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PEMFC electrode preparation by electrospray: Optimization of catalyst load and ionomer content

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ABSTRACT

Electrodes for proton exchange membrane fuel cell (PEMFC) have been prepared by means of electrospray deposition, using different ionomer contents and catalyst loads. The electrodes have been mounted in single PEMFC, and tested as cathode. The electroactive platinum area of electrosprayed electrodes has been measured by the hydrogen underpotential deposition method. Polarization curves have been measured to determine the optimal concentration for the platinum catalyst (Pt/C, 20 wt.%) and the ionomer (Nafion®). Best performance is observed with 15% ionomer content in the electrosprayed cathode due to minimal cell internal resistance. This optimal concentration is lower than that found for electrodes prepared by other standard methods, like airbrushing or impregnation, which is attributed to the improved ionomer distribution within the electrospray deposited catalyst layer. On the other hand, the optimum value for catalyst load is similar to that encountered for electrodes prepared by the other methods, which reflects that electrospray has little or no effect neither on the catalyst nor on the electronic resistance of the catalyst layer.

1. Introduction

The gas diffusion electrodes of proton exchange membrane fuel cells (PEMFC) are complex structures, comprised of different layers [1,2]. Considering as electrode all the materials filling the space between the flow field channels of the current collector and the electrolyte membrane, at least two layers can be distinguished: the gas diffusion and the catalyst layer. The gas diffusion layer consists of a carbonaceous substrate (carbon cloth, carbon paper), also called 'backing layer', with a meso–microporous layer on top (carbon black). PTFE is used to provide mechanical stability and hydrophobic character to this layer. Over the gas diffusion layer, the catalyst, or active layer, contains the electrocatalyst (Pt nanoparticles supported on carbon, Pt/C) immersed in a solid ionomer to facilitate proton conduction within this layer. Such electrode structure must allow for the easy transport of water and gases from and back to the flow field, and proton exchange with the membrane, maintaining at the same time three-phase boundary regions (i.e. areas with the liquid, solid and gas phases in very close proximity) within the catalyst layer for the electrochemical reactions [1,2].

There is an important research effort nowadays directed towards the optimization of the catalyst layer, because it has the highest impact on cost and durability of a PEMFC. In particular, two key parameters of the catalyst layer are the platinum and the ionomer (Nafion®) concentrations. Different works have been carried out towards the optimization of these parameters, using experimental measurements in aqueous solution contact [3], single cell measurements [4–9], as well as by modelling [2,10]. The optimal ionomer concentration found by different studies falls in the range 30–36%, for electrodes prepared by well known, standard, methods, like airbrushing [3,4], or impregnation [8]. This parameter has been found to depend on electrode Pt load [6] and on the Pt weight percent in the electrocatalyst powder [7], the reason being attributed to an optimal thickness of the ionomer film on the platinum surface of around 200 nm, determined from a rotating disk electrode study [11]. Thicker ionomer films give rise to oxygen diffusion limitation, and increase the resistance to electron circulation among carbon particles, i.e. the electronic resistance of the catalyst layer. Porosity measurements have shown that the ionomer incorporates into the secondary pores (40–200 nm) formed between agglomerates in the catalyst layer, leaving primary porosity (20–40 nm) unchanged [12]. It may be inferred from the optimal ionomer concentration, that a film thickness of a few 7–8 nm is deposited over the external surface of carbon agglomerates, too thin for O_2 diffusion limitation [11], so it

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is most probable that the electronic resistance is the first factor limiting at high ionomer concentrations.

Recently we have developed a new method for catalyst layer deposition, based on the electrospray effect [13,14]. Electrospray consists of the pulverization of a liquid sample or a suspension under the influence of a strong electric field [15,16]. The electric field, imposed between the ejector needle and the substrate, gives rise to the formation of a mist of ionised droplets and particles which deposit very homogeneously. A photograph of the electrospray needle is shown in Fig. 1. At the needle end, the meniscus adopts an inverse cone shape ('Taylor cone') where particles become ionised; in the apex of the cone, repulsion forces among charges are stronger than the liquid surface tension so charges are abruptly separated ('Coulomb explosion') to form a mist of particles and solvent droplets. For PEMFC electrode preparation, the electrospray suspension contains the catalyst, Pt/C particles, and the ionomer (Nafion®) in colloidal form, which are codeposited on the electrode gas diffusion layer. The resulting film morphology shows typical dendritic growth shape, due to the electrical interactions among mist components and with the substrate during the electrospray process. This morphology may be responsible for the enhanced activity encountered with these electrodes as cathode of PEMFC [14].

In this work, the electrospray deposition technique has been used to prepare PEMFC electrodes with different Pt and ionomer contents. For this task, Pt/C and ionomer suspensions have been prepared in isopropanol solvent and electrosprayed onto a commercial carbon cloth gas diffusion layer. Membrane electrode assemblies (MEA) have been prepared, with the electrosprayed electrodes as cathode, and tested in single cells. Polarization curves and electroactive catalyst area have been obtained as a function of Pt load and ionomer concentration in the electrosprayed cathodes.

2. Experimental

2.1. Electrode preparation by electrospray deposition

Electrodes preparation with 4 cm × 4 cm area has been carried out by electrospray deposition, from a suspension of Pt/C (E-TEK, 20 wt.% Pt) and Nafion® (Aldrich, 5% solution in aliphatic alcohols), in isopropanol (Panreac). The substrate was an uncatalysed carbon cloth covered with a microporous carbon black layer (LT1200W, PEMEAS, E-TEK). For the electrospray deposition process, a DC voltage (6000–9000 V) is imposed (Bertran, Model 205B-10R) between the substrate and the ejector needle. The suspension is placed in a beaker under ultrasonic stirring, thermostatised at 22 °C, and pressurised (0–0.2 bar) with N_2. The beaker is connected to the needle through a silica capillary (150 μm diameter). The substrate is heated at 50 °C, and placed on a computer controlled *x*–*y* stage (Physik Instrument). Electrospray current is continuously monitored with a picoammeter (Keithley).

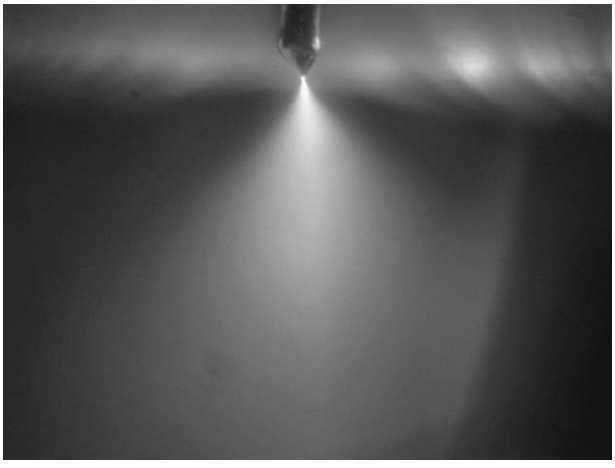

Fig. 1. Photograph of the electrospray mist and the ejector needle.

2.2. MEA preparation and characterisation

Membrane electrode assemblies (MEA) were prepared with the electrosprayed electrode in the cathode side, a standard electrode (PEMEAS E-TEK, 0.25 mg_{Pt} cm^{-2}) in the anode side, and Nafion® 112 membrane (Aldrich). The membrane was previously activated by successively immersing in hot H_2O_2 (10%) solution and H_2SO_4 (0.5 M) solution for 1 h, respectively. The MEAs were mounted in single cells using graphite plates with serpentine flow field for gas distribution, gold plated copper current collectors, and thermostatised end-plates. Characterisation was carried out with a home-made test bench under control of different variables. Standard values for testing parameters were used: 80 °C cell temperature, 80 °C hydrogen and oxygen lines temperature, 100% humidification for both gases, 1 bar_G back pressure in both gas lines, and constant stoichiometric factor $\lambda = 1.5$ for hydrogen and $\lambda = 3$ for oxygen. Previous to acquisition of the polarization curves, the cell is started-up and preconditioned at the above referred parameters under 1 A current demand, during 24 h. For polarization curves, the cell is first submitted to the maximum allowable demand (0.3 V cell voltage) and left until stabilization; afterwards, the demand is decreased in 50 mA cm^{-2} steps and the stable values of cell potential and 1 kHz internal resistance (HP 4338B milliohmmeter) are recorded. For cathode electroactive area measurements, the hydrogen underpotential deposited desorption charge was measured by means of voltammetries, under 30 cm^3 min^{-1} H_2 flow in the anode and 50 cm^3 min^{-1} N_2 flow in the cathode, at 30 °C cell temperature, using a potentiostat (EG&G, PARC, model 263A).

3. Results and discussion

3.1. Nafion® concentration

Polarization curves corresponding to single cells with the electrosprayed cathodes prepared using variable concentration of ionomer, are shown in Fig. 2. The values of the Tafel slope (b), the exchange current density (i_0), and the internal resistance of the cell

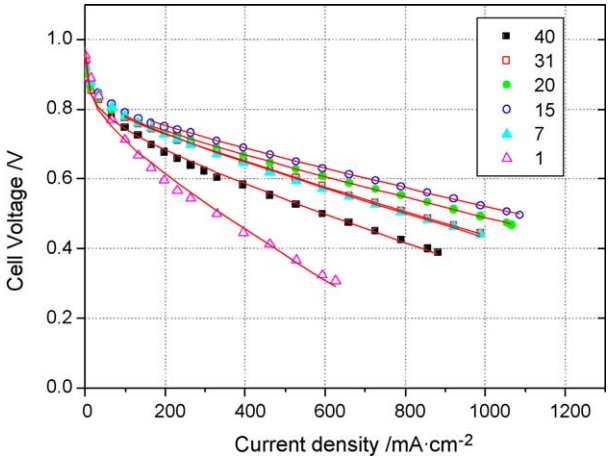

Fig. 2. Polarization curves corresponding to MEAs with cathode deposited by electrospray, using different ionomer contents in the catalyst layer as indicated (values are given in weight percentage within the catalyst layer). Cathode Pt load: 0.20 mg cm^{-2}.

(R_i) were determined by fitting to the equation:

$$V = E^0 - b\log\left(\frac{i}{i_0}\right) - R_i i \quad (1)$$

where V is the cell voltage, E^0 (=1.19 V) the thermodynamic potential, and i the cell current density. Values of R_i, cell voltage at 0.5 A cm^{-2}, b and i_0 are plotted in Fig. 3 as a function of ionomer concentration. A maximum is observed in the cell voltage with 15% Nafion® concentration, which corresponds to a minimum in the internal resistance (R_i) (Fig. 3a). This result shows that electronic resistance effects are predominant above 15% Nafion® concentration. Electrode kinetics is affected to some extent by Nafion® concentration, as reflected by Tafel slope and exchange current density plots (Fig. 3b). Values at extreme ionomer concentrations (1% and 40%) show larger changes, whereas at intermediate concentrations the dependence is less significant. In fact, the effect of Nafion® concentration on cathode kinetics affects to opposed factors, principally the improvement of proton transport to platinum particles, on the one hand, and the decrease in oxygen diffusivity and probable less favoured interaction on platinum surface, on the other.

The Pt specific area was measured from hydrogen underpotential deposited desorption charge (H_{UPD}). The values as a function of ionomer concentration are shown in Fig. 4. It is observed maximum specific area (31 m^2 g^{-1}) at 20% ionomer concentration. The corresponding Pt utilization may also be read in the same figure, considering a nominal specific area of 76.3 m^2 g^{-1}

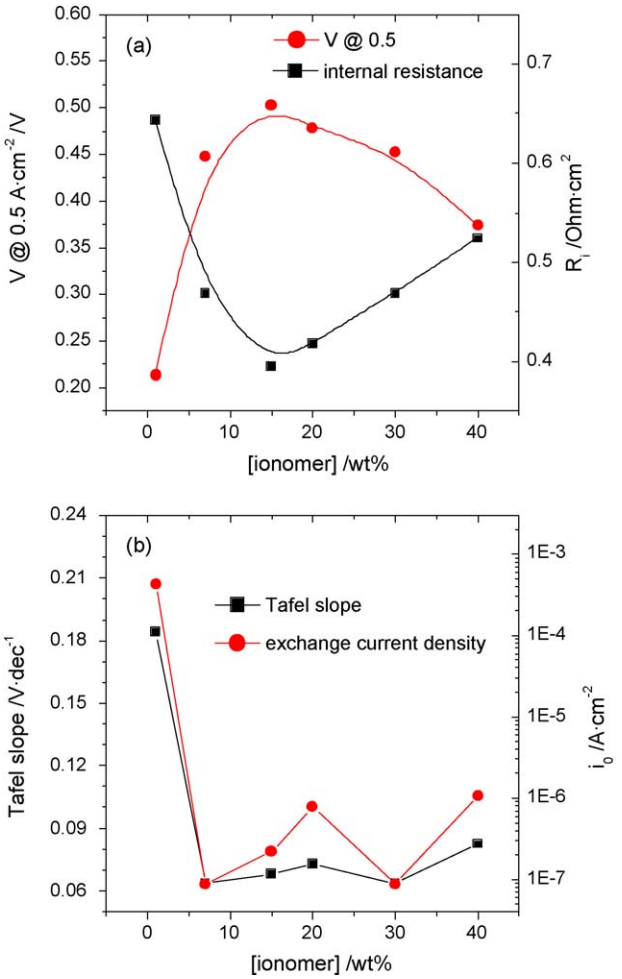

Fig. 3. (a) Cell voltage at 0.5 A cm^{-2} and internal resistance, and (b) Tafel slope and exchange current density, as a function of ionomer concentration in the electrospray deposited active layer, determined from polarization curves in Fig. 2.

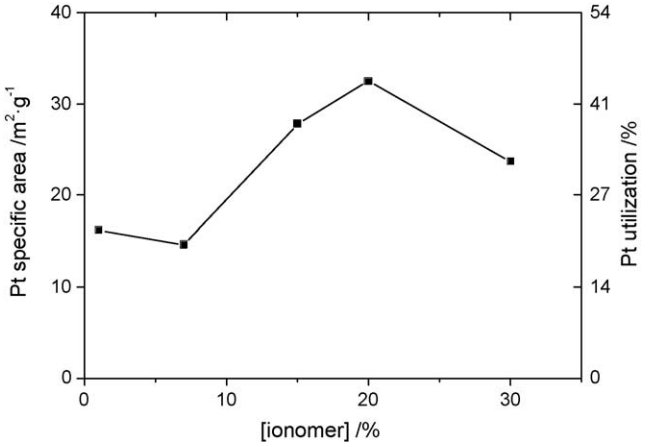

Fig. 4. Plot of the Pt specific area of electrosprayed electrodes, as a function of ionomer content.

for spherical particles of 3.8 nm diameter measured by TEM [14]. A maximum in the specific Pt area as a function of Nafion® concentration has been observed by some authors [3,4]. For instances, Sasikumar et al. [6] find a range of values between 21% and 50% Pt utilization, depending on Nafion® concentration, for electrodes prepared by the airbrushing method. Higher specific area values are encountered by Antolini et al. [3] (70–110 m^2 g^{-1}) also on electrodes prepared by airbrushing, however these authors used in their measurements the hydrogen adsorption charge, instead of desorption charge, which may give rise to overestimation of the area due to the overlapping with the current from adsorption of species on the Pt surface. On the other hand, if the ionomer is sprayed on the active catalyst layer after Pt/C deposition, instead of being deposited mixed with the catalyst, a continuous increase in the Pt area is observed with ionomer concentrations, until above 40% [17], reflecting less efficient proton conduction.

The optimal ionomer concentration in the catalyst layer (15 wt.%) is reflected by minimal internal resistance of the cell, i.e. maximal ionic conductivity in the catalyst layer [5]; this value is close to, but not the same, the highest Pt utilization (Fig. 4). Above this concentration, other factors predominate, mainly the electronic resistance among catalyst particles. It is significant that the optimal ionomer content obtained for the electrosprayed electrodes is, significantly lower than that encountered for electrodes prepared by other methods, usually between 30% and 40% [3,6,7,8,10]. This result may reflect different ionomer distributions inside electrosprayed catalyst layer, giving rise either to enhance proton conductivity, or to higher electronic resistance within the catalyst layer. Both effects would give rise to a decrease in the optimal ionomer concentration, however it is most probably the enhance proton conductivity responsible as reflected by the lower resistance of electrosprayed electrodes compared with airbrushed electrodes (see below). It is very probable that a stronger ionomer–catalyst particle interaction results within the catalyst layer, as a consequence of the electric interactions among Pt/C particles and Nafion® colloids occurred during electrospray deposition, that gives rise to more efficient proton conduction. More in depth study of this effect is being currently carried out.

3.2. Platinum load

Polarization curves corresponding to single cells with cathodes prepared by electrospray with different platinum loads are shown in Fig. 5. A curve corresponding to a cathode prepared by airbrushing is also included for comparison. The curves were

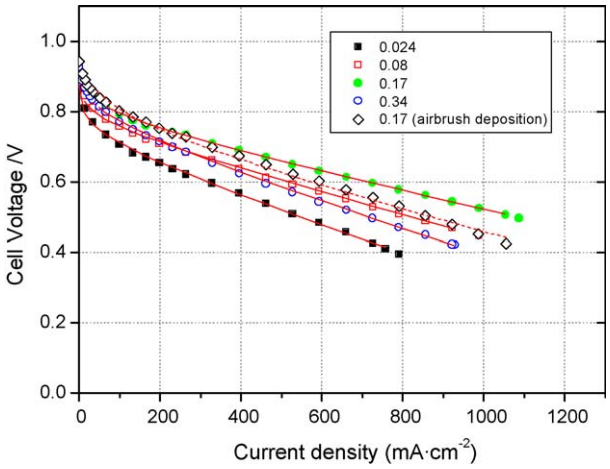

Fig. 5. Polarization curves corresponding to MEAs with cathode deposited by electrospray, using different Pt loads, as indicated (values are given in Pt mg cm^{-2}). Nafion® content in catalyst layer: 17 wt.%.

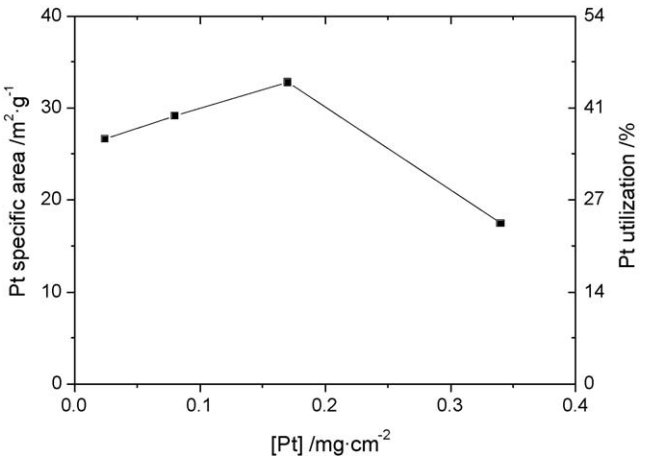

Fig. 7. Plot of the Pt specific area of electrosprayed electrodes, as a function of platinum load.

analysed in the same way as those in Fig. 2, and the resulting parameters are plotted in Fig. 6. The internal resistance is minimised around 0.17 mg cm^{-2}, giving rise to a peak in the performance of the cell (Fig. 6a). On the other hand, Tafel slope shows a smooth minimum at 0.17 mg cm^{-2}, whereas exchange current density increases steeply with catalyst load, as expected. The specific area of Pt (Fig. 7) shows a maximum at 0.17 mg cm^{-2}, and decreases above as a consequence of the increase amount of inactive Pt particles [18].

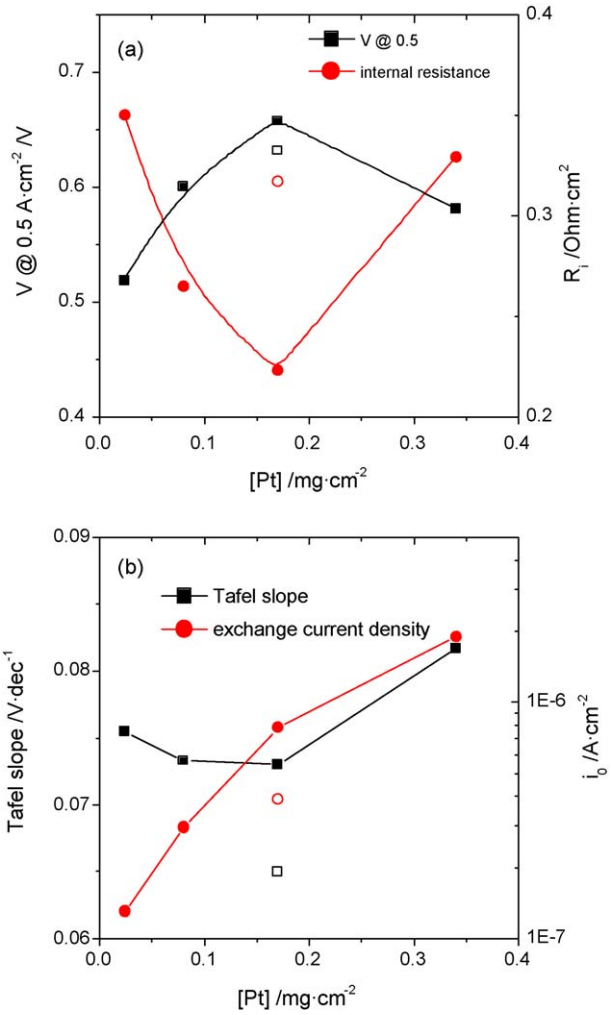

Fig. 6. (a) Cell voltage at 0.5 A cm^{-2} and internal resistance (R_i), and (b) Tafel slope and exchange current density, as a function of Pt load, determined from polarization curves in Fig. 5. Hollow symbols correspond to values for a single cell with airbrush deposited cathode.

Upon variation of Pt load, two fundamental parameters of the catalyst layer are being changed: the amount of catalyst and the thickness of the layer (our ex situ measurements with a profilometer show that the thickness of the electrosprayed catalyst layer varies from 0 to 40 μm for catalyst loads between 0 and 0.5 mg cm^{-2}). Results in Fig. 6 show that the cell performance improves with catalyst amount as a consequence of better electrode kinetics (i_0), together with some decrease in the internal resistance. A peak value at 0.17 mg cm^{-2}, indicates that the electronic resistance of the catalyst layer, proportional to its thickness, starts to be limiting. Above this value, increasing catalyst concentrations will have a positive effect only at very low current densities (<50 mA cm^{-2}).

The optimal catalyst load measured in this work for electrosprayed electrodes is close to that observed for electrodes prepared by conventional methods using the same weight percent catalyst (Pt/C, 20 wt.%) [7]. That result seems to reflect that the electrospray effect has little or no influence on catalyst activity, neither on the (thickness dependent) electronic resistance of the catalyst layer.

4. Conclusions

The ionomer content and catalyst load have been optimized for cathodes prepared by electrospray deposition. An optimal 15% Nafion® concentration is found for electrospray deposited cathodes, which is lower than that observed for electrodes prepared by standard methods (airbrushing). This is explained as a consequence of the improved interaction of the ionomer with catalyst particles after electrospray deposition. Further research is being carried out to have more insight into this interaction. The catalyst load also shows an optimal value, 0.17 mg cm^{-2}, which corresponds with a minimum in the resistance of the catalytic layer. In this case, the value is similar to that found for cathodes prepared by other deposition methods, which implies that the electrospray effect does not change the catalyst activity neither the electronic resistance of the catalyst layer.

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