



Electrospray deposition of catalyst layers with ultra-low Pt loadings for PEM fuel cells cathodes

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ABSTRACT

Suspensions of Pt/C catalyst nanoparticles in Nafion®-alcohol solutions have been electrosprayed over carbon paper to prepare cathodes for proton exchange membrane fuel cells (PEMFC). Catalyst layers with platinum loading ranging from 0.1 mg_{Pt} cm⁻² down to 0.0125 mg_{Pt} cm⁻² and different Nafion® contents were obtained by this method. Morphological studies of the catalyst layers by SEM inspection showed fractal structures with a high dispersion of catalyst. Fuel cell performance of membrane-electrode assemblies (MEAs) made from these cathodes revealed a strong dependence on the Nafion® concentration in the electrosprayed suspension. In the platinum loading range 0.1–0.025 mg_{Pt} cm⁻² and optimal Nafion® content, a linear relation between fuel cell power density and platinum loading has been found, such that a reduction of platinum content by a factor 4 only reduces the performance by roughly a factor 2. However for the lowest platinum loading investigated, 0.0125 mg_{Pt} cm⁻², a sharp drop in performance was noticed.

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1. Introduction

One major factor limiting the large-scale commercialization of proton exchange membrane fuel cells (PEMFC) is the platinum content in the electrode catalyst layers. The goal is to decrease the platinum content without sacrificing performance of the fuel cell. For this purpose, several techniques have been developed to optimize the utilization of platinum. Among these techniques, vacuum deposition methods (chemical vapour deposition [1], physical or thermal vapour deposition [2], and sputtering [3–5]) have been successful in achieving ultra-low platinum loadings (lower than 0.1 mg_{Pt} cm⁻²). However, the strict atmosphere control and vacuum conditions required by these methods make them relatively expensive and not easily adaptable to bulk production. The electrohydrodynamic atomization or electrospray [6–8] is another promising method that leads to an electrostatic deposition of the catalyst and may be used to optimize the utilization of platinum. This technique is based on the atomization of a liquid or suspension subjected to an electric field. Electrospray method has been applied recently in fuel cells to generate catalyst layers with a high dispersion of the catalyst [9]. Compared to other deposition methods, this technique has no vacuum requirements, is easily scalable

to any size and has a simple experimental set up. However further research is required to evaluate its capabilities and improve reproducibility [10].

Literature on the application of an electrospray to produce electrodes for PEMFC is scarce. Baturina and Wnek [11] reported about the application of this technique for electrode preparation. In this study, catalyst layers with platinum loading of 0.09 and 0.36 mg_{Pt} cm⁻² were prepared by electrospraying the catalyst suspensions directly on the membrane. At about the same time, Umeda et al. [12] explored the feasibility of the same technique and later Umeda et al. [13] characterized membrane-electrode assemblies (MEAs) prepared by this method with 0.1, 0.5 and 1.0 mg_{Pt} cm⁻². On the other hand, Benítez et al. [14] used an electrospray to produce the catalyst layers on carbon cloth obtaining electrodes of 0.5 mg_{Pt} cm⁻². Finally, Chaparro et al. [15] studied the influence of the solvent in electrospray deposition and prepared electrodes on carbon cloth with a platinum content of 0.3 mg_{Pt} cm⁻². In spite of the promising results obtained in these works, little effort seems to be invested to make this new technique a competitive option for electrode production. In particular, lower platinum loadings have to be investigated in relation to the Nafion®¹ content in the catalyst layers. Studies on the existence of an optimum Nafion® content have already been reported in the literature [16,17] concluding that this optimum value depends indeed on platinum loading. In

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¹ Dupont™ Nafion® is a trademark product of DuPont Company.

electrosprayed electrodes this kind of optimization study is still lacking. Additionally, other effects like the platinum loading of the catalyst particles and the influence of the control parameters during hot pressing (pressure, temperature and time) have to be evaluated and optimized.

In the present study, electrodes prepared by electrospray with platinum loadings of 0.1, 0.05, 0.025 and 0.0125 mg_{Pt} cm⁻² were tested as cathodes whereas anodes were prepared by impregnation with a platinum loading of 1 mg_{Pt} cm⁻² and 30 wt% of Nafion[®] in solids. These electrodes were used to prepare MEAs by hot pressing the two electrodes with a Nafion[®] 112 membrane between them. Morphological studies of these electrodes were carried out by means of a scanning electron microscope (SEM) before and after hot pressing. Current–voltage characteristics of MEAs with cathodes prepared by electrospraying were compared to a MEA made by impregnation (both electrodes) and, for each platinum loading, the optimum Nafion[®] content was determined.

2. Experimental

2.1. Electrospray setup

A schematic of the electrospray experimental setup is shown in Fig. 1. It consists of a needle and a substrate, both connected to a DC high voltage supply (Bertan 205B-10R). A syringe pump (KDS 100) drives a liquid suspension (the catalyst ink indicated in next section) through a capillary tube into the needle at the selected flow rate. Two voltmeters (Isotech IDM67) measure the charge emitted by the needle and the charge collected by the substrate.

When an electrical potential difference is imposed between the needle and the substrate, the suspension pumped through the needle breaks up in a spray of charged droplets. The electric field drifts these charged droplets toward the substrate, with the solvent (alcohol) evaporating along the flight. As a consequence of this evaporation, the electrostatic repulsion forces between ions in a droplet can overcome the surface tension forces (the so-called Rayleigh limit) and the droplet undergoes a Coulomb explosion and breaks up into smaller droplets. Thus, depending on the operating conditions, aggregates or even single particles can reach the substrate generating a porous deposit with high roughness and fractal structure [9,18–20].

2.2. Preparation of the catalyst inks

Catalyst inks were prepared with platinum supported on carbon powder (Pt 10 wt% on Vulcan XC-72R). Pt/C powder was mixed with ethanol as solvent and Nafion[®] (Aldrich, 5 wt% in lower aliphatic alcohols and water) as ionomer. These suspensions were ultrasonically dispersed for 2 h before starting the electrospray deposition.

2.3. Electrode and MEA preparation

The electrospray setup of Fig. 1 was used for dispersing the catalyst inks on a 5 cm² area of untreated (not hydrophobized with PTFE) carbon paper (Toray TGP-H-060) to serve as cathodes. Electrospray of the catalyst ink was carried out at the selected flow rate of 0.3 ml h⁻¹ which leads to fractal deposits [18]. The distance between the needle and the substrate (electrode) was fixed at 7 cm (long enough to ensure the complete ethanol evaporation of the electrosprayed droplets) and the spraying voltage drop kept at 9000 V (to get a stable electrospraying cone-jet mode). Platinum contents of 0.1, 0.05, 0.025 and 0.0125 mg_{Pt} cm⁻² were applied and suspensions were prepared with different Nafion[®] concentrations for each platinum loading. On the other hand, the electrodes that served as

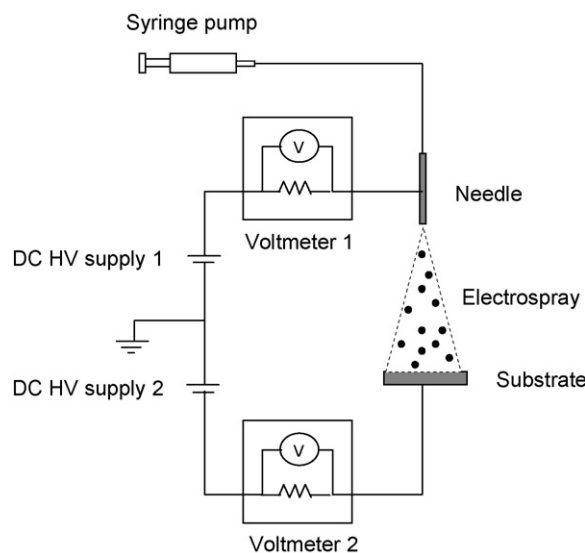


Fig. 1. Scheme of the experimental setup for electrospray deposition.

anode were prepared by impregnation with a platinum loading of 1 mg_{Pt} cm⁻² and Nafion[®] content of 30%. This high platinum loading ensured that the anode was not limiting the performance of the MEA allowing the direct evaluation of the cathode efficiency.

For the MEAs preparation, a Nafion[®] 112 membrane was sandwiched between the two electrodes and bonded by hot pressing at a pressure of 10 MPa and a constant temperature of 120 °C applied for 2 min. The electrochemical performance of these MEAs was evaluated in a commercial fuel cell hardware accommodating a 5 cm² single cell geometry (FC05-01SP Electrochem, Inc.) connected with an external electronic load (Hocher & Hackl PL306). The fuel cell hardware employs machined graphite flow field plates with serpentine flow patterns and copper gold-plated current collectors. The current–voltage characteristics of the cell were obtained at 40 °C and ambient pressure. Feeding gases were dry oxygen and dry hydrogen supplied by mass flow controllers (Bronkhorst Hi-Tec).

To characterize the morphology of the electrosprayed electrodes, samples were observed using a SEM. A coating of Au/Pd was applied to these samples by means of a sputter-coater instrument (Polaron Range SC7620). Moreover, some samples were fractured to observe their cross-section on the SEM. A clean cut was achieved by placing these samples in an aluminium sealed bag and immersing them in a liquid nitrogen bath at ambient pressure (77 K, 1 atm) after which the samples were dry fractured.

3. Results and discussion

3.1. Characterization of the catalyst layer

The morphology of the catalyst deposits was analyzed by means of a scanning electron microscope (Hitachi S-3000N). In Fig. 2, SEM micrographs with the same magnification show the morphology of the catalyst layer on two electrodes, one of them (Fig. 2a) prepared by impregnation and the other one by electrospraying (Fig. 2b). As seen, the electrode made by the electrospray method shows a porous character with very open structures and large exposure of the catalyst which are desirable properties for a catalyst layer. A large exposure of the catalyst leads to an increased active area and hence a better use of it. Moreover, a large porosity will reduce the limitations by mass transport phenomena. The fractal structure of the electrode deposited material can be characterized after image seg-

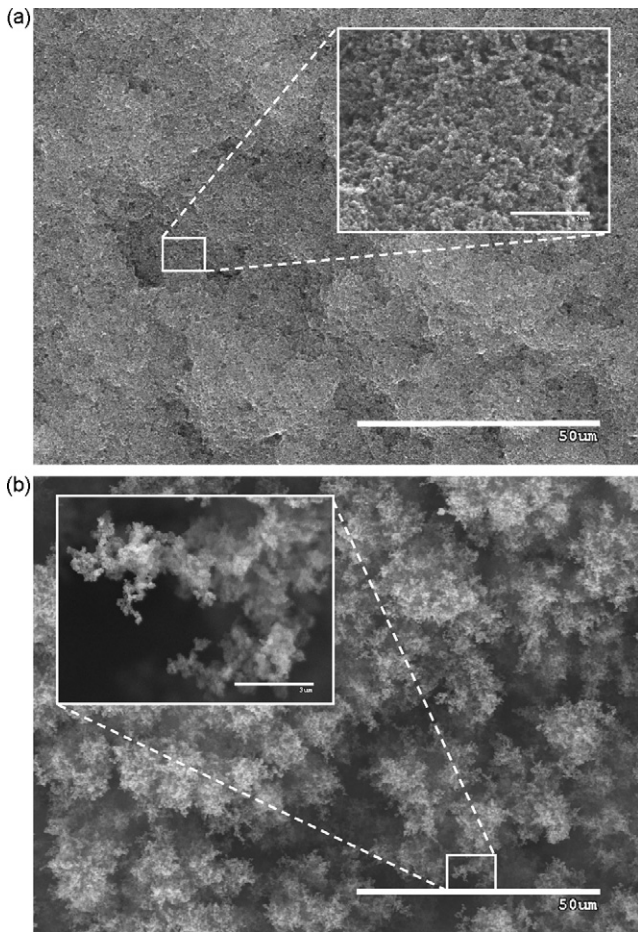


Fig. 2. SEM micrographs of an electrode prepared by impregnation (a) and an electrode prepared by electrospray (b). Same magnification on both images. In both figures the horizontal micron bar corresponds to a 50 μm length at the main image and to 3 μm at the enlarged inset.

mentation of the side view using a box-counting method. For this kind of electrosprayed deposits the fractal dimension of the 2D projected structures was measured [9] leading to a fractal dimension of the catalytic surface in the range 2.10–2.20. By contrast, the electrode prepared by impregnation is more compact and less porous than the electrosprayed electrode.

The macrostructure of the catalyst layer in an electrosprayed electrode is shown in Fig. 3. As it can be appreciated, the catalyst layer exhibits a great homogeneity that is preserved throughout the electrode surface.

Images of the catalytic surface at different platinum loadings and the same Nafion[®] content are presented in Fig. 4. For a platinum loading of 0.1 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ (Fig. 4a) the catalyst covers completely the carbon fibres resulting in a pseudo-continuous layer. However, for a platinum loading of 0.0125 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ (Fig. 4b), the electrosprayed material is not enough to fill out the void regions between the carbon fibres but it covers only the surface of the individual and outermost fibres of the substrate.

Fig. 5 shows the images of the catalyst layers of both kinds of electrodes after hot pressing. As noted, the structure of the electrosprayed electrode has changed significantly (Fig. 5a). Thus, the fractal structures shown in Fig. 2(b) are collapsed by hot pressing as the fractal structures are pressed and incorporated into a more compact structure. Nevertheless, the surface roughness (given by the characteristic particle size in the pressed catalytic layer) remains almost unchanged. However, the final structure of the electrode

prepared by impregnation is quite different. In this latter case, after hot pressing, the characteristic length of surface roughness is much larger due to the agglomeration of the impregnated catalyst particles in larger units covered by a gluing Nafion[®] layer (Fig. 5b). As a consequence, after hot pressing, the remaining active surface in the electrode prepared by the impregnation method is lower than the active surface for the electrosprayed catalyst because a large amount of the catalyst material becomes inaccessible for the reactant gas.

3.2. Evaluation of fuel cell performance

Current–voltage characteristics of fuel cell electrodes with cathode platinum loadings of 0.1, 0.05, 0.025 and 0.0125 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ and different concentration of Nafion[®] are presented in Fig. 6(a–d). For platinum loadings of 0.1, 0.05 and 0.025 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$, the electrode performance increases with the Nafion[®] concentration until a maximum performance is reached. Further increase in the amount of Nafion[®] results in a decrease of performance. This effect has also been reported by other authors [16,17,21–23] using thin-film methods for electrode preparation. The low performance at low Nafion[®] content is explained by the poor contact between the catalyst and the membrane. There is not enough ionomer connecting the catalyst sites to the membrane and the platinum utilization is relatively low. In the case of high Nafion[®] content several factors contribute to the loss of performance because voltage losses by mass transport may be caused by effects occurring at different

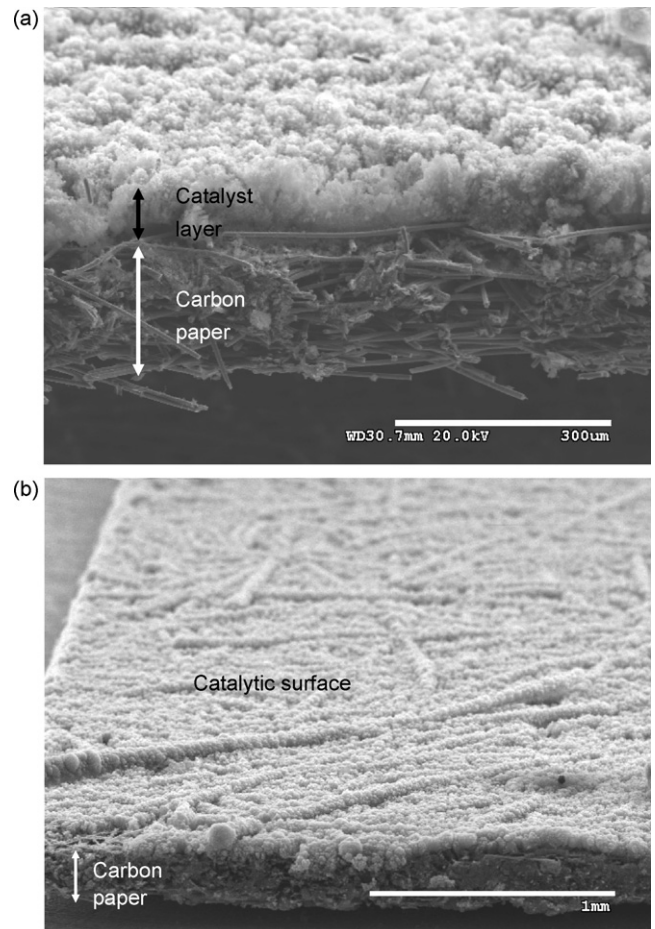


Fig. 3. Cross-sectional (a) and tilted (b) SEM micrographs of an electrosprayed electrode. The micron marker bars are 300 μm and 1 μm for (a) and (b), respectively.

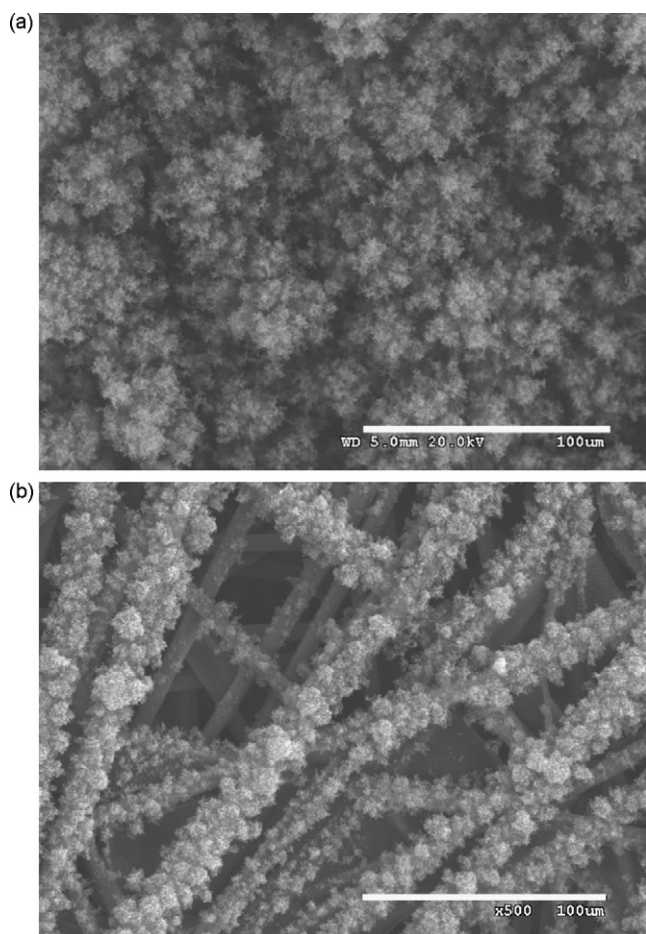


Fig. 4. SEM images of catalyst layer applied by electro spray with the same Nafion[®] content and platinum loadings of $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ (a) and $0.0125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ (b). Same magnification on both images. In both figures the horizontal micron bar is $100 \mu\text{m}$ length.

scales. On the one hand, an increased thickness of Nafion[®] covering the catalyst particles forces oxygen to diffuse a longer way through the ionomer to reach the catalyst site. Also, a high Nafion[®] content decreases the porosity of the catalyst layer which results in a lower permeability, that is, a larger mass transport resistance in the gas phase. On the other hand, a too high concentration of Nafion[®] leads to underutilization of catalyst because the catalyst particles may be electrically isolated by Nafion[®].

Fig. 7 shows the maximum fuel cell power density versus Nafion[®] content for the four platinum loadings depicted in Fig. 6. For each platinum loading, the maximum performance is seen to be attained at different Nafion[®] contents. For 0.1, 0.05, and $0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ loadings, the Nafion[®] content required to yield maximum power increases with the platinum loading. These results are in qualitative agreement with Sasikumar et al. [16,17] who studied the optimum Nafion[®] content in PEMFC electrodes for different platinum loadings. However the optimum values for the same platinum loading differ quantitatively from Sasikumar et al.'s results because the optimization depends on the electrode fabrication method. Fig. 7 also shows a change in the electrochemical behaviour that happens for the lower platinum loading of $0.0125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. This platinum loading does not present a sharp peak in performance but behaves smoothly in the range 20–40% of Nafion[®] content. The reason may be related to the fact that at such low platinum loading a qualitative change occurs in the structure of the catalytic layer because the amount of deposited material is not enough to form a thick and continuous catalytic layer (see the

SEM image in Fig. 4b). The catalyst material only covers the surface of the outermost fibres leaving large void regions between the fibres. In this situation, after the hot pressing stage, most of the catalyst particles are in direct contact with the membrane and so the effects of the Nafion[®] added to the catalytic ink are relatively weak. Anyway, when the Nafion[®] concentration is large enough (as in the 50% case), the electrode performance decreases due to the electric insulation effect mentioned above.

Fig. 8 depicts current–voltage characteristics (Fig. 8a) and power curves (Fig. 8b) of MEAs with cathodes prepared by electro spray (EL) – and optimal Nafion[®] content – compared to a reference MEA with both electrodes prepared by impregnation and platinum loading of $1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ (IM). This (IM) large platinum content MEA leads to an overall performance greater than the performance of the MEAs prepared by electro spray. However, the electro sprayed MEA with platinum loading of $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ attains two-thirds the maximum power output of the reference MEA with only one-tenth of the platinum loading. On the other hand, a sharp drop in the performance is observed for the platinum loading of $0.0125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ as could be anticipated from the poor characteristics of the catalytic layer. The SEM micrograph in Fig. 4(b) shows that the space between fibres is almost devoid of catalyst. The consequence of this is a significant decrease on the effective electrode area that causes a drop in performance greater than the expected linear decrease. Moreover, hot pressing conditions may be also partially responsible for the extra drop in performance. All MEAs were hot pressed

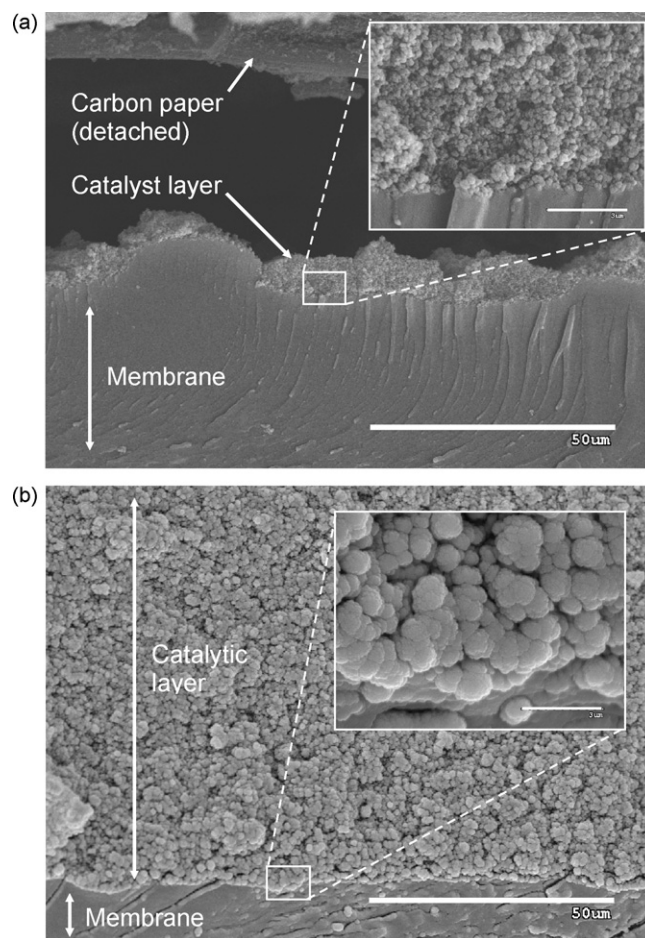


Fig. 5. Cross-sectional SEM micrographs of catalyst layer after hot pressing for an electro sprayed electrode (a) and an electrode prepared by impregnation (b). Same magnification on both images. In both figures the horizontal micron bar corresponds to a $50 \mu\text{m}$ length at the main image and to $3 \mu\text{m}$ at the enlarged inset.

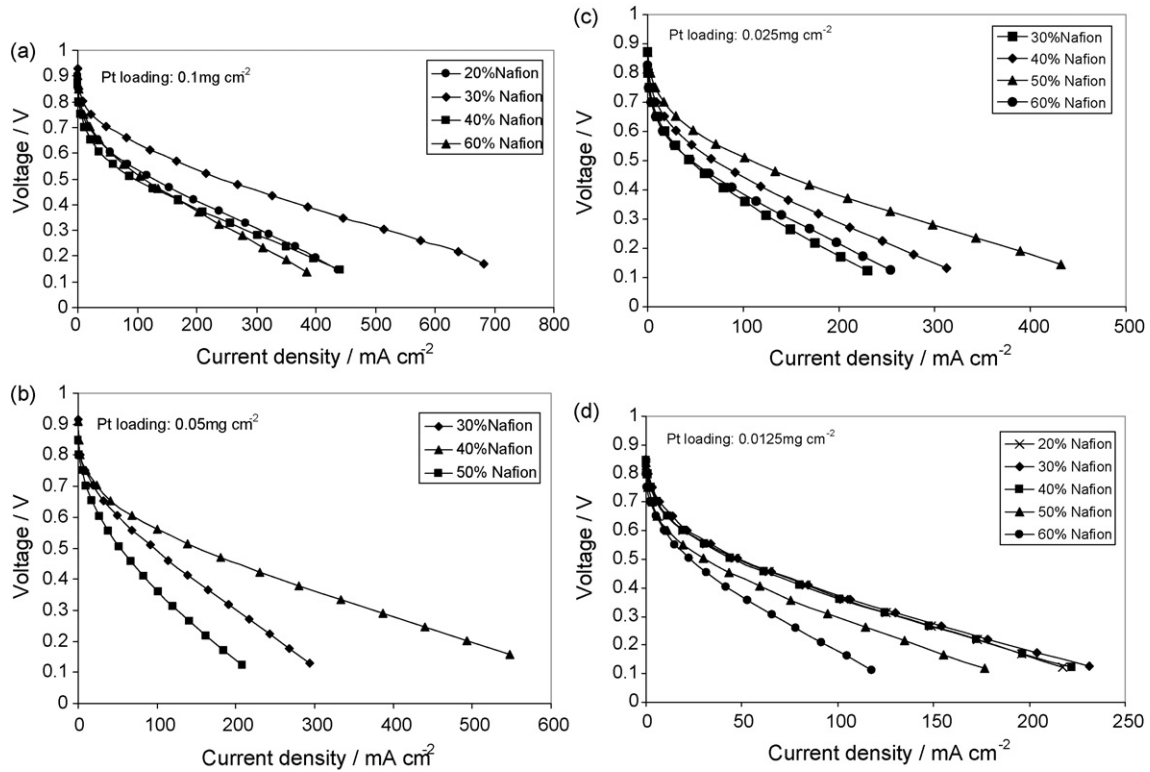


Fig. 6. Current–voltage characteristics corresponding to MEAs assembled with electro sprayed cathodes having different Nafion® content for several platinum loading: (a) $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, (b) $0.05 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, (c) $0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ and (d) $0.0125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. All measurements were carried out with dry (non-humidified) H_2/O_2 at ambient pressure and temperature of 40°C .

under the same external force but as it was remarked above, for this platinum loading, the effective catalyst area was smaller. Hence, for maintaining the same pressure in this case, a weaker force had to be applied during the pressing stage.

Comparison of the performance between the different MEAs is better achieved accounting for the relative platinum utilization. Thus, the monotonous decrease of the power density curves versus Pt loading shown by Fig. 8b is reverted in Fig. 9 when the power is referred to the amount of platinum on each MEA. This figure shows clearly the benefits of the electro spray method with

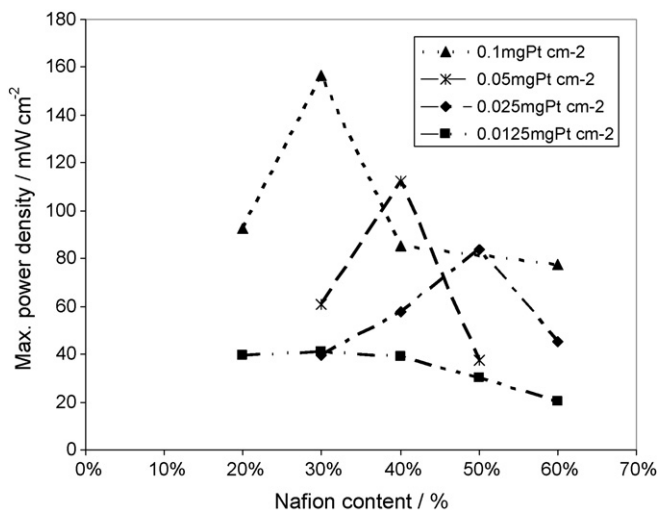


Fig. 7. Effect of Nafion® content on maximum power density of MEAs with electro-sprayed cathodes (results from Fig. 6).

respect to the impregnation technique. The optimal performance is now reached by the MEA with $0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ and a saturation effect is evident at lower Pt loadings. This trend is made clearer by focusing attention only to the maxima of the power curves. The maxima of these curves (Figs. 8b and 9) are plotted versus the Pt loading in Fig. 10. The continuous curve (left axis) in Fig. 10 depicts the experimental (EL) maxima in Fig. 8b, with the dash-dotted line depicting the linear approximation of this continuous curve for the larger Pt loadings investigated here. In the range $0.025\text{--}0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ the continuous curve almost coincides with the dash-dotted line. Therefore, the maximum power density provided by a fuel cell built with this type of electrodes would grow linearly with the Pt content in the electrodes. However, for the lowest platinum content investigated here ($0.0125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) the experimentally measured maximum power density is relatively weaker (the solid line lies below the dash-dotted line) because other effects start to play a role, like the existence of uncovered voids in the catalytic layers discussed above. However, in the linear response region, where the maximum power output behaves linearly with respect to the amount of platinum loading, the slope of this linear relation is relatively low. Therefore the maximum power density per platinum mass is achieved at the lower platinum loadings, as it is shown by the discontinuous dashed curve in Fig. 10 (referred to the right axis). Both solid and dashed curves show that a reduction of the Pt loading by a factor of 4 (from 0.1 to $0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) causes just a decrease of the maximum power density close to a factor 2, doubling the electrode performance relative to Pt loading. Note that the reference (IM) MEA is not included in Fig. 10 because the results will be far from the used scales. Anyway, its relative performance is much lower than the maximum power per Pt loading achieved by any of the (EL) electrodes (see Fig. 9).

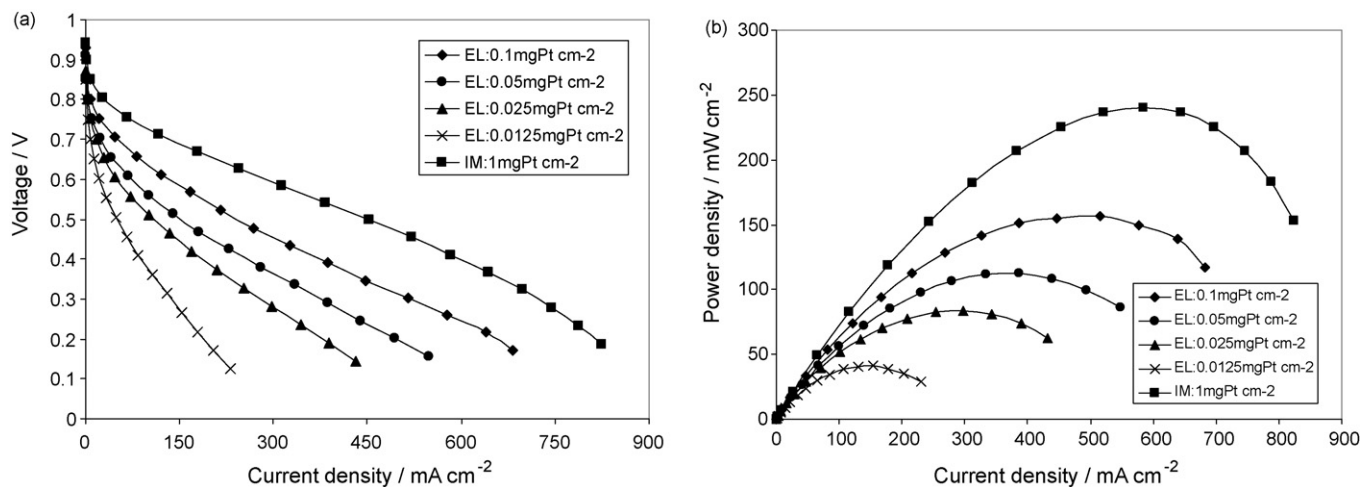


Fig. 8. Current–voltage characteristics (a) and corresponding power density curves (b) of MEAs with electrospayed cathodes and a reference MEA prepared by impregnation with platinum loading of $1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. All measurements were carried out with dry (non-humidified) H_2/O_2 at ambient pressure and temperature of 40°C .

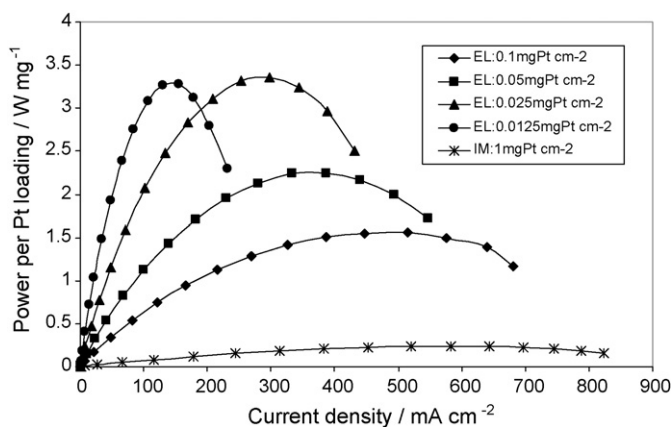


Fig. 9. Power output per Pt loading versus the current density for each MEA in Fig. 8.

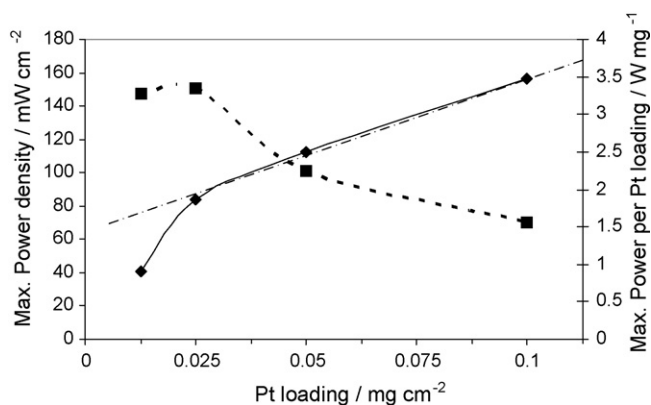


Fig. 10. Maximum power density (solid line, left axis) and maximum power per Pt loading (dashed line, right axis) achieved by the four MEAs prepared by the electrospay method. The dash-dotted line indicates the linear trend of the maximum power density for sufficiently large Pt loadings.

4. Conclusions

The electrospay method has been used to prepare catalyst layers on electrodes for use as PEM fuel cells cathodes. Several platinum loadings ranging from 0.1 to $0.0125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ were studied. For each platinum loading different Nafion[®] contents were considered.

The SEM micrographs of the catalyst layers obtained by this electrospay method reveal the generation of fractal structures at the electrospaying conditions applied. However this fractal character is seriously affected by hot pressing during MEA assembling.

The conclusions of the present study concerning the dependence on Nafion[®] content of the catalyst layers are consistent with the observations reported by other authors [16,17]. The performance of the MEAs shows a strong dependence on the Nafion[®] concentration in the electrospayed solution. From 0.1 to $0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, there is an optimum Nafion[®] content for attaining a maximum performance. Moreover, these optimum values depend on platinum loading. For a platinum loading of $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ the optimum Nafion[®] content was 30% while for electrodes with 0.05 and $0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ the optimum Nafion[®] loading were 40% and 50%, respectively.

Comparison between electrodes prepared by the electrospay (EL) method – with loadings 0.1 – $0.0125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ – and by impregnation (IM) method – with platinum loading of $1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ – was carried out. As expected, the overall power density increases with the amount of platinum in the electrode and it is larger for the impregnation electrode. However, the platinum utilization, i.e., the power density relative to the platinum loading, is substantially higher for any of the electrospayed electrodes. A noticeable power per platinum loading is achieved for the ultra-low Pt loading considered here (from 0.1 to $0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$), increasing as the platinum loading decreases until the amount of catalyst is not able to form a pseudo-continuous layer ($0.025 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ in our case).

One may expect that a larger coverage of the electrode surface (and thus a better electrode performance) could be achieved for the smallest platinum loading investigated here (and even smaller) by using catalyst with lower platinum loading per particle ($<10 \text{ wt}\%$). This topic will be the subject of follow on studies.

All these results together with the simplicity and easy scale-up of the process, allow us to conclude that the electrospay technique is a promising method suitable for mass production of PEM fuel cells electrodes with ultra-low Pt loadings.

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