The Effect of Substrate Nature Gas Diffusion Layer PTFE Content and Catalyst Layer Platinum Loading on the Performance of Low Temperature Proton Exchange Membrane Fuel Cell

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Abstract

The nature of the substrate, the content of Polytetrafluoroethylene (PTFE) and platinum (Pt) loading are the key factors to determine the heat transfer characteristics and hydrophobicity of the gas diffusion layer (GDL) and to enhance hydrogen oxidation and oxygen reduction kinetics which directly affect the performance of the proton exchange membrane fuel cell (PEMFC).

Here, we carried out-of-cell studies of the effect of the nature of the substrate, carbon black and PTFE loading in the GDL on the cell performances. Performances of double layered cathodes are evaluated from the current density-voltage (i-V) characteristics of the single cell. In addition, the behaviour of Pt loading on the amount of electroactive catalyst area is studied using cyclic voltammetry (CV).

Keywords: polymer electrolyte membrane fuel cell, Membrane electrode assembly, Nafion®, Gas diffusion layer.

1. Introduction

Modern fuel cell shows great promise for research and development technology for more clean and effective energy sources. A fuel cell converts hydrogen and oxygen to electricity directly by an electrochemical reaction. Among several fuel cell systems, PEMFC is a popular choice for mobile, portable and stationary power systems such as for automobiles and cellular phones. Compared with other fuel cell systems they have the advantage of high-power densities at relatively low operating temperatures small and lightweight (Wu et al., 2016; Chen et al., 2016).

A PEMFC consists of two porous electrodes: an anode, to which hydrogen fuel is supplied, a cathode to which oxygen or air is supplied, and a perfluorosulfonic acid electrolyte membrane that permits the flow of protons from the anode to cathode. Nafion® produced by DuPont is one of the most popular polymer electrolyte films today (Young et al., 2017).

The porous GDL in a PEMFC consists of a thin layer of carbon black mixed with PTFE that is coated onto a sheet of macro-porous carbon backing cloth. This GDL ensures that reactants effectively diffuse to the CL. In addition, the GDL is the electrical conductor that transports electrons to and from the GDL. Although the diffusion layer is an apparently slight component in a fuel cell, it has been shown that varying the composition of the diffusion layer can lead to substantial improvements in the performance of the cell (Deke et al., 2018). The improvements reported relating to the thickness and the porosity of the layer which functions as the electrical

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contact resistance and rejects liquid water from the membrane electrode assembly (MEA) (Sassin et al., 2016).

In H_2/O_2 (air) PEMFC, platinum has proven to be the best catalyst for both anodic and cathodic reactions. In order to lower the platinum loading and to increase further the electrode performance, it is necessary to prepare an electrode with high platinum utilization. The electrodes with the platinum layer at the front surface have been developed because the structure of the electrode determines the electrochemically active surface areas (EAS) in the fuel cell (Łukaszewski et al., 2016). The use of a solid polymer as an electrolyte causes the problem of non-active catalysts in the electrode. Therefore, the Nafion® solution is impregnated on the electrode surface to extend the catalytic reaction area by forming passages of ionic transfer (Jacobs et al., 2016).

In this work, GDLs were made of carbon paper or prepared by applying porous GDLs to each face of a carbon cloth support. The CL was prepared using a simple method that consists of mixing supported catalyst with Nafion® solution and water and spraying the ink so obtained onto the GDL. This method was not only simpler, safer and more economical, but also achieved better performance.

Performances of double layered cathodes were evaluated from the i-V characteristics of a single cell. The influence of platinum loading on the amount of electroactive catalyst area is studied using CV.

2. Experimental details
2.1. Reagents
Commercial electrocatalysts powders (E-TEK Johnson Matthey) consisting of 20 wt. % platinum nanoparticles supported by Vulcan XC-72 were chosen here because of their current use in PEMFC technology. They offer rather well-defined catalytic particle sizes (2.5-3 nm) and specific surface areas. The Nafion® solution is a 5 w/w 1100 EW solution from DuPont. Pure Vulcan XC-72 (Cabot), was used to prepare mixtures with E-TEK powders. High purity nitrogen gas and 99.999 % pure oxygen, pure hydrogen, and air gas were used.

2.2. Electrode preparation
The electrode was composed of a gas diffusion layer and a catalyst layer. The GDL was prepared on wet-proofed carbon cloth with PTFE. It is obtained by filing the carbon cloth with a mixture composed of carbon powder (Vulcan XC-72) and PTFE 30 wt. % and isopropyl alcohol (IPA). The viscous mixture was screen-printed on to the wet-proofed carbon cloth and then dried for 24 hours.

The mixture composing the CL (ink of Pt/C -20 wt. % Pt on Vulcan XC-72, IPA, PTFE 30 wt. % and 5 wt. % Nafion® solution was then sprayed on one side of the GDL. The spraying method allows easy control of the platinum ratio on the electrodes.

2.3. Electrode and membrane assembly
Nafion® 117 polymer electrolyte membrane was treated with boiling H_2O_2 and H_2SO4 to remove organic and metallic impurities for 1 h respectively and then washed in distilled water for 1 hour (Kaufman et al., 2002; Giorgi et al., 1998; Jordan et al., 2000). For the performance evaluation, an anode and a cathode are re-impregnated with electrolyte Nafion® solution in order to obtain loadings of approximately 0,5 mg/cm² and then hot-pressed on each side of the proton exchange membrane at 140 °C under 50 kg/cm² for 5 minutes.

2.4. Test cells and electrochemical instrumentation
The obtained EMAs were inserted in the fuel cell hardware consisting of two graphite blocks with parallel flow field channels for the reactants, two copper current collectors and an end plate assembly.

Two types of single cells test fixture (5 and 50 cm²) purchased from Globetech Inc. (USA) were used in this study. We note that on the 5 cm² cell test (Figure 1) anodic and cathodic potentials are separately determined thanks to an internal reference consisting of a platinum wire which relates to a piece of electrode stuck on the membrane at the anode side. The reference electrode is supplied with hydrogen gas by a derivation in the cell. This single cell is incorporated in a test station fabricated in our laboratory with all its peripheral components (temperature controller, humidification, flow meter, pressure regulator, etc...). During the performance evaluation the fuel cell is connected in series with power supplies for their operations under galvanostatic load and cell voltages, as well as half-cell potentials, were recorded versus current

densities. Measurements were made at 80 °C and under 3-atmosphere pressure of H_2 at the anode and 5-atmosphere pressure O_2 or air at the cathode. The humidification of the anode/cathode gas streams was realized by diverting the streams through heated water-filled bottles that were usually kept at 95 °C for H_2 and O_2 or air. We impose on the cell a current density of 200 mA/cm² during 20 hours. The i-V density characteristic curves were then plotted using a dc Electronic Load for every electrode model. Cyclic voltammetry (CV) was carried out with a Wenking potentiostat-galvanostat in order to determine the electrochemically-active surface area (ESA). For CV studies, nitrogen was passed through the 5 cm² test electrode and hydrogen was passed through the counter electrode chamber. The counter electrode was also used as the reference electrode because of the negligible overpotential for hydrogen oxidation and reduction on platinum. The potential was then scanned between 100 and 1400 mV versus the reversible hydrogen electrode (RHE) at a scanning rate of 50 mV/s. The ESA of the Pt catalyst was evaluated from the voltammogram by dividing the charge is expressed in units of microcoulomb that corresponded to the area under the hydrogen desorption region by 210 µC (Srinivasan et al., 1990; Ticianelli et al., 1988 and Giorgi et al., 1999).
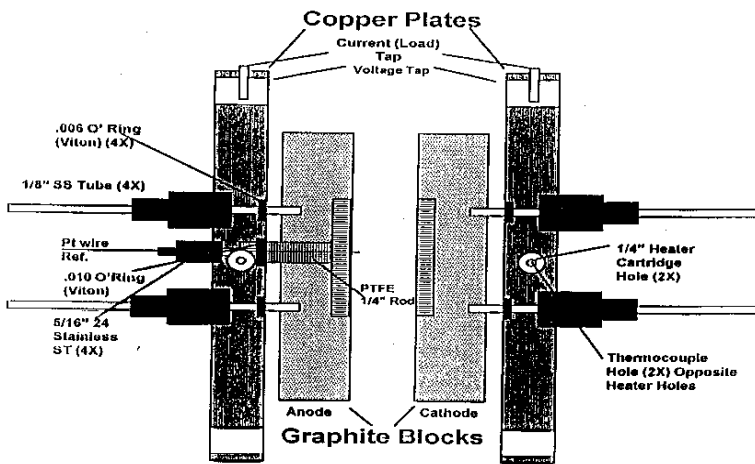

Fig. 1. Schematic diagram of the single cell test fixture (5 cm²) (Globtech Inc)

The experimental roughness factor (RF_{exp}) was calculated by dividing the ESA by the geometric area (5 cm²) of the electrode. Knowing that the surface determined by the adsorption of CO is 112 m² per gram of platinum (for Vulcan XC-72 - 20 wt.% in platinum) the theoretical roughness factors RF_{th} of an electrode according to its load in catalyst L_{Pt} are given by:

$$RF_{th} = 1120(cm^2/mg\ Pt) \times L_{Pt}(mg/cm^2)$$

Utilization of the Pt catalyst was evaluated by dividing the experimental roughness factor (RF_{ex}) of the electrode by the theoretical one (RF_{th}) (Watanabe et al., 1995). From both roughness factors, theoretical and experimental, it is possible to estimate the platinum utilization (η_{Pt}) by:

$$\eta_{Pt} = 100 \times \frac{RF_{ex}}{RF_{th}}$$

3. Results and discussion
3.1. Preliminary test

In order to qualify cell test under our experimental conditions, we studied the performances of cells exclusively made with commercial E-TEK electrodes. These electrodes containing Pt loading of 0,4 mg/cm² will be afterward chosen as "reference" for the present study. The polarization curves recorded with both 5 and 50 cm² cells are recorded in Figure 2. We note a good concordance of the results obtained with two types of a single cells test fixture.
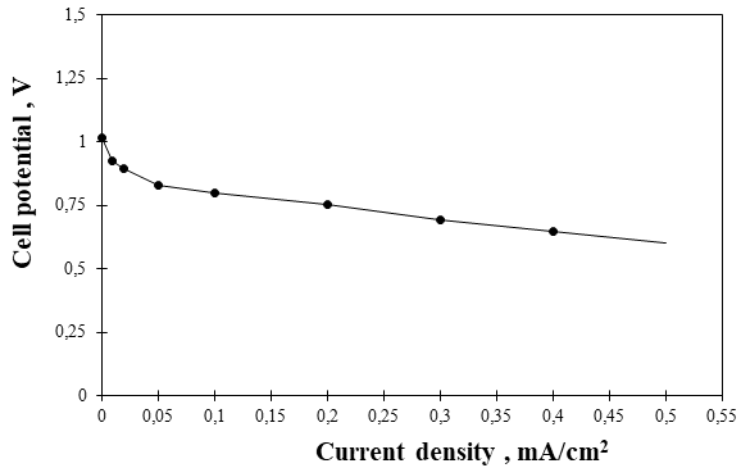
Fig. 2. Polarization curves of 5 cm² (-) and 50 cm² (•) O$_2$ E-TEK /Nafion® / H$_2$ E-TEK PEMFC$_s$

Figure 3 gives polarization curves of the same cells supplied with air. The influence of the partial pressure of oxygen is appreciably identical in both 5 and 50 cm² electrode surfaces.
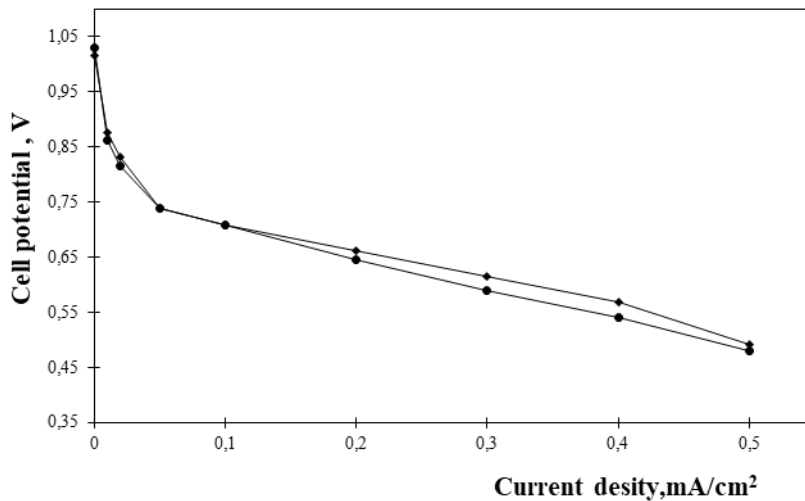

Fig. 3. Polarization curves of 5 cm² (♦) and 50 cm² (•) air E-TEK /Nafion® / H$_2$ E-TEK PEMFC$_s$

Figure 4 giving anodic and cathodic partial performances show that the biggest party of the cell polarization is due to cathode kinetics.
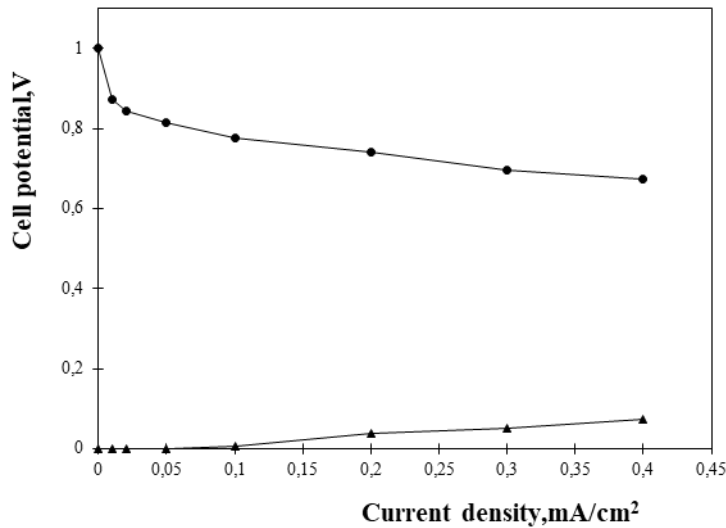
Fig. 4. 5 cm² O₂ E-TEK /Nafion® / H₂ E-TEK PEMFC performances.
(•) cathodic polarization curve; (▲) anodic polarization curve

3.2. Gas diffusion layer
3.2.1. Effect of substrate

The effect of the substrate on the PEMFC performance using PWB3 cloth and Toray paper is shown in Figure 5. As can be seen, in H₂/O₂ operation, the best cell performance was obtained with PWB3 cloth. The characteristics of the different backings differ with respect to the pore size and the grade of hydrophobicity reached by impregnating the backing with PTFE-suspension. Generally, a compromise between unhindered gas access (large, hydrophobic pores) and removal of product water (hydrophilic pores, problems of condensing or flooding the electrode) must be found. Large pores, on the one hand, provide a "free barrier" gas access. On the other hand, at the interface between the hydrophobic backing and the hydrophilic active layer the pores will probably resist the intrusion of water and a droplet will be formed. The larger the pore size, the greater is the expected size of the droplet and the reactant diffusion barrier, whereas in case of micropores only very small droplets are formed (Sasikumar et al., 2004) which can escape through the pores because of capillary forces. Dealing with the PTFE content one faces the same conflict between a highly hydrophobic layer, which is expected to provide unhindered gas access and the fact that water cannot be efficiently removed through the hydrophobic pores consequently flooding the active layer.
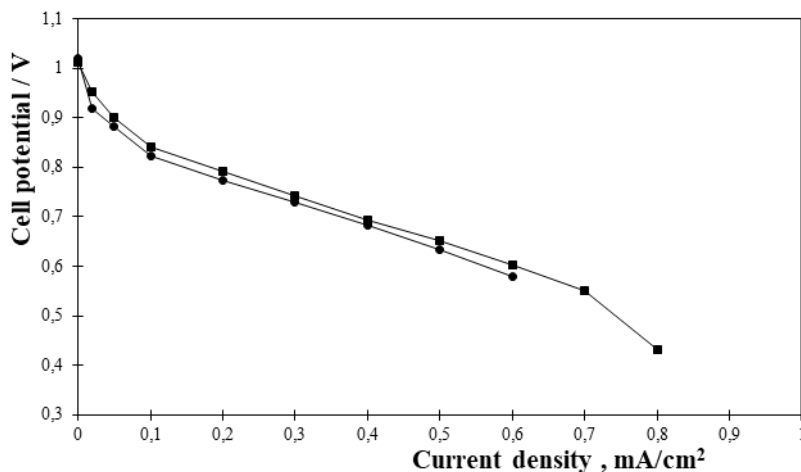

Fig. 5 Effect of the kind of substrate on the performance of O₂ /Nafion® / H₂ E-TEK PEMFC.
(■) PWB3 cloth; (•) Toray paper

3.2.2. Influence of carbon black

Using PWB3 as a substrate, we studied the influence of the powder placed in the GDL. The three carbon powder types investigated were Black Pearls 2000, Vulcan XC-72 (oil-furnace carbon black) and Shawinigan (acetylene-black) carbon powder (Bevers et al., 1996).

Black Pearls 2000 differs essentially from Vulcan XC-72 by its high specific conductivity and very high specific surface. Shawinigan Black also presents a very good specific electric conductivity and a structure getting closer very strongly to some graphite. Figure 6 shows cathode performances which GDL were prepared with these various products. We found that an electrode featuring Vulcan carbon powder performed substantially better than an electrode containing Shawinigan carbon powder and lower cell performances are obtained with acetylene black.
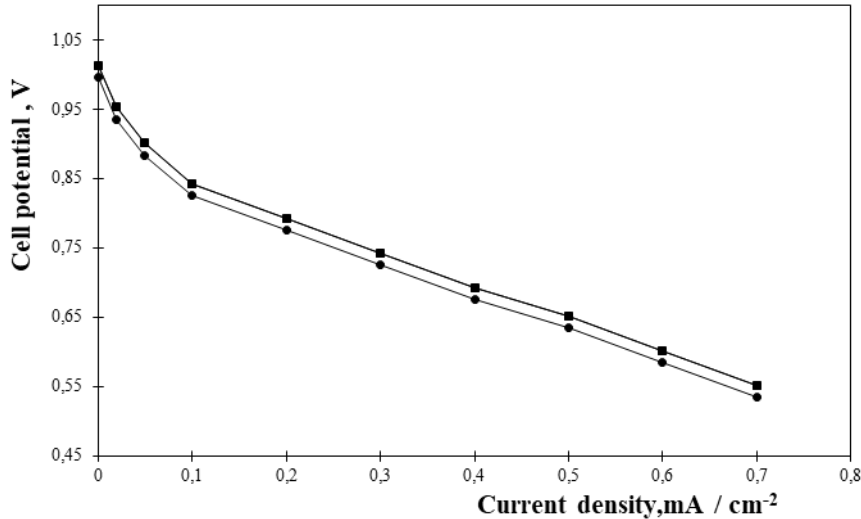

Fig. 6. O_2 /Nafion® / H_2 E-TEK PEMFCs PEMFC performances. GDLs were prepared with : (♦) Vulcan XC72 ; (■) Black pearles 2000 and (●) Shawinigan Black

3.2.3. Polytetrafluoroethylene (PTFE) content

Cell performances according to different PTFE loading in GDL of the cathode are given in Figure 7. The loading of the hydrophobic material in the GDL affects the mass transport properties of the electrode and thus the cell activity. We can note that at low current densities (lower than 0.25 A/cm²) higher cell voltages values are obtained with cell corresponding to 10 % wt. PTFE in the GDL. These best performances are attributed to a good hydration balance of the membrane obtained thanks to the retro diffusion of the water produced in the cathode. This one remains in great quantities, thanks to the partial hydrophobic character of this GDL. At high current densities, this tendency is inverted.

Figure 7 shows the effect of PTFE loading on the current density at 0.5 V. The maximum cell performance is obtained at about 30 % wt. PTFE. This behavior results from the effects of gas diffusion and ionic resistance.
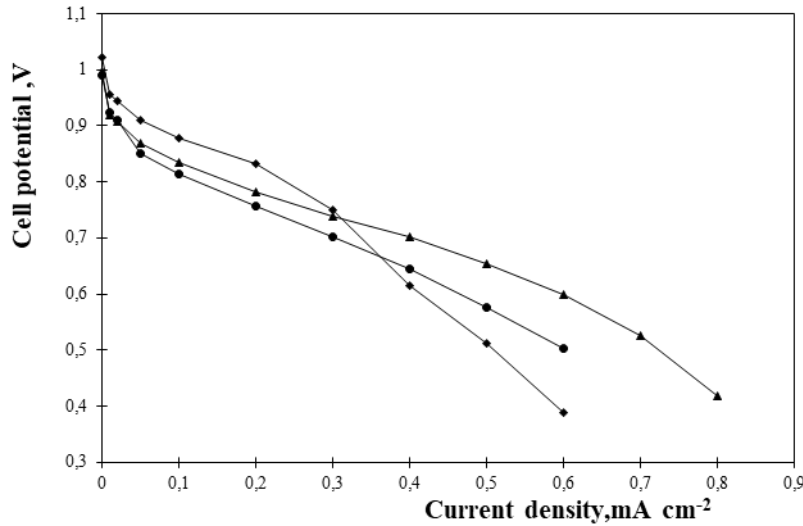
Fig. 7. O_2 /Nafion® / H_2 E-TEK PEMFC performances.
GDLs contain: (♦) 10 % wt. PTFE ; (▲) 30 % wt. PTFE ; (●) 50 % wt. PTFE

These two phenomena related to the transport of water depend greatly on the PTFE loading. Dependence of current density on polytetrafluoroethylene (PTFE) content of GDL given in Figure 8, shows that a maximum cell performance at 0.5 V is obtained at about 30 % wt. PTFE. It seems that the lower performance of cathodes containing 10 % and 50 % wt. PTFE is caused by its flooding and the increased ionic strength of the membrane and the electronic resistance of the electrode, respectively.The type of GDL material sample with 30 % corresponds certainly to a good specific electric conductivity and reinforced the hydrophobic character of the GDL (Passalacqua et al., 1998).
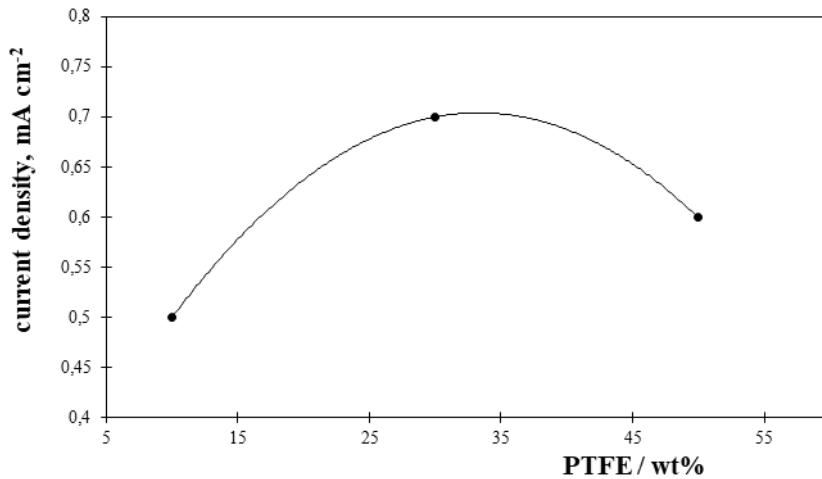

Fig. 8. Dependence of current density on polytetrafluoroethylene (PTFE) content of the GDL at cell voltage 0,5 V

3.3. Catalytic layer
Large area electrodes of about 500 cm² were prepared according to the manufacturing method described above, then samples of 5 cm² and 50 cm² were cut and tested. Figure 9 giving polarization curves of a 50 cm² and à 5 cm² single H_2/O_2 cell shows a very good reproducibility of the performances.

The thickness of the CL should be proportional to the quantity of catalyst as far as the structure does not change. The variation of this thickness is realized by the pulverizing of various quantities of a mixture (ink of Pt/C, IPA PTFE, and Nafion®) (Antonili et al., 2002).

Using a 5 cm² H₂/O₂ single PEMFCs were tested and polarization curves are plotted in Figure 9 for various platinum loading. The utilization of Pt catalyst can be provided by variation of current density at 0,65 V according to platinum loading.
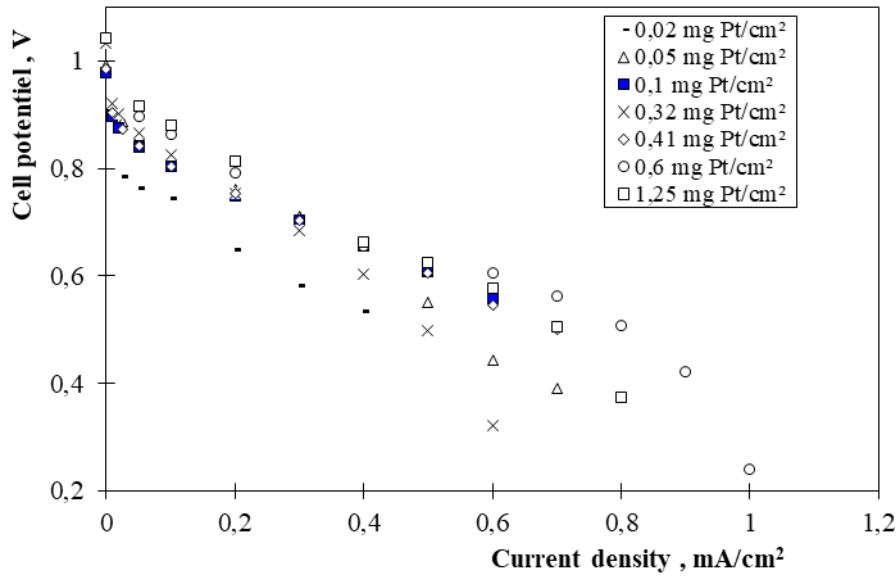

Fig. 9. (O₂ electrode/Nafion/H₂ E-TEK) cell performances for cathodic CL prepared using various Pt caralyst loading

The curve plotted in Figures 10a, 10b shows that it is possible to reduce catalyst loading close to 0.2 mg/cm² without changing significantly cell performances.
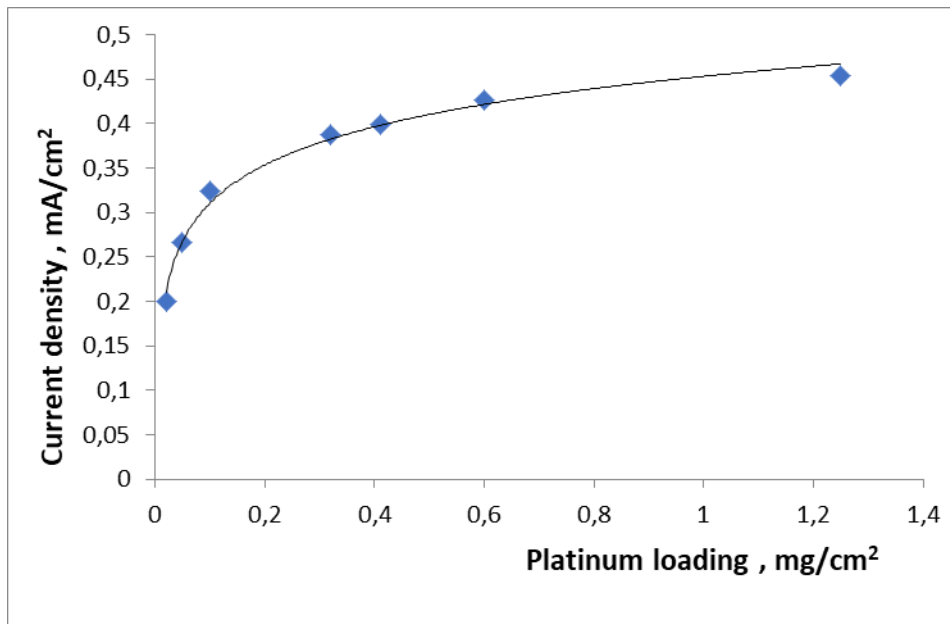

Fig. 10a. Dependence of current density on Pt catalyst loading of the cathodic CL at 0,75 V.

The electrochemically active surface area in CL has been evaluated by cyclic voltammogram studies and typical cyclic voltammogram with a scan rate of 50 mV/s of a cathode with 0,54 mg/cm² loading is given in Figure 10b.
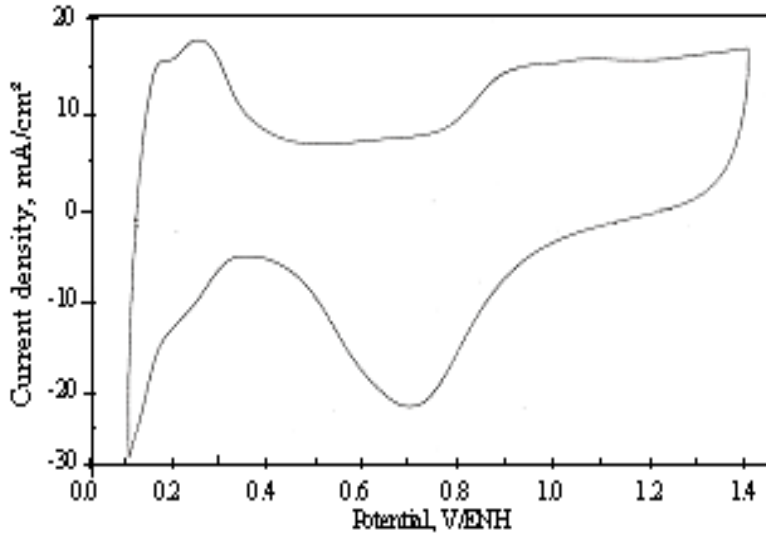
Fig. 10b. Typical cyclic voltammogram at a scan rate of 50 mV/s

The really active surface so determined is that of all the particles in ionic and electronics contact with the membrane and the support.

Figure 11 shows that the variation of RF_{th} according to L_{Pt} is a right-hand side passing by the origin and of equal hillside in 1120 cm² of platinum per mg of catalyst. On the same figure, this right-hand side is compared with that of the experimental roughness factor RF_{ex} obtained by CV. At lower platinum loads than 0,1 mg/cm² the experimental points are closer to the theoretical right-hand side. Beyond a Pt loading of 0,4 mg/cm² the experimental roughness factors go away from the theoretical right-hand side. The difference between both curves is evaluated the Pt utilization.
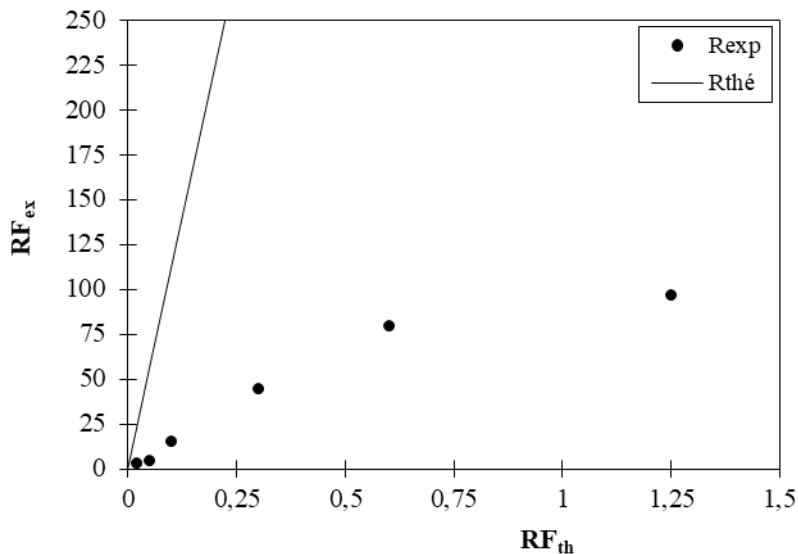

Fig. 11. Dependence of theoretical and experimental roughness factor on platinum loading in the active layer of the oxygen electrode

The dependence of the Pt utilizationon its loading plotted in Figure 12 shows that $_{Pt}$ passes from a constant value of 14 % for L_{Pt} < 0,4 mg/cm² to 8% for L_{Pt}> 1,25 mg/cm². For platinum loadings higher than 0,4 mg.cm⁻², the catalyst particles are not completely accessible to the protons transported through the electrolyte incorporated in the catalytic layer. It is thus not interesting to manufacture electrodes containing Ptloadings higher than 0,45 mg.cm⁻².
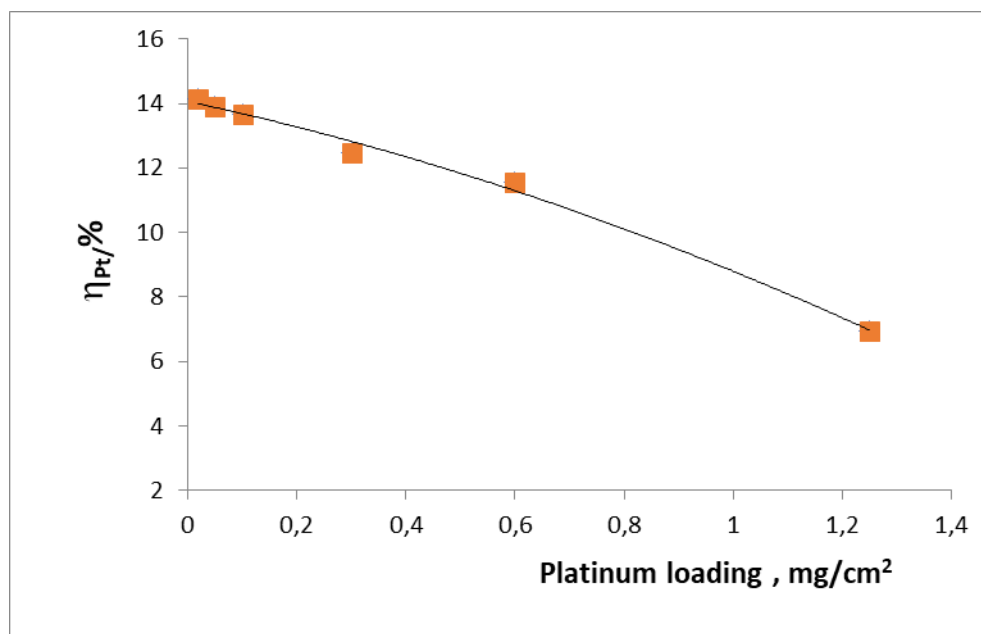
Fig. 12. Dependence of platinum utilization on its loading in the active layer of the oxygen electrode

4. Conclusion
The influence of substrate nature, carbon black, PTFE content in gas diffusion layer and catalyst layer platinum loading on the performance of PEMFC was investigated. The results presented show that:

1. The best cell performance was obtained using PWB3 cloth.
2. Using PWB3 as substrate electrode featuring Vulcan carbon powder performed substantially better than an electrode containing Shawinigan carbon powder and lower cell performances are obtained with acetylene black.
3. It is possible to reduce catalyst loading close to 0.2 mg/cm² without changing significantly cell performances. We note that for platinum loadings higher than 0.4 mg/cm², the catalyst particles are not completely accessible to the protons transported through the electrolyte incorporated in the catalytic layer.

5. Conflict of Interest
The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere.

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