Improvement of the sputtered platinum utilization in proton exchange membrane fuel cells using plasma-based carbon nanofibres

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Abstract
Proton exchange membrane fuel cells are complex nanostructures containing a catalyst (usually platinum), proton and electron conductors and pores. Their electrode performance is strongly influenced by the size, the repartition and the orientation of the nanoseparated materials used and the pores. This paper investigates the electrical performance achieved by three designs of plasma-prepared Pt/C electrodes with low Pt loadings (from 0.01 to 0.1 mgPt cm\(^{-2}\)). A plasma sputtering process was used for the synthesis of Pt nano-clusters in three different microporous supports: a single oriented layer based on aligned carbon nanofibres (CNFs, custom-made by plasma), a single convoluted layer based on Vulcan carbon particles (LT1600, known as a gas diffusion layer—GDL) or a double layer composed of CNFs covering a GDL. Membrane electrode assemblies (MEAs) were prepared by hot-pressing one of these three electrodes with a commercial electrode (0.5 mgPt cm\(^{-2}\)) and a commercial Nafion 115 membrane, and compared with a reference MEA (from Electrochem Inc. with a Pt loading per electrode of 0.5 mgPt cm\(^{-2}\) and a maximum power density of 425 mW cm\(^{-2}\)). The cathodic Pt utilization efficiency in the best performing plasma-prepared cathode (based on the double layer GDL/CNF) with a Pt loading per electrode of 0.5 mgPt cm\(^{-2}\) and a maximum power density of 425 mW cm\(^{-2}\)). The cathodic Pt utilization efficiency in the best performing plasma-prepared cathode (based on the double layer GDL/CNF) with a Pt loading per electrode of 0.5 mgPt cm\(^{-2}\) and a maximum power density of 425 mW cm\(^{-2}\)). The cathodic Pt utilization efficiency in the best performing plasma-prepared cathode (based on the double layer GDL/CNF) with a Pt loading per electrode of 0.5 mgPt cm\(^{-2}\) and a maximum power density of 425 mW cm\(^{-2}\)). The cathodic Pt utilization efficiency in the best performing plasma-prepared cathode (based on the double layer GDL/CNF) with a Pt loading per electrode of 0.5 mgPt cm\(^{-2}\) and a maximum power density of 425 mW cm\(^{-2}\)). The cathodic Pt utilization efficiency in the best performing plasma-prepared cathode (based on the double layer GDL/CNF) with a Pt loading per electrode of 0.5 mgPt cm\(^{-2}\) and a maximum power density of 425 mW cm\(^{-2}\)). The cathodic Pt utilization efficiency in the best performing plasma-prepared cathode (based on the double layer GDL/CNF) with a Pt loading per electrode of 0.5 mgPt cm\(^{-2}\) and a maximum power density of 425 mW cm\(^{-2}\)).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is the most promising fuel cell candidate for a wide variety of power applications (portable, stationary power supply and transportation) due to a series of advantageous features such as a low-operating temperature, low weight, compactness, potential for low cost and volume, long stack life, fast start-ups and suitability for discontinuous operation. Over the past few years, fuel cell, electronic and automotive companies have announced several new technologies or prototype vehicles adopting PEMFC supplied with hydrogen or methanol. The main limitations for a large-scale application of the PEMFC is the cost and some technological barriers such as the limited...
supply, the stability and the lifespan. The fabrication cost can be reduced through several approaches such as economy-of-scale effects in production, a more efficient use of materials, particularly the platinum catalyst in the PEM fuel cells electrode [1–3] and by achieving a more effective membrane electrode assembly (MEA) [4]. Nowadays, the platinum utilization efficiency in a commercial electrode is close to 1 gPt kW−1 which represents a cost of $48 kW−1 (considering a Pt cost of $48 gPt−1 on December 2007). According to the US Department of Energy [5], this Pt cost must be decreased to 0.110 mgPt cm−2 for a MEA delivering a maximum power density of 1 W cm−2. On this basis, we will evaluate the electrical performance achieved by our MEA when the Pt loading is reduced to around 0.01 mgPt cm−2 in the anode and 0.1 mgPt cm−2 in the cathode by using a combination of plasma processes.

A commercial electrode is usually prepared by ink processes and is composed of a macroporous carbon support (typically carbon paper or cloth), a gas diffusion layer (GDL—typically carbon Vulcan and PTFE nanoparticles) and an active layer (typically a mixture of carbon Vulcan particles chemically coated by Pt catalyst nano-clusters) [6–8]. A proton conductive polymer (typically Nafion®) is generally added to the active layer to provide ample contact between the proton exchange membrane (typically Nafion®) and the Pt catalyst sites. The Nafion® polymer addition encapsulates Pt/C particles to form agglomerates (more or less spherical with a diameter in the 200–1000 nm range) in the active layer, which unfortunately leads to a decrease in the catalyst accessibility [9–12]. Powders based on carbon nanotubes (CNTs) or nanofibres (CNFs) have been proposed as a replacement of the carbon Vulcan particles in the catalytic inks [13–16]. However, these results have not yet shown any significant advantages over conventional carbon particles. The feasibility of growing CNTs directly on carbon paper has recently been demonstrated using a silica gel to catalyze the CNT growth [17–19] or using a process of electro-deposition of Pt on CNTs grown by chemical vapour deposition on carbon paper after an initial electro-deposition of cobalt catalyst [20–23]. In previous studies [24], we demonstrated a new protocol process for a homogeneous growth of CNFs. The carbon substrate (GDL or carbon paper) is covered by oriented CNFs surrounded by Pt nano-clusters directly grown on a (macroporous or microporous) carbon substrate. This process consisted of a combination of plasma steps.

The objective of this work is to report on the performance achieved by a MEA fitted with different carbon nanostructures catalyzed by plasma sputtering (on the anode or on the cathode side) when varying the Pt loading and the operating gas pressure. Three active layers based on different carbon nanostructures are compared: a single oriented layer based on aligned CNFs grown by plasma processes (CNF/Pt), a single convoluted layer based on Vulcan carbon particles (GDL/Pt) and a double layer with Pt covered CNFs laid on carbon Vulcan particles (GDL/CNF/Pt). These electrodes are compared with a commercial electrode by measuring their performance in an MEA. Finally, the Pt utilization efficiency is discussed.

2. Experimental

2.1. Plasma-controlled synthesis of aligned CNFs

Different pieces of 5 cm2 microporous layer composed of Vulcan carbon particles supported on woven web (GDL, LT1600, purchased at BASF Fuel cell Inc.) and of 5 cm2 carbon paper (TP060 toray carbon paper purchased at Fuel Cell Store) are covered by oriented CNFs in a low pressure plasma system called Southern Cross [25, 26]. In summary, a helicon plasma source is attached to the top of a deposition chamber shaped as a cross (55.5 cm × 55.5 cm). The typical base pressure in the system before the gas is introduced is less than 5 × 10−6 mbar. The helicon plasma is created by a double saddle antenna [27] surrounding the tubular glass source and powered by a 13.56 MHz radio frequency generator. An uncatalyzed carbon support (a microporous GDL or a macroporous carbon paper) is placed on a circular substrate holder which can be dc biased, heated, manually rotated on its axes and moved along the vertical axis. Two 5 × 5 cm2 targets (Ni and Pt) are placed 13 cm below the plasma source on either side of the substrate holder and 8 cm away from the vertical reactor axis. Two successive plasma processes schematized in figure 1 are required for the CNF growth. Initially, nickel nano-clusters are deposited on the carbon support by plasma sputtering in an argon plasma. This nickel acts as a catalyst for the CNF growth [28–30]. Subsequently, the CNFs are synthesized on the Ni coated carbon support using a methane/hydrogen radio-frequency helicon plasma.

For the first step (figure 1(a)), argon is introduced in the system to reach a pressure of 5 mTorr and the plasma is coupled using 500 W RF power. The argon ions strike the Ni target biased at −300 V and sputtered Ni atoms are ejected from the target. Ni atoms are deposited on the carbon support after collisional transport through the plasma phase. For these conditions, the Ni deposition rate measured by Rutherford backscattering spectroscopy (RBS) is 15 × 1015 Pt atoms cm−2 min−1 [26] (which corresponds to 1.5 nm min−1 considering a dense Ni layer). Atomic force microscopy (AFM) experiments have shown that the diameter of the Ni nano-clusters is about 25 nm for the 8 min long Ni deposition performed in this study. When the Ni deposition is completed, the RF plasma is switched off and the argon is pumped out of the reactor.

The second step (figure 1(b)) begins by clamping the Ni-covered carbon support on the substrate holder (10 cm below the source) with a 4 cm2 open area grid. This grid is required for a homogeneous growth of CNFs. The carbon support temperature is then increased to 400°C under the base pressure over a period of 15 min. The system is then fed with methane and hydrogen at 5 mTorr with a 1:4 flow ratio and a 500 W plasma is ignited. With the substrate dc biased at −100 V, aligned CNFs (typically in a stacked-cup structure [31, 32] and following a tip growth mechanism [33]) are grown for a period of 90 min. At the end of the process, the carbon support (GDL or carbon paper) is covered by oriented CNFs over a surface of 4 cm2.
Figure 1. Schematic of the two plasma steps required to grow the catalytic layer based on CNFs: (a) Ni nano-clusters deposition by plasma sputtering and (b) CNFs growth by plasma enhanced chemical vapour deposition.

2.2. Plasma deposition of platinum on carbon nanostructured layer (convoluted, oriented or both)

The Pt deposition on PEM fuel cell electrodes by plasma sputtering has been previously studied [34–41]. However, only electrodes based on Vulcan particles are generally used as a substrate. In this study, Pt nanoclusters are grown on three types of porous carbon nanostructured layers: on a single convoluted layer of Vulcan carbon particles (GDL), on a single oriented layer of CNFs supported on carbon paper (CNF) or on a double layer of CNFs and Vulcan particles (GDL/CNF). The $\pm 300$ V biased Pt target is sputtered by ions coming from an argon plasma at 5 mTorr pressure and 500 W RF power conditions. During the deposition, the substrate holder is manually rotated to provide a deposition rate uniformity of $\pm 10\%$. The Pt deposition rate measured by RBS and simulated by a Monte Carlo model called SpaTinG [42] is $15 \times 10^{15}$ atoms cm$^{-2}$ min$^{-1}$ (i.e. 0.005 mgPt cm$^{-2}$ min$^{-1}$). The Pt deposition time varies from 1 to 20 min, which results in a Pt loading ranging between 0.005 and 0.1 mgPt cm$^{-2}$.

Figure 2 displays a schematic of the Pt deposition scheme (on CNFs).

A cold field scanning electron microscope (SEM, Hitachi S4500) is used to characterize the CNFs based layer before and after the growth of Pt nano-clusters. The apparent mean diameter $\langle d \rangle$ is calculated from at least 50 randomly chosen isolated clusters using the following equation:

$$\langle d \rangle = \frac{\sum n_i d_i}{n},$$

where $n$ is the total number of measured particles or clusters, $n_i$ the number of particles or clusters with a diameter of $d_i$.

Assuming that each Pt nano-cluster is perfectly spherical, the platinum dispersion $D$ can be estimated by dividing the number of Pt atoms on the spherical surface by the number of total Pt atoms in the spherical volume:

$$D = \frac{1}{\langle d \rangle \sqrt{N_a m_{Pt}/M_{Pt}}} \frac{4 \pi (d/2)^2}{(N_a m_{Pt}/M_{Pt})} \times \frac{4 \pi}{3} \langle d/2 \rangle^3 \approx \frac{1.48 \times 10^{-9}}{\langle d \rangle},$$

where $N_a$ is Avogadro’s number and $M_{Pt}$ the molar mass of Pt.
where $m_{Pt}$ is the Pt mass density ($g_{Pt} \text{ m}^{-3}$), $M_{Pt}$ the Pt molar weight ($g_{Pt} \text{ mol}^{-1}$) and $N_A$ the Avogadro number (at mol$^{-1}$).

2.3. Custom-made MEA

Each custom-made MEA is composed of one of the three 5 cm$^2$ plasma-prepared electrodes (GDL/Pt, CNF/Pt or GDL/CNF/Pt) and a 5 cm$^2$ commercial electrode purchased at BASF Fuel cell Inc. (ELAT$^\text{TM}$ GDEs, LT 120E-W) containing 0.5 mg$\text{Pt cm}^{-2}$ of platinum.

Firstly, the Nafion$^\text{TM}$ 115 membrane (Electrochem. Inc.) is treated according to a standard procedure [43] and stored in de-ionized water.

Secondly, a Nafion$^\text{TM}$ 5 wt% (PowerIon Inc.) solution is spread on the electrode without CNFs (GDL/Pt and commercial electrode) using a pipet to ensure proton access from the membrane to the Pt catalyst site. After the Nafion$^\text{TM}$ application, the electrodes are dried in an oven at 50 $^\circ \text{C}$ for 1 h.

Nafion$^\text{TM}$ solution is not added on the electrodes with CNFs (single—CNF—or double layer—CNF/GDL).

Finally, two 5 cm$^2$ electrodes and the humidified and treated Nafion$^\text{TM}$ 115 membrane placed in between are assembled in a manual hot press (purchased at Rondol technology Ltd) at 130 $^\circ \text{C}$ for 120 s under a pressure of 2 kN cm$^{-2}$.

2.4. Reference MEA

All the custom-made MEAs are compared with a reference MEA (FC05-MEA, Electrochem. Inc.) composed of a commercial Nafion$^\text{TM}$ 115 membrane and two commercial electrodes with a platinum loading of 0.5 mg$\text{Pt cm}^{-2}$ (per electrode) supported on carbon paper. The geometric surface area of this MEA is 5 cm$^2$.

2.5. Fuel cell tests

To obtain an operating cell with a surface area of 5 cm$^2$, 10 mil thick silicon gaskets (EC-GS-SIL-10-05SP, Electrochem. Inc.), carbon bipolar plates (FC05-MPR, Fuel cell store) and gold plated current collectors copper plates (FC-05-CP, Electrochem. Inc.) are added on each side on the MEA. A torque of 2 N m is applied on each of the eight bolts clamping the fuel cell. The tests are carried out using a MTS 150 Fuel Cell Station manufactured by Quintech. Details about the station are given elsewhere [43]. In this study, pure hydrogen and pure oxygen are used as fuel and oxidant. All polarization curves are obtained at a cell temperature of 80 $^\circ \text{C}$ without gas humidification. The anode backpressures ($P_a$) and the cathode backpressure ($P_c$) are set at the same value.

We analyse the electric data up to the end of the linear region of the $E(j)$ curves. The square of the correlation coefficient is always higher than 0.95. In this treatment, the mass transport limitations are not considered. In addition, we assume that the reactants act as ideal gases and that the activity of water is 1. The activation overpotential at the anode is assumed to be negligible.

3. Results and discussion

3.1. Characterization of the sputtered Pt catalyst

Figure 3 displays the SEM observations of the CNF layer before (figure 3(a)) and after (figure 3(b)) a 4 min long Pt deposition resulting in a Pt loading of 0.02 mg$\text{Pt cm}^{-2}$. The same CNF morphology is obtained on carbon paper or GDL. For these CNFs growth parameters, previous microscopy analysis has shown that their length, diameter and the space between each CNF are about 2 $\mu \text{m}$, 37 nm and 67 nm, respectively. The CNF density on GDL surface is estimated...
to be about $2.2 \times 10^{10} \text{ cm}^{-2}$. The platinum atoms form nano-clusters on the top and side wall of each CNF as shown in figure 3(b). The mean diameter ($d$) of these nano-clusters decreases from 8 to 3 nm between 100 and 600 nm from the top to the bottom of the CNF [24] and the mean diameter over the whole CNFs is about 5 nm. Hence, the Pt dispersion calculated from equation (2) increases from 18% to 50% with a mean Pt dispersion of 29%. The Pt loading represents 25.1 wt% of the carbon weight in this 2 $\mu$m thick catalytic layer with a Pt loading of 0.020 mgPt cm$^{-2}$, by assuming a carbon density in a CNF of 2.25 g cm$^{-3}$. In this study, the Pt loading sputtered on the CNF layer will vary from 0.010 to 0.1 mg Pt cm$^{-2}$, which gives a local Pt/C ratio ranging from 12.6 to 125.7 wt%.

We have previously shown that on a GDL (without CNF layer) sputtered platinum atoms form nano-clusters with an average diameter ($d$) of 5 nm for an argon pressure of 0.5 Pa [26]. For a Pt loading of 0.02 mgPt cm$^{-2}$, these Pt nanoclusters coalesce to form a hillocked surface and the coverage of the carbon particles at the GDL surface is close to 100%. The Pt dispersion is lower on the GDL than on the CNF layer. This is related to the convoluted porosity of the GDL which avoids a deep penetration of the platinum atoms during the deposition process (not the case with the oriented porosity of the CNF layer). The decrease in the Pt density into the microporous GDL follows a stretched exponential [46,47] up to a depth of 2 $\mu$m with 90% of the total platinum amount spread over a depth of 400 nm. A SEM analysis has shown that the GDL thickness is about 50 $\mu$m, the estimated local Pt/C catalyst ratio is in the 23–230 wt% range over the 400 nm GDL depth. Consequently, the local Pt/C ratio in the catalytic layer with Vulcan particles is higher than that in the CNFs based catalytic layer.

Cyclovoltametry experiments have been previously performed on the electrodes based on Pt sputtered on GDL (without CNF layer). The measured electrochemical active surface area ($a_{\text{Pt}}$) was about 7–8 m$^2$ g$^{-1}$ for a Pt loading of 0.1 mgPt cm$^{-2}$ which is in accordance with a recent study [48]. In this study, Kim et al claimed that this active surface area is slightly higher than that obtained on conventional electrode (2.8–7.5 m$^2$ g$^{-1}$) but much lower than that obtained on electrode based on CNTs (9.1–20.6 m$^2$ g$^{-1}$). This latest electrode structure is similar to our GDL/CNF/Pt electrode. Consequently, it can be assumed that our GDL/CNF/Pt electrodes and their CNT based electrodes lead to similar Pt active areas for the same CNT (or CNF)/Vulcan ratio.

### 3.2. Electrical performance of the three nanostructured cathodes prepared by plasma processes

The influence of the Pt loading sputtered on the three types of plasma-prepared cathode is studied. Four different Pt loadings (0.01, 0.02, 0.04 and 0.1 mgPt cm$^{-2}$) are deposited on the Vulcan based layer, on the CNFs based layer and on the Vulcan and CNFs based layer. Each cathode is hot pressed with a commercial anode (0.5 mgPt cm$^{-2}$ Pt loading) against a Nafion® 115 membrane.

Figure 4 displays the polarization curves obtained with these twelve custom-made MEAs and with the reference MEA.
The highest current density $j_0$ with the double microporous layer GDL/CNF is always lower than that for the single layer based on Vulcan. This is due to the mass transport limitation at high current density, even if the current density $j_0$ is higher with the CNF layer for the highest Pt loadings (0.04 and 0.1 mgPt cm$^{-2}$).

Figure 5 displays the power density obtained with the reference MEA (dashed line) and with the three cathode designs (GDL/Pt—squares, CNF/Pt—triangles and GDL/CNF/Pt—diamonds) for two different cathodic Pt loadings contained in the cathode and expressed in kW gPt$^{-1}$.

Table 1. Electrode kinetic parameters for oxygen reduction drawn from $E(j)$ curves of figure 4.

<table>
<thead>
<tr>
<th>Carbon nanostructures in the cathode</th>
<th>Pt loading sputtered on the cathode (mgPt cm$^{-2}$)</th>
<th>$E_c$ (V)</th>
<th>$j_0$ ($\times 10^6$ A cm$^{-2}$)</th>
<th>$b$ (mV decade$^{-1}$)</th>
<th>$E_0$ (V)</th>
<th>$R_{cell}$ ($\Omega$ cm$^2$)</th>
<th>Maximum power density (mW cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan (ref. MEA)</td>
<td>0.5</td>
<td>0.97</td>
<td>400</td>
<td>60</td>
<td>0.82</td>
<td>0.36</td>
<td>425</td>
</tr>
<tr>
<td>Vulcan</td>
<td>0.01</td>
<td>0.84</td>
<td>0.7</td>
<td>50</td>
<td>0.57</td>
<td>0.64</td>
<td>137</td>
</tr>
<tr>
<td>Vulcan</td>
<td>0.02</td>
<td>0.89</td>
<td>2</td>
<td>54</td>
<td>0.62</td>
<td>0.48</td>
<td>203</td>
</tr>
<tr>
<td>Vulcan</td>
<td>0.04</td>
<td>0.92</td>
<td>3</td>
<td>58</td>
<td>0.66</td>
<td>0.46</td>
<td>238</td>
</tr>
<tr>
<td>Vulcak</td>
<td>0.1</td>
<td>0.95</td>
<td>10</td>
<td>60</td>
<td>0.70</td>
<td>0.45</td>
<td>270</td>
</tr>
<tr>
<td>CNFs</td>
<td>0.01</td>
<td>0.85</td>
<td>0.0001</td>
<td>49</td>
<td>0.40</td>
<td>0.65</td>
<td>66</td>
</tr>
<tr>
<td>CNFs</td>
<td>0.02</td>
<td>0.9</td>
<td>0.2</td>
<td>58</td>
<td>0.56</td>
<td>0.60</td>
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<tr>
<td>CNFs</td>
<td>0.04</td>
<td>0.91</td>
<td>7</td>
<td>61</td>
<td>0.66</td>
<td>0.57</td>
<td>177</td>
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<tr>
<td>CNFs</td>
<td>0.1</td>
<td>0.94</td>
<td>60</td>
<td>63</td>
<td>0.74</td>
<td>0.47</td>
<td>230</td>
</tr>
<tr>
<td>CNFs on Vulcan</td>
<td>0.01</td>
<td>0.85</td>
<td>10</td>
<td>50</td>
<td>0.65</td>
<td>0.60</td>
<td>180</td>
</tr>
<tr>
<td>CNFs on Vulcan</td>
<td>0.02</td>
<td>0.86</td>
<td>31</td>
<td>54</td>
<td>0.67</td>
<td>0.55</td>
<td>219</td>
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<tr>
<td>CNFs on Vulcan</td>
<td>0.04</td>
<td>0.90</td>
<td>40</td>
<td>57</td>
<td>0.71</td>
<td>0.45</td>
<td>289</td>
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<tr>
<td>CNFs on Vulcan</td>
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<td>100</td>
<td>60</td>
<td>0.76</td>
<td>0.45</td>
<td>310</td>
</tr>
</tbody>
</table>

The Pt utilization efficiency in the cathode (defined by the power density delivered by the assembly devised by the Pt loading contained in the cathode and expressed in kW gPt$^{-1}$).
is displayed in figure 6 for these six custom-made MEAs and for the reference MEA. It reaches 18 and 3.1 kW g\textsuperscript{−1} in the two best performing plasma-prepared cathodes (based on GDL/CNF/Pt) with a respective Pt loading of 0.01 and 0.1 mgPt cm\textsuperscript{−2}, which is 20 and 3.6 times higher than that obtained for the reference MEA (0.85 kW g\textsuperscript{−1}). However, the inferior histogram in figure 6 shows that the maximum power density achieved by the best performing cathode prepared by plasma (GDL/CNF/Pt with 0.1 mgPt cm\textsuperscript{−2}) is 27% lower than that obtained with the reference MEA (310 mW cm\textsuperscript{−2} versus 425 mW cm\textsuperscript{−2}). At low current density where fuel cells operate in all likely applications (<300 mA cm\textsuperscript{−2}), the decrease in performance with this plasma-prepared cathode is two times lower: only 13% at 300 mA cm\textsuperscript{−2} (190 mW cm\textsuperscript{−2} with the best performing cathode prepared by plasma prepared versus 220 mW cm\textsuperscript{−2} for the reference MEA). At 300 mA cm\textsuperscript{−2}, the Pt utilization in the cathode based on the GDL/CNF/Pt nanostructure is 4.3 times higher than that in the commercial cathode for these operating conditions.

In summary, a decrease in the Pt loading in the FC cathode from 0.5 to 0.1 mgPt cm\textsuperscript{−2} can be achieved by the plasma deposition of CNFs as catalyst nano-supports on the Vulcan particles based microporous layer. For such a cathode prepared by plasma, the cathodic platinum utilization efficiency is increased by a factor of 3.6 (from 0.85 to 3.1 kW g\textsuperscript{−1}).

3.3. Electrical performances of the three nanostructured anodes prepared by plasma processes

The three catalytic nanostructured layers (GDL/Pt, CNF/Pt and GDL/CNF/Pt) are tested on the anode side. As the hydrogen oxidation requires less Pt active surface area than the oxygen reduction, the amount of plasma-sputtered platinum on the anode is reduced to 0.01 mgPt cm\textsuperscript{−2} (Pt deposition time of 2 min). Figure 7 displays the electrical performance obtained with the three custom-made MEAs and with the reference MEA (solid line). The anodes prepared by plasma processing lead to the same performance as that of the reference assembly, except for the anode with CNF (triangles) where the cell voltage drops at high current density (>600 mW cm\textsuperscript{−2}).

Figure 8 displays the $E−j$ curves achieved by these four MEAs (the three custom-made and the reference one) when the operating gas backpressure $P$ is decreased to 2 bar (figure 8(a)) and 1 bar (figure 8(b)). For both cases, the decrease in performance is more important for our custom-made MEAs (triangles, circles and diamonds) than for the reference MEA (dashed and dotted line). At low current density (up to 100 mA cm\textsuperscript{−2}), the $E−j$ curves obtained with the three custom-made MEAs and for the reference MEA are similar. At medium current density (from 100 to 400 mA cm\textsuperscript{−2}) in figure 8(a) and from 100 to about 200 mA cm\textsuperscript{−2} in figure 8(b), the three custom-made MEAs keep the same cell voltage which is lower than that obtained for the reference MEA. All the MEAs display an ohmic behaviour characterized by a similar negative slope. At higher current density (from 400 mA cm\textsuperscript{−2} in figure 8(b) and from 200 mA cm\textsuperscript{−2} in figure 8(b)), the cell voltage achieved by the two MEAs based on a single nanostructured anode (CNF/Pt in triangles and GDL/Pt in diamonds) drops quickly, whereas the MEA with the double nanostructured anode (circles) keeps an ohmic behaviour.

Starting with the lowest performance MEA (CNF/Pt anode—triangles), an additional study is carried out where three different amounts of Pt (0.01, 0.02 and 0.04 mgPt cm\textsuperscript{−2}) are deposited on the CNFs based layer covering the macroporous carbon paper. The polarization curves of the three custom-made MEAs are displayed in figure 9 for three
operating backpressures: 1 bar (figure 9(a)), 2 bar (figure 9(b)) and 3 bar (figure 9(c)). The MEA performance increases with the Pt loading for all backpressures over the whole range of current density. At 1 bar, the $E(j)$ curve obtained with the Pt loading of 0.04 mgPt (triangles) reaches that of the reference MEA at low current density (up to 200 mA cm$^{-2}$). At higher backpressure, the cell voltage obtained with the custom-made MEAs and with the reference MEA are similar at low current density for lower Pt loading: 0.02 mgPt cm$^{-2}$ at 2 bar (circles in figure 9(b)) and 0.01 mgPt cm$^{-2}$ at 3 bar (diamonds in figure 9(c)). Hence, the Pt loading required in the CNF based anodes to maintain the reference MEA performance at low current density decreases when the operating backpressure is increased.

In summary, the Pt loading can easily be decreased in the anode by using plasma techniques. The anode with 0.01 mgPt cm$^{-2}$ of platinum deposited on GDL or on the GDL/CNF layer leads to the same performance as the reference MEA for an operating backpressure of 3 bar.

4. Conclusion

Three PEMFC electrode designs with a low Pt loading (from 0.01 to 0.1 mgPt cm$^{-2}$) have been prepared by plasma
processing and compared in terms of electrical performance and platinum utilization efficiency. The platinum nano-clusters are grown by plasma sputtering in three different carbon nanostructured layers: a microporous layer based on Vulcan particles (GDL), a microporous layer based on plasma-prepared CNFs and a double layer made of Vulcan particles covered by CNFs. These three electrode designs have been hot pressed with a commercial electrode (from BASF Fuel cell Inc. and containing 0.5 mgPt cm$^{-2}$ of platinum) and a Nafion® 115 membrane.

The plasma-prepared electrodes were initially used on the cathode side of the custom-made MEAs. The FC tests performed at 80 °C and 3 bar showed that the performance achieved by these MEAs is lower than that of the reference MEA (purchased at Electrochem Inc., Nafion® 115 membrane and two electrodes with 0.5 mgPt cm$^{-2}$ of platinum). However, the Pt utilization efficiency in the three designs of low Pt loaded cathodes is much higher, especially with the cathode based on the microporous double layers (CNF and Vulcan). The efficiency in such a cathode with 0.1 mgPt cm$^{-2}$ (3.1 kW Pt$^{-1}$) of platinum is 3.6 times higher than that in the commercial cathode of the reference MEA (0.85 kW gPt$^{-1}$). The maximal power densities achieved by these two respective MEAs are 310 and 425 mW cm$^{-2}$ (performance decrease of 27%). For the current density range used in a commercial fuel cell (≤300 mA cm$^{-2}$), this performance decrease is half reduced (about 13%).

The three anodic designs prepared by plasma with a sputtered Pt loading of 0.01 mgPt cm$^{-2}$ lead to the same electrical performance than that of a reference assembly at an operating backpressure of 3 bar. At a lower backpressure, the CNF/Vulcan based electrode is the best performing anode prepared by plasma processes.

This study has shown that a combination of plasma techniques leads to an effective method for preparing thin oriented and porous active layers (based on aligned CNFs surrounded by Pt nano-clusters) on GDLs for highly efficient and low Pt loaded fuel cells.

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