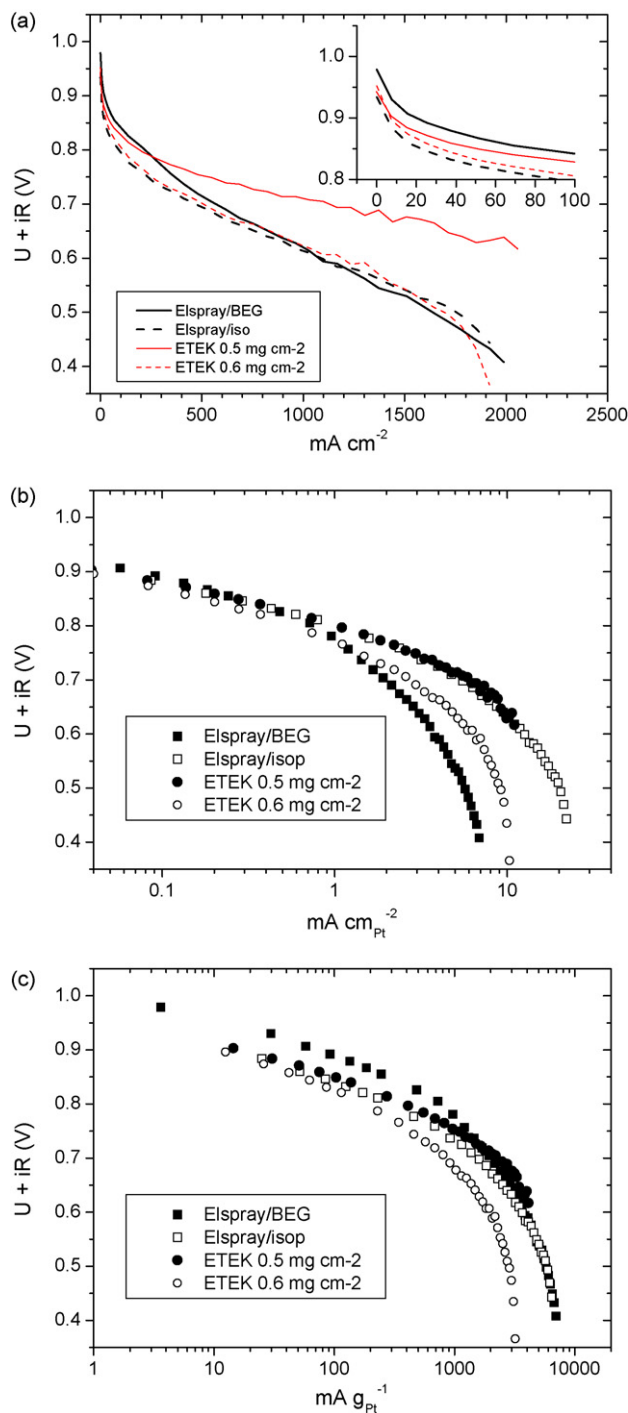


Fig. 7. (a) Polarisation curves corresponding to MEAs with electro sprayed cathodes using two solvents for preparation (isopropanol and BEG), and two MEAs prepared with commercial electrodes (ETEK). The inset shows the low current regime enlarged. Conditions are anode/cathode feed: H_2/O_2 (1.5/9.5), full humidification at 80°C . (b and c) are the same polarisation curve as a function of Pt area (b) and platinum mass (c).

the performance with air feed decreases at high current densities, due to oxygen transport limitation. Losses are comparative with more severe limitation for the electro sprayed electrode prepared with isopropanol (0.4V at 600 mA cm^{-2}).

The time behaviour of an electro sprayed electrode prepared with BEG solvent suspension is shown in Fig. 9. The volt-

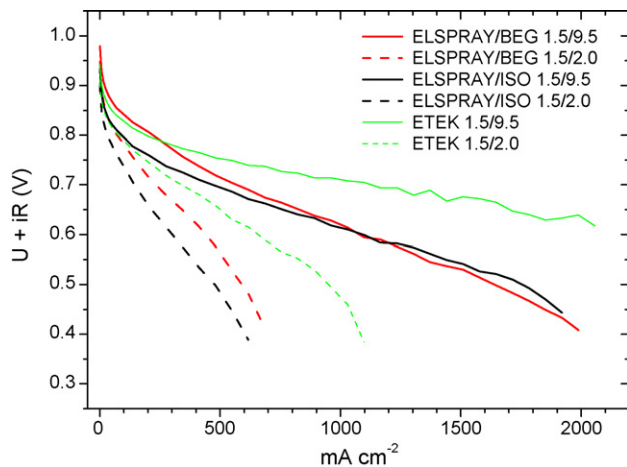


Fig. 8. Polarisation curves corresponding to MEAs with electro sprayed cathodes using two solvents for preparation (isopropanol and BEG), and two MEAs prepared with commercial electrodes (ETEK). The curves are obtained with two different gas feeds: H_2/O_2 (1.5/9.5) and H_2/air (1.5/2.0).

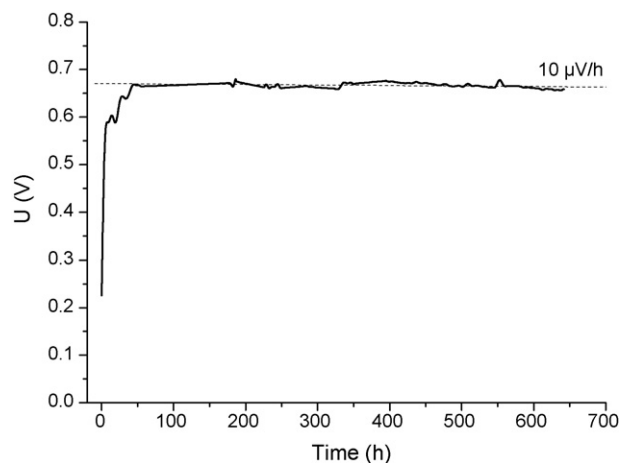


Fig. 9. Single cell voltage evolution at a constant current demand (500 mA cm^{-2}) for a MEA prepared with electro sprayed (BEG suspension) cathode.

age decays with a slope of $10\ \mu\text{V h}^{-1}$. During this time, the single cell was submitted to a constant current demand of 500 mA cm^{-2} , with some interruptions for test measurements (polarisation curves and internal resistance measurements).

4. Discussion

4.1. Solvent influence on electro spray deposition

During electro spray, the Pt/C suspension is submitted to a high electric potential that gives rise to the generation of ions at the meniscus of the needle (Fig. 1b). This process depends on liquid dispersant properties (Table 1), and may affect the different components of the suspension, i.e. Pt/C particles and Nafion[®] ionomer, in a complex way. As a hypothesis to explain ionization in the suspension, Nafion[®] predominates in colloidal state in both solvents [20], and electro spray ionisation should affect mainly surface charges of colloids. At the same time, ion-

isation may occur on the Pt/C particles, most probably involving oxygenated carbon groups, like $-\text{COOH}$, $-\text{COH}$.

Probably the most important difference in the solvents used in this work for electro spray deposition resides in their evaporation temperature (Table 1). Solvent evaporation takes place predominantly in the aerosol state, and gives rise to the reduction in the size of the droplets. XPS results show that isopropanol evaporation is complete, whereas the BEG solvent remains within the film (Fig. 5), due to higher evaporation temperature.

In addition, solvent evaporation during deposition may have another effect. Although the electro spray method produces mainly the disruption of non-covalent interactions, weaker covalent bonds may also be affected by collisions in the electro spray mist [8]. Such collisions are more efficient among desolvated gas phase ions to promote fragmentation, which occurs when using a low evaporation temperature and a high dielectric constant solvents. This may be the case when using isopropanol, as reflected by the XPS results, showing weaker backbone Nafion[®] signal (Fig. 5).

Therefore, the different properties of the solvent used, mainly the evaporation temperature, give rise to qualitatively different results on electro sprayed Pt/C films. Some fragmentation in Nafion chains is observed when depositing with more volatile solvent (isopropanol). On the other hand, the BEG suspension yield deposited films with unaltered ionomer structure, although in this case the solvent is not completely eliminated and remains in the film. Such different electro spray deposition characteristics must have an effect on the cathode behavior in MEAs, as will be discussed in the next section.

4.2. MEA results with electro sprayed cathodes

Electro sprayed electrodes were mounted in MEAs in the cathode side, which is the more demanding electrode in terms of electrocatalysis. Very significant differences are observed in the specific Pt area value of the cathodes (Table 3). Electro sprayed electrodes deposited from BEG solvent, i.e. low dielectric constant and high evaporation temperature, show the highest surface area, almost $290 \text{ cm}^2 \text{ cm}^{-2} \text{ Pt}$. This high value may in principle be attributed to the dendritic morphology of electro sprayed electrodes (Fig. 1b), which after MEA preparation, exhibits the highest electrochemical area. It is not clear to us at this moment why isopropanol as a solvent does not produce such a high surface area electrode, in spite of the same dendritic morphology observed in the films. One reason may be the Nafion[®] fragmentation effect mentioned above, which may decrease the amount of platinum contributing to the effective area.

On the other hand, internal resistance measurements show slightly higher values with electro sprayed electrodes, that seem to indicate lower conductivity of these electrodes. In principle, fragmentation of Nafion[®] chains shown from XPS results (Fig. 5) may give rise to a decrease in the proton conductivity. It explains that in this case a higher internal resistance for the isopropanol deposited suspension is observed, as reflected by the current pulse resistance measurements in Table 3.

Polarisation curves show a better response for electro sprayed cathodes in the low current regime. Under these conditions, acti-

vation polarisation is the most limiting factor. On the other hand, at higher current demands the performance of electro sprayed cathodes decreases, if compared with standard MEAs, which may reflect a limitation by diffusion of oxygen inside the electro sprayed structure, and/or lower proton conductivity. Enhanced mass transport losses with electro sprayed electrodes has already been observed, and attributed to poor water management [12].

5. Conclusions

The electro spray deposition of Pt/C and Nafion suspensions has been used for the preparation of PEMFC electrodes. The method gives rise to the growth of films with a high specific area and dendritic morphology. Two solvents have been used for the preparation of the suspensions, isopropanol and a mixture of butylacetate, ethanol, and glycerol (BEG). It is apparent that the Nafion[®] ionomer may be altered during electro spray deposition in suspensions prepared with isopropanol due to its low evaporation temperature. On the other hand, electro sprayed cathodes prepared with BEG solvent show a high mass specific area of $101 \text{ m}^2 \text{ g}^{-1}$. Single cell tests on MEAs prepared with the electro sprayed electrodes (0.3 mg cm^{-2}) in the cathode side show that, at low current densities the performance is slightly improved with respect to MEAs with commercial cathode and higher Pt loading (0.5 mg cm^{-2}). However, at high current densities the performance decreases due to mass transport polarisation (H^+ or oxygen) in the electro sprayed cathodes. Stability of the electrodes show a promising low decay rate of $10 \mu\text{V h}^{-1}$.

Acknowledgements

This research was financed by project NECATPEM (MAT2002-03125) from Ministerio de Educación y Ciencia of Spain. A.M.C. acknowledges a grant from MEC (Programa Nacional de Ayudas para la Movilidad de Profesores e Investigadores Españoles y Extranjeros, PR2005-0067) for his stay at the Paul Scherer Institut.

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