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Comparison of Pt/C Electrocatalyst Deposition Methods for PEM Fuel Cells

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In recent years, in order to solve the environmental problems associated with electricity production, alternative systems to traditional methods have been developed. In this contest, fuel cells are widely considered to be an efficient and non-polluting power source and therefore, they are considered to be promising energy devices for the transport, mobile, and stationary sectors. At the current stage of technology, among different types of developed fuel cells, proton exchange membrane fuel cells (PEM) deserve major attention. Pt/C deposited on Nafion membrane is the most used electrocatalyst for PEM due to the highest oxygen reduction catalytic activity. The most used conventional deposition methods on Nafion polymeric membranes for commercial PEM are screen printing and transfer printing. In order to improve the specific activity of Pt, alternative and cheap techniques are under investigation.
Therefore, in this work the performances of Pt/C samples deposited by dipping method and spray coating method have been compared, using a commercial system, as reference. Experimental tests were performed using a commercial Pt/C catalyst (20 wt. % Pt on Carbon Vulcan XC-72) deposited on Nafion membrane and tested in the 100 cm^2 single-cell testing kits. At the same cell voltage (0.3 V) and Pt loading (0.12 mg_{Pt} cm^{-2}), the results showed that the spray coating provided both a higher current density and a higher maximum power density (90 $mW \cdot cm^{-2}$) compared to the dipping method (38 $mW \cdot cm^{-2}$). Subsequently, the influence of Pt/C electrocatalyst load on PEM by spray coating method has been investigated and a Pt loading equal to 0.12 $mg_{Pt} \cdot cm^{-2}$ has guaranteed the best performances.
Moreover, the performances of a commercial PEM containing a Nafion membrane functionalized by screen printing method with 0.5 $mg_{Pt} \cdot cm^{-2}$ has been compared to the PEM with the membrane prepared by spray coating method loaded with 0.12 $mg_{Pt} \cdot cm^{-2}$. Experimental results showed that, at the same cell voltage, the PEM prepared with spray coating method allowed to obtain an electrical power higher than that obtained using commercial PEM.
Finally, the use of PEM at 0.12 $mg_{Pt} \cdot cm^{-2}$ obtained by spray coating method showed a remarkable stability because there was no decrease in the generated current also for long test time (higher than 30 h).

1. Introduction

Energy is the primary element of modern civilization and a prerequisite for sustainable development. It is known that global primary energy consumption is increasing with rapid urbanization. In fact, it has been predicted that global energy demands will grow about 36 % over the current level by the year 2030 (Islam et al., 2014). Because of fossil fuels such as oil, natural gas and coal are running out, fuel cells are widely considered to be an efficient and non-polluting power source, offering much higher energy densities and energy efficiencies compared to any other current energy storage devices. Fuel cells are electrochemical energy conversion devices that convert chemical energy directly into electrical energy. They are therefore considered to be promising energy devices for commercial and transport sectors (Sammes and Editor, 2006). Among different types of fuel cells, polymeric electrolyte membrane fuel cells (PEM) are the most efficient technologies to convert hydrogen into electricity (Saebea et al., 2017). The gaseous hydrogen, supplied to the anode, is oxidised into protons and electrons. The protons pass through the conducting membrane electrolyte whereas the electrons go around the external electrical circuit to the cathode. Oxygen is reduced to produce water at the cathode. At the current stage of technology, among different types of developed fuel cells, proton

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exchange membrane fuel cells (PEM) deserve major attention. In fact, PEM have many advantages such as low temperature operation (below 100 °C), high power density, lower corrosion, simple stack design and increased ruggedness (Feroldi and Basualdo, 2012). At our knowledge, electrocatalysts based on platinum (Pt) particles supported on porous carbon materials (Pt/C) deposited on Nafion membrane (Louh et al., 2007), have been reported to be efficient for PEM fuel cells due to the highest catalytic activity for the oxygen reduction reaction.
However, the large-scale implementation of this technology is hindered by the high cost of electrocatalysts with platinum because they represent for over 55% of the total cost (Lin et al., 2012). Thereby, there is a strong incentive to develop a novel processing technique in order to enhance the loading efficiency of the electrocatalysts and their distributions on the electrodes. Instead of conventional deposition technique on Nafion polymeric membranes for commercial PEM such as screen printing (Kim et al., 1998), brushing, or transfer printing (Antolini et al., 1999), in this paper, the dipping and spray coating deposition methods are proposed as an alternative and cheap techniques to deposit the catalyst ink on the conductive substrates in order to investigate the power performance of Pt/C electrocatalysts on Nafion polymeric membranes.

2. Experimental

2.1 Deposition of Pt/C electrocatalyst on Nafion membrane

450 mg of Pt/C catalyst powder (20 wt. % Pt on Carbon Vulcan XC-72, Fuell Cell Earth) were dispersed in 18 mL of 2-propanol (Sigma-Aldrich) and 9 mL of 5 wt% Nafion solution (Fuell Cell Earth). After the ultra-sonication, the resultant suspension coated the Nafion membrane (square shape with an area of 100 cm^2) through two different deposition methods: dipping method and spray coating method. In first case, Nafion membrane was immersed in the catalytic ink for one minute and subsequently left to dry at room temperature for about 1 h. The same procedure has been repeated several times until to reach the desired catalyst loading deposited on PEM. Spray coating method is instead a technique in which the printing ink is forced through a nozzle whereby a fine aerosol will be formed (Krebs, 2009).
Specifically, a commercial spray gun, maintained at a distance of about 10 cm from the membrane surface, has been connected to a compressed air line in order to have an optimal nebulization of the suspension containing the catalyst. As for the dipping method, the catalytic ink on Nafion membrane was dried for about a 1 h at room temperature and the same procedure was used until the desired catalyst load was reached. In particular, the amount of Pt/C deposited on both sides of the Nafion membrane was equal to 60 mg that corresponds to a Pt loading of 0.12 $mg_{Pt} \cdot cm^{-2}$.

2.2 Fuel cell tests

Experimental tests were carried out in a single plastic square cell (100 cm^2) with a stainless steel cover (PaxiTech). The oxygen present in the surrounding air can access the fuel cell through the number of slits on cathode side of the cell. Humidified H_2 stream (flow rate equal to 40 $Ncc \cdot min^{-1}$) was provided to the anode side of the cell from a hydrogen gas reservoir.
The cell has one hydrogen gas input and one exit. A porous carbon cloth material (gas-diffusion layer) is placed inside the kit for the homogeneous diffusion of hydrogen over the whole surface area of the membrane electrode assembly. Moreover, the fuel cell system is composed by current collectors. To measure the electric current or the cell voltage data, an electronic load was used (PaxiTech). The latter consists of an electronic variable resistor which can work in constant current or constant voltage mode. The performance of the fuel cell is shown by a graph of its output voltage versus the drawn current density (polarization curve).

3. Results

3.1 Comparison between spray coating and dipping method on PEM performances

The polarization curves and the corresponding power density for the spray coating and dipping method are presented in Figure 1a and in Figure 1b, respectively. In the same working conditions (cell voltage of 0.3 V and Pt loading of 0.12 mg_{Pt} cm^{-2}), the spray coating was able to reach both a higher current density (Figure 1a) that a higher maximum power density of 90 $mW \cdot cm^{-2}$ (Figure 1b) compared to the dipping method (38 $mW \cdot cm^{-2}$). The improvement in fuel cell performances for the spray coating method could be related to the good catalyst ink dispersion on Nafion membrane.
In general, the coating methods have been shown to provide higher performances because they offer better ionic connection between the membrane and the ionomer in the catalyst layer (Litster and McLean, 2004).

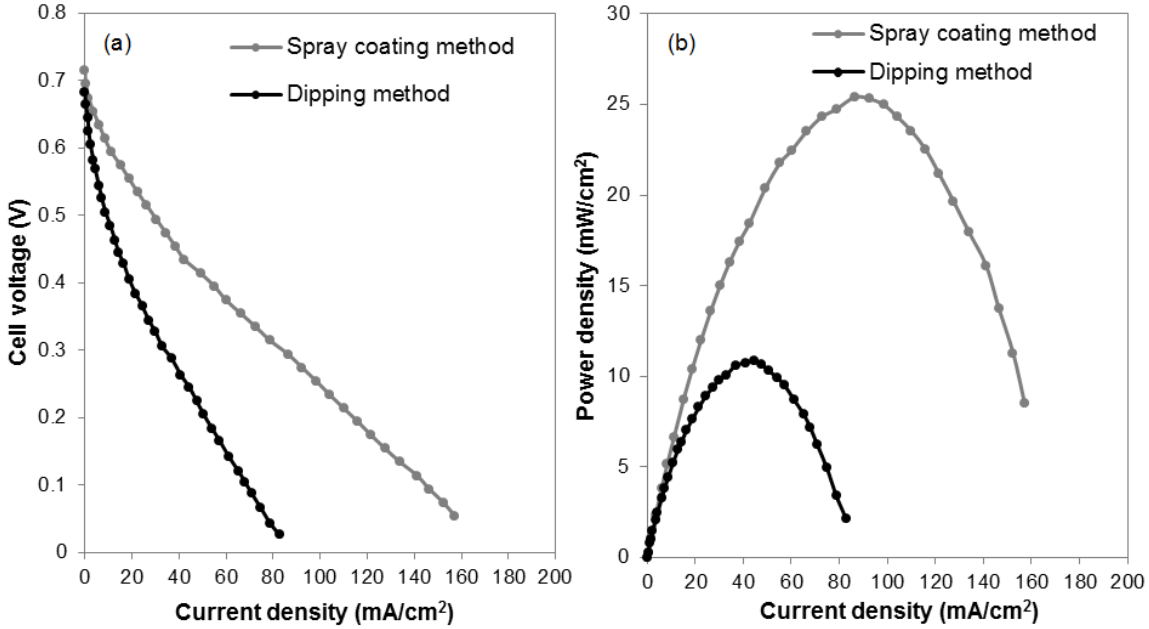

Figure 1: Comparison of polarization curves (a) and electrical power (b) for spray coating method and dipping method

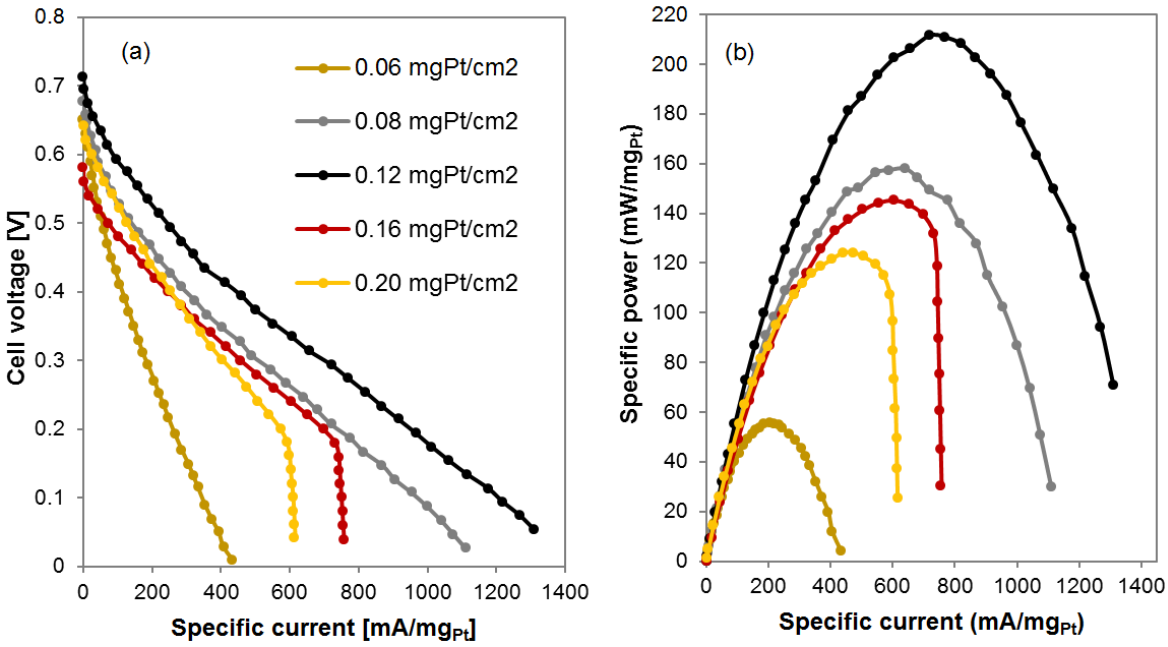

Figure 2: Influence of Pt/C electrocatalyst load in terms of polarization curves (a) and electrical power (b)

3.2 Influence of Pt/C electrocatalyst load on PEM

The influence of Pt/C electrocatalyst load on PEM by spray coating method has been investigated in the range of 0.06-0.2 $mg_{Pt}\cdot cm^{-2}$. Figure 2 shows that an increase in the Pt/C electrocatalyst load up to 0.12 $mg_{Pt}\cdot cm^{-2}$ clearly improved electrode performances, while further increases from 0.16 to 0.2 $mg_{Pt}\cdot cm^{-2}$ led to a significant drop in PEM performances.

For this reason, the best performance in terms of both current (Figure 2a) and electric power with a higher maximum power specific current of about 200 $mW\cdot mg_{Pt}^{-1}$ (cell voltage of 0.294 V) (Figure 2b), was obtained with a Pt loading equal to 0.12 $mg_{Pt}\cdot cm^{-2}$.

The thickness of the catalytically active region is usually determined by the depth of proton penetration, which is a function of the specific protonic conductivity, the volume fraction and the distribution of the ionomeric electrolyte within the electrode structure (Wilson and Gottesfeld, 1992b). However, by increasing the thickness of the electrode, mass transfer effects through the catalyst layer become more important with negative effects on PEM performances.
The effect of catalyst layer thickness could be explained considering that, at high cell current densities, gas permeability limitations within a thicker catalyst layer would allow activity only in the part of the layer closest to the gas supply and furthest from the ionomeric membrane (Wilson and Gottesfeld, 1992a). This could explain the results obtained for Pt loadings higher than 0.12 $mg_{Pt} \cdot cm^{-2}$.

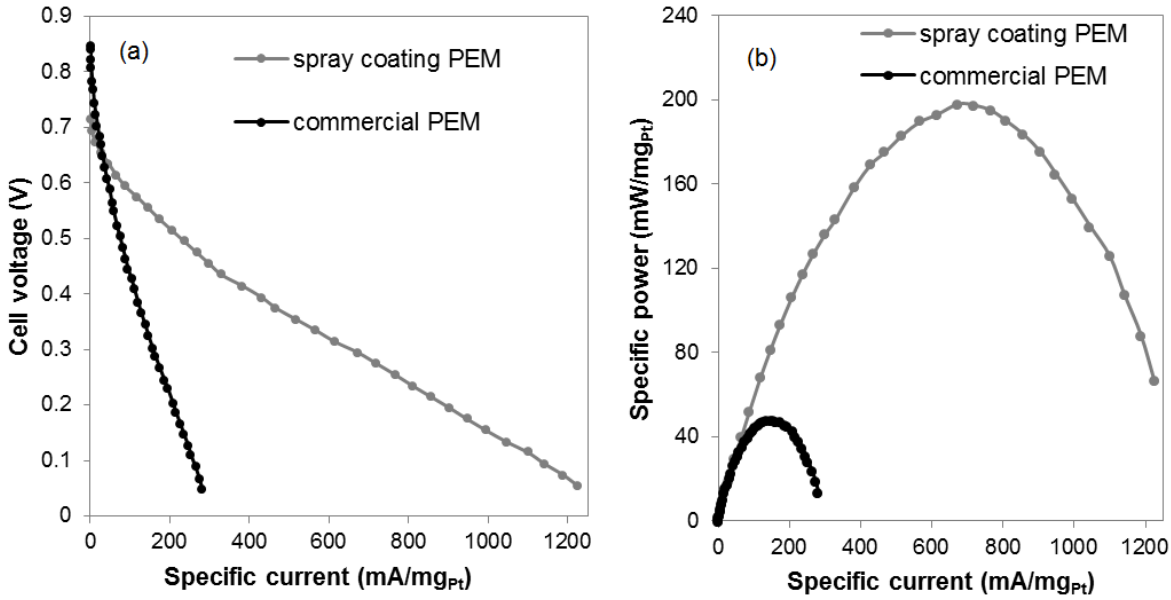

Figure 3: Comparison of polarization curves (a) and electrical power (b) for spray coating PEM and commercial PEM

3.3 Comparison between spray coating and screen printing method on PEM performances

The performances of a commercial PEM containing a Nafion membrane functionalized by screen printing method with 0.5 $mg_{Pt} \cdot cm^{-2}$ has been compared to the PEM with the membrane prepared by spray coating method loaded with 0.12 $mg_{Pt} \cdot cm^{-2}$. Figure 3a shows that, at the same cell voltage, the PEM prepared with spray coating method allowed to obtain an electrical power higher than that obtained using commercial PEM. This is an important result because the amount of Pt on PEM obtained by spray coating is less than a quarter of the commercial PEM. In Figure 3b is evident that PEM functionalized by spray coating method was able to achieve a higher maximum power specific current of about 200 $mW \cdot mg_{Pt}^{-1}$ for a cell voltage of 0.294 V instead of commercial PEM (44.5 $mW \cdot mg_{Pt}^{-1}$ for a cell voltage of 0.344 V).
This result is very interesting considering that, in other works, the comparison with PEM obtained by screen printing has led to the same level of power efficiency (Louh et al., 2007). A further comparison, shown in Figure 4, was carried out in order to check the PEM stability until to 14 h. The results showed that both membranes achieved a stable value within 4 h of test. It is worthwhile to note that, the PEM obtained by spray coating (with Pt loading lower than the value of PEM commercial) showed higher performances compared to PEM functionalized with screen printing method. Specifically, the specific current generated by the PEM functionalized by spray coating (about 800 $mA \cdot mg_{Pt}^{-1}$) was much higher than the value obtained by the commercial PEM (about 130 $mA \cdot mg_{Pt}^{-1}$).
Finally, the specific current obtained from the stability test (Figure 4), has been compared with the literature data. In particular, it is clear that our PEM, functionalized by spray coating method, is able to guarantee the highest specific current compared to the values reported in the scientific literature.

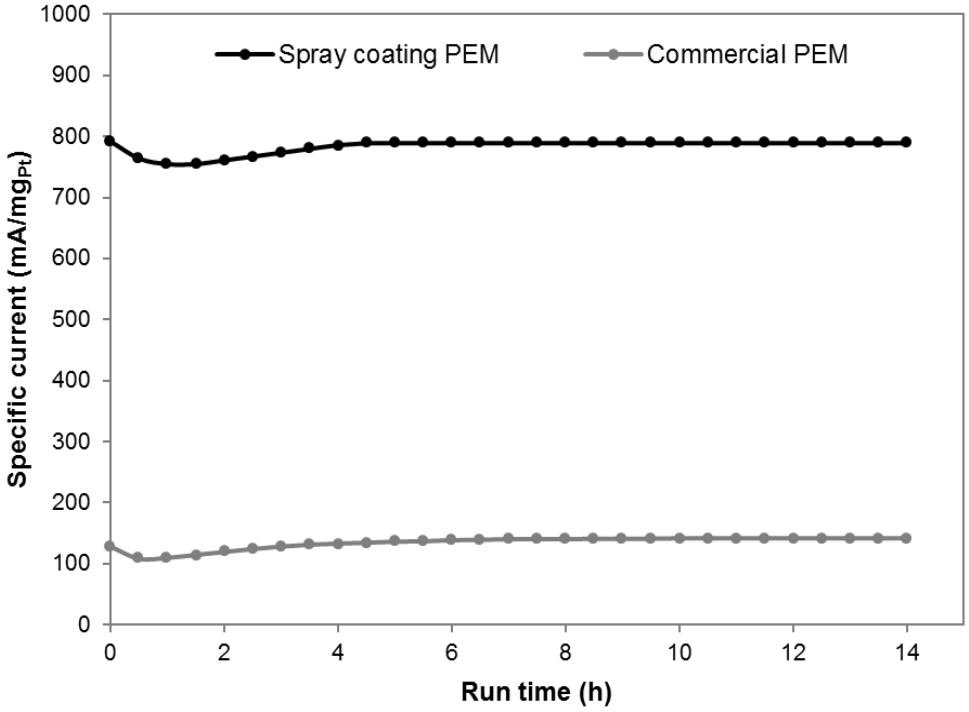

Figure 4: Stability tests (cell voltage of 0.294 V for spray coating PEM and cell voltage of 0.344 V for commercial PEM)

Table 1: Comparison of stability test results with scientific literature

PEM deposition method	Catalyst ink	Specific current [$mA \cdot mg_{Pt}^{-1}$]	Reference
spray coating	Pt/C	800	Our work
screen printing	Pt/C	141.7	(Litster and McLean, 2004)
vacuum deposition	Pt/C	708.3	(Litster and McLean, 2004)
screen printing	Pt/C	675	(Louh et al., 2007)
screen printing	Pt/C	440	(Wang et al., 2015)
screen printing	Pt/C	425	(Yarlagadda et al., 2017)
ultrasonic spray coating	Pt/C	360	(Yarlagadda et al., 2017)
vacuum filtration	Pt/C	290	(Yarlagadda et al., 2017)

4. Conclusions

In this paper Pt/C deposited on Nafion membrane through spray coating method has proved as an alternative and cheap technique to deposit catalyst ink on PEM fuel cells. In particular, with a cell voltage of 0.3 V and Pt optimal loading of 0.12 mg_{Pt} cm^{-2}, it was able to reach both a higher current density that a higher maximum power density (90 $mW \cdot cm^{-2}$).

Moreover, spray coating method has been demonstrated higher performances also compared to the PEM functionalized with conventional method such as screen printing. In fact, compared to commercial PEM, spray coating method allowed to achieve both a higher maximum power specific current (200 $mW \cdot mg_{Pt}^{-1}$ with a cell voltage of 0.294 V) that a higher specific current attained from stability test (about 800 $mA \cdot mg_{Pt}^{-1}$). In this last case, PEM functionalized by spray coating method was able to ensure the highest specific current than those reported in the scientific literature. The improved performances obtained by spray coating method could be the starting point for future research activity aimed to formulate innovative electrocatalysts (e.g. by further reduce the Pt loading and changing the carbon support for active phases) in order to make PEM fuel cell cheaper and competitive with the traditional methods used for the generation of the electricity.

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