Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 102–103 (2005) 50–57

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Electrocatalytic performances of nanostructured platinum–carbon materials

M. Gangeri [a,c,*], G. Centi [a,c], A. La Malfa [a,c], S. Perathoner [a,c,**],
R. Vieira [b,c], C. Pham-Huu [b,c], M.J. Ledoux [b,c]

[a] Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, University of Messina, Salita Sperone 31, 98166 Messina, Italy
[b] Universite Louis Pasteur Strasbourg, Strasbourg, France
[c] ELCASS, European Laboratory for Surface Science and Catalysis, Salita Sperone 31, 98166 Messina, Italy

Abstract

The performances of platinum supported on carbon nanofibers (Pt/CNFs) and Pt nanoclusters on carbon Cloth (Pt_{nano}/CC) as alternative electrodes for PEM fuel cells are compared with those of a commercial Pt-carbon black on carbon Cloth electrode in a 1 cm^2 fuel cell working at room temperature. Carbon nanofibers were grown by chemical vapour deposition on two different types of microshaped carbon supports (Felt and Cloth) and then Pt was deposited on these nano/micro composite carbon supports. The analysis of the results and in particular of the polarization curves indicate that (i) both Pt_{nano}/CC and Pt/CNFs materials are better electrocatalysts than commercial one and (ii) Pt_{nano}/CC gives the lowest ohmic losses while Pt/CNFs materials give the lowest mass transfer losses. Further studies and a better membrane and electrodes assembly (MEA) engineering are necessary to further validate the results, but these preliminary analysis pointed out that new electrode materials based both on Pt nanoclusters and carbon nanostructures (nanofibers/nanotubes) could be very interesting for fuel cells applications.

Keywords: Electrocatalysis; Carbon Cloth; Nanofiber; Fuel cell; PEM

1. Introduction

Recently, the study of nanostructured catalysts has become one of the most active areas in the field of advanced materials, due to their exceptional properties that make them suitable for many potential applications in sustainable technologies, for example, for the gas phase photo-electrocatalytic reduction of carbon dioxide backs to fuels, that can be implemented in a photo-electrocatalytic reactor (PEC) [1–4]. Moreover, in particular, they could replace the conventional electrocatalysts used for fuel cells.

Fuel cells have received increasing attention recently because they are able to convert chemical energy directly into electricity in an efficient way without environmental pollution. Among them polymer electrolyte membrane (PEM) fuel cells are the most promising in particular for mobile applications. The heart of a PEM fuel cell is the membrane and electrodes assembly (MEA): the membrane used as electrolyte, usually hydrated poly-perfluorosulphonic acid polymer such as Nafion®, is placed between two porous electrodes containing the electrocatalyst.

Recently, electrode structure in PEM fuel cells has been improved from a two layers to a three layers system [5] constituted by a conductive porous support, a diffusion layer and the catalyst itself. The performances of the electrodes depend on many parameters [6,7]: (1) type of macroscopic carbon support (carbon paper, carbon Cloth, etc.) and its characteristics (porosity and thickness); (2) type of catalyst (metal, metal amount, metal particles size, type of catalyst support); (3) thermal treatment; (4) thickness of diffusion and catalytic layers; (5) fabrication process (screen-printing, rolling, brushing, filtering or spraying).

Electrocatalysts for PEM fuel cells have to fulfill various requirements: primarly, a high specific activity is necessary for the electrochemical oxidation of hydrogen at the anode as well as for oxygen reduction at the cathode.

---

[*] Corresponding author.
E-mail address: mgangeri@ingegneria.unime.it (M. Gangeri).
[**] Co-corresponding author.

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2005.02.035

High performance cathode electrocatalysts must improve the slow oxygen reduction kinetics by reducing the high overpotential of this four-electron-reaction. Anode electrocatalysts, which catalyse the hydrogen oxidation process, should be resistant to poisoning caused by CO, CO_2 and other contaminants in the feed.

At present, platinum or platinum alloys are the catalysts of choice for PEM fuel cells due to their high catalytic activity [8] and their stability in the fuel cell environment; these electrocatalysts are expensive and thus, there is a need to minimize the catalyst loading and maximize the catalyst utilization, without sacrificing catalytic activity. As the catalytic reduction of oxygen and the catalytic oxidation of hydrogen are surface processes, a way to maximize catalyst utilization is to maximize the specific surface area of platinum. The most efficient way to achieve this is to reduce the size of the platinum particles.

Metal nanoclusters, near monodispersed particles that are generally less than 10 nm in diameter, have generated intense interest over the past decade [9]. Metal nanoclusters have a significant potential as new type of higher activity and selectivity catalysts than those of today because a large percentage of metal atoms lies on the surface; furthermore, the electrons are confined to spaces that can be as small as a few atom-widths across, therefore they have high surface electron density. Electrocatalytic oxidation of hydrogen and reduction of oxygen are multi-electron transfer reactions, in fact they needs four electrons, therefore, they are favoured by catalysts with high electron density.

Besides, the nature of the conductive carbon support and a high surface area are fundamental and conductivity is essential for good electrocatalytic performances [10]. Nanostructured carbon materials have stimulated an intense research interest in the scientific community. Since the discovery of carbon nanotubes (CNTs) in 1991, they have been the object of numerous theoretical and experimental studies in order to determine their physical and chemical properties [11]. The peculiar electronic, adsorption, mechanical and thermal properties suggest that CNTs are suitable materials for electrodes and catalysts supports in PEM fuel cells [12]. It should be also noted that the good and reversible hydrogen storage capacity of CNTs makes such materials very interesting for application in the PEM fuel cells.

In conclusion, there are several parameters influencing the performances of the anode electrocatalyst and in turns the PEM fuel cell behavior. While the largest part of these studies have been focalized on the engineering of the PEM fuel cell and the preparation methodology of the electrodes (including aspects such as the effect of Pt particles size), few attention has been devoted to the understanding of the role of carbon support and of the Pt particles/carbon interface. The aim of the work presented here was to analyze these aspects. In this first study, the electrocatalytic performances of electrodes based on (i) platinum supported on carbon nanofibers (Pt/CNFs) and (ii) platinum nanoclusters deposited on carbon Cloth (Pt_{nano}/CC) are compared with those of a reference commercial Pt electrode from E-TEK, in order to derive indications on the role of the carbon and of the Pt particles/carbon interface which can be used to prepare new types of improved electrodes for PEM fuel cells. The electrodes based on platinum supported on carbon nanofibers (Pt/CNFs) used in this work are effectively nano/micro composites, because the carbon nanofibers were grown by chemical vapour deposition on two different types of micro-shaped carbon fibers supports (Felt and Cloth) and then Pt was deposited by incipient wetness impregnation on these nano/micro carbon fibers supports.

2. Experimental

2.1. Preparation of the electrocatalysts

2.1.1. Platinun over nano/micro carbon fibers composites (Pt/CNFs)

Different electrocatalysts based on platinum supported on carbon nanofibers were prepared (Table 1). They differ on the metal loading and type of micro-shaped carbon support. CNFs were prepared starting from two different types of micro-shaped carbon supports (in the form of Felt and Cloth of carbon microfibers) supplied from Carbone Lorraine Co. Carbon nanofibers were then grown on these carbon supports by chemical vapour deposition method, obtaining finally a nano/micro carbon fibers composite support, briefly indicated here and after as F-CNFs when derived from Felt-type carbon microfibers and C-CNFs when derived from Cloth-type carbon microfibers.

The growing of the nanofibers by chemical vapour deposition method is realized as follows. A mixture of ethylene and hydrogen (1:5, v/v ratio) was passed for 2 h over these supports (on which 1 wt% nickel was previously deposited by incipient wetness impregnation) and then heated at 973 K [13]. CNFs composites (see later) are obtained. Platinum (5, 20, 40 wt%) was then deposited on these CNFs composites (F-CNFs and C-CNFs) by incipient wetness impregnation using H_2PtCl_6 as metal precursor.

Table 1
List of the electrodes based on platinum supported on carbon nanofibers (Pt/CNFs) used in the PEM fuel cell

Electrode code	Type of micro-shaped carbon support[a]	Platinum loading (wt%)
F5	Felt	5
F20	Felt	20
F40	Felt	40
C5	Cloth	5
C20	Cloth	20

[a] On which carbon nanofibers were then grown by chemical vapour deposition.

2.1.2. Platinun nanoparticles over carbon Cloth (Pt_{nano}/CC)

Four shell type Pt nanoclusters were prepared by a metal salt reduction method and stabilized against aggregation into larger particles by steric stabilization using bathophenantroline sulfonic acid that surrounds the metal center providing a steric barrier which prevents close contact of the metal particle centers. An ethanol solution of H_2PtCl_6 and bathophenantroline sulfonic acid in a molar ratio of 7:1 was stirred under H_2 until gas absorption ceased (5 h). The brown–black reaction solution was then exposed to an oxygen atmosphere to oxidize the free surface atoms. The resulting black solid was separated using a laboratory centrifuge, washed several times with ethanol and after removal of the solvent under vacuum, the Pt nanoclusters were stored under nitrogen.

For the final preparation of the electrocatalyst, pieces of E-TEK ELAT carbon Cloth (gas diffusion membrane—GDM, e.g. a carbon Cloth on which teflon was deposited on one side) were coated with a Nafion® SE-5112 suspension of the noble metal nanoclusters and cured at 180 °C. The final amount of Pt electrocatalyst was 20 wt% in order to permit comparison with commercial 20% Pt (0.4 mg/cm^2) on GDM electrodes from E-TEK.

2.2. Nafion membrane pretreatment and preparation of membrane and electrodes assembly (MEA)

Different MEAs were prepared for electrochemical measurements using different electrodes for the anode and always the same electrode for the cathode. The different electrodes used as anode were Pt/F-CNFs (5, 20, 40 wt%), Pt/C-CNFs (5, 20 wt%) and Pt_{nano}/CC. The cathode was a commercial gas diffusion electrode (E-TEK Inc.) consisting of carbon Cloth “A” with a thickness of 350 μm, wet-proofed with a layer of carbon/teflon and on one side of it a catalyst layer of Pt/carbon black (0.4–0.6 mg/cm^2, 20 wt%) was deposited. The platinum particles size is about 2 nm and specific metal surface area is 128 m^2/g.

Before being used in manufacturing MEAs, the polymer electrolyte membrane, Nafion® 112 (Du Pont Chemical), was cleaned by immersing in 3% H_2O_2 for 1 h at 80 °C to remove organic impurities and then in 0.5 M H_2SO_4 for 1 h at 80 °C; the H_2SO_4 was removed by repeated washing in boiling distilled water.

The assembly of the electrodes and the membrane was hot pressed between two metallic plates, heated at 100 °C, with a pressure of 20 kg/cm^2; at this pressure the temperature was raised to 130 °C and the assembly maintained in these conditions for 90 s.

2.3. Electrochemical measurements

The MEAs obtained had a geometric area of 1 cm^2 and were tested in a fuel cell working at room temperature and atmospheric pressure. Hydrogen and oxygen were passed through humidifiers to wet the gases, in order to maintain the high ionic conductivity of the Nafion membrane, and fed at the anode and at the cathode at a flow rate of 9 ml min^{-1} and 50 ml min^{-1}, respectively. Characteristic polarization curves V (cell potential) versus I (current density) were recorded connecting the two electrodes electrochemical cell to a potentiostat/galvanostat (AMEL 2049) where the anode represented both reference electrode and counter electrode and the cathode acted as the working electrode. The electrochemical measurements were carried out in galvanostatic way, setting negative polarity of the working electrode respect to the reference one and taking the cell potential by varying the electric load.

2.4. Characterization methods

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were made using a JEOL JMS 840 and a TOPCON EM-002B UHR or CM12 Philips microscopes, respectively. BET surface area of the macroscopic carbon supports, before and after the synthesis of CNFs, was measured by a COULTER SA 3100 instrument.

X-ray diffraction (XRD) analysis were carried out using an ItalStructures APD 2000 diffractometer and Cu Kα radiation. Diffraction peaks of crystalline phase were compared with those of standard compounds reported in the JCPDS Data File.

3. Results and discussion

3.1. Characterization of the electrocatalysts

Scanning electron microscopy images of the Felt (Fig. 1a) show that the base carbon micro fibers (microfibers of the Felt used as the support on which then the carbon nanofibers – CNFs – have been successively grown by chemical vapour deposition method) after the synthesis of CNFs were fully covered with a thick network of carbon nanofibers forming a layer of 3 μm around each one of the carbon microfibers, increasing their diameter of about 20% (Fig. 1b).

BET surface area of the Felt increased from 1–2 to 80 m^2/g, due to the large external (geometrical) surface area of the CNFs; no significant change was observed after the metal charge. The structure of CNFs was studied by transmission electron microscopy and some images are reported in Fig. 2. Low magnification image confirmed the lack of an hollow cavity in some parts and evidenced that no residual metallic particles, coming from the CNFs production process, could be observed because they were encapsulated by the carbon; whereas in the high magnification TEM image, it was evident that carbon nanofibers were herringbone (CNF-H), that means graphene layers are stacked obliquely (75°) with respect to the growth axis and regularly spaced by a distance of about 0.34 nm. Moreover,

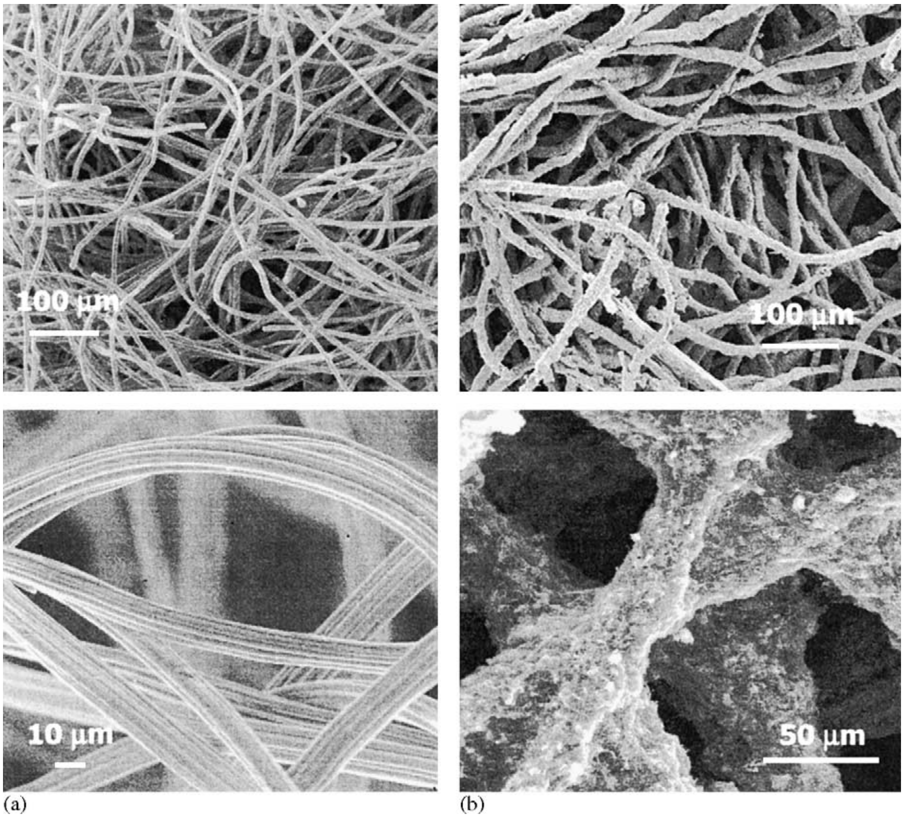


Fig. 1. SEM images of the microshaped carbon support, Felt-type (a) before and (b) after the synthesis of carbon nanofibers (CNFs).

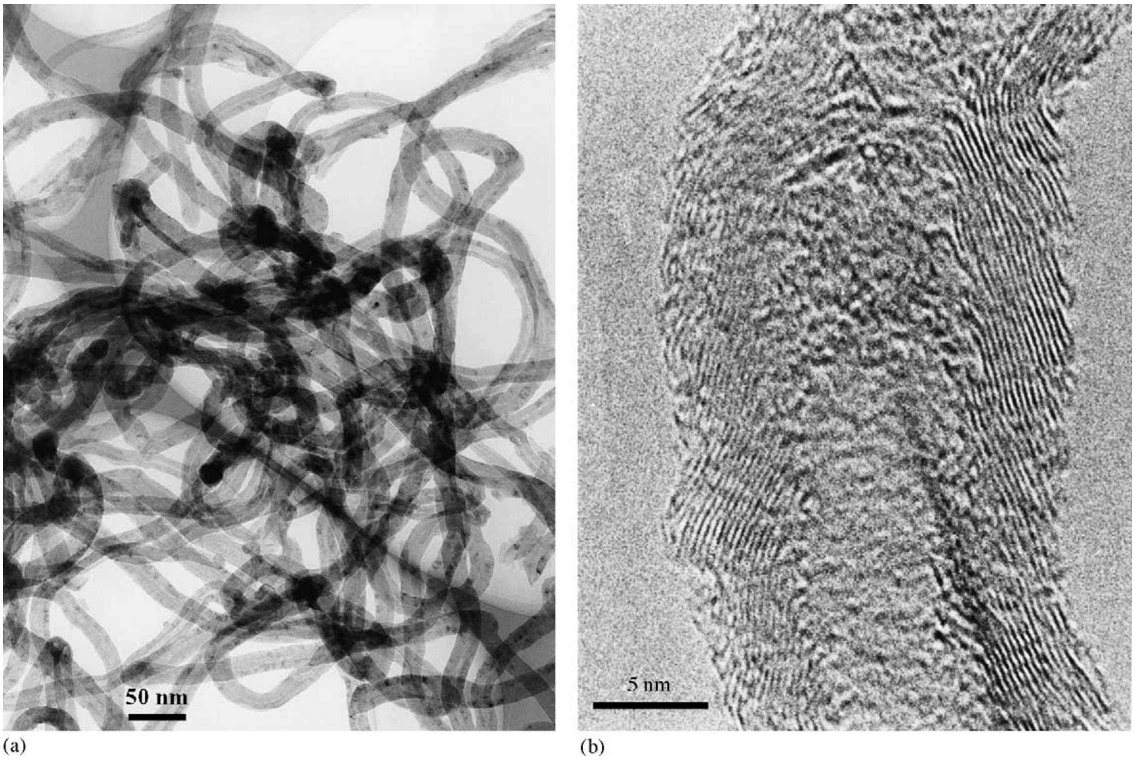


Fig. 2. TEM images of CNFs at low and high magnification.

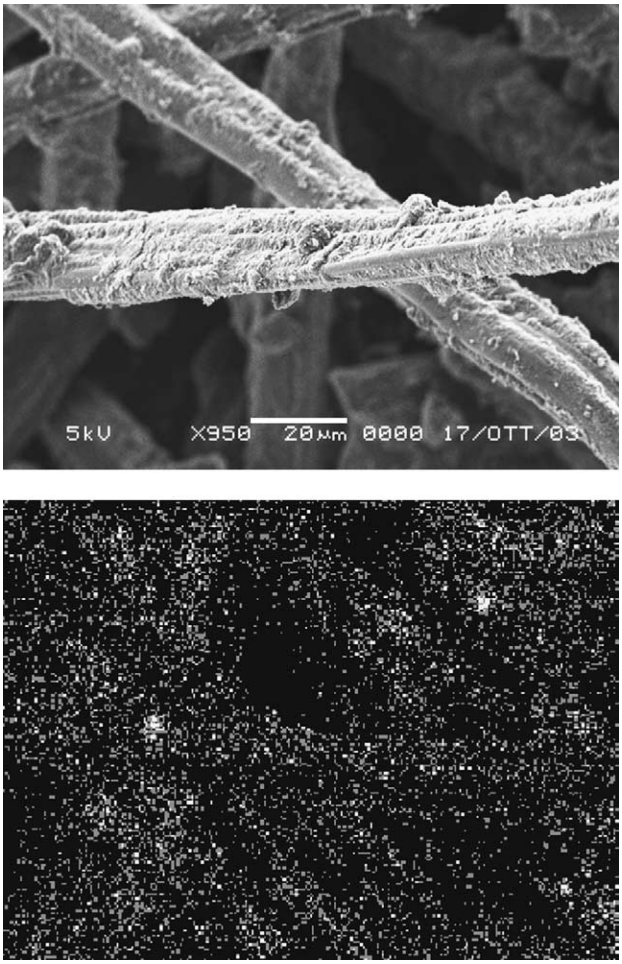


Fig. 3. SEM image of Pt/Felt-CNFs (20 wt%) electrocatalyst (top) and platinum distribution on carbon nanofibers (bottom).

Pt particles size for all samples reported in Table 1, determined by TEM analysis, was about 10 nm.

EDX compositional analysis of Pt/F-CNFs (20 wt%) electrode confirmed the presence of Pt without any trace of Ni, used as catalyst for the growth of CNFs, and the map of Pt dispersion shows that noble metal particles were very homogeneously distributed on CNFs composite (Fig. 3).

Pt nanoclusters based electrocatalysts were characterized using X-ray diffraction and TEM analysis. Fig. 4a reports the XRD patterns of Pt nanoclusters and reflections correspond to metallic Pt. The broadening of platinum $d_{1\,1\,1}$ reflection indicates a mean diameter of the metal particles of about 2 nm. TEM investigations are displayed in Fig. 4b where good spherical shaped particles are evident with a narrow distribution in the range 1–5 nm centered at 2 nm, which was in good agreement with XRD results.

3.2. *Electrocatalytic performances of Pt/F-CNF, Pt/C-CNF and Pt_{nano}/CC based MEAs*

Fig. 5a and b show the dependence of the cell potential versus current density (typical polarization curve, *I–V* curve) measured for the PEM fuel cell. Increasing current density there is a decrease of cell potential as usually observed in PEM fuel cells. Generally speaking, less pronounced is this decrease, better are the fuel cell performances, because higher is the maximum power densities of the cell.

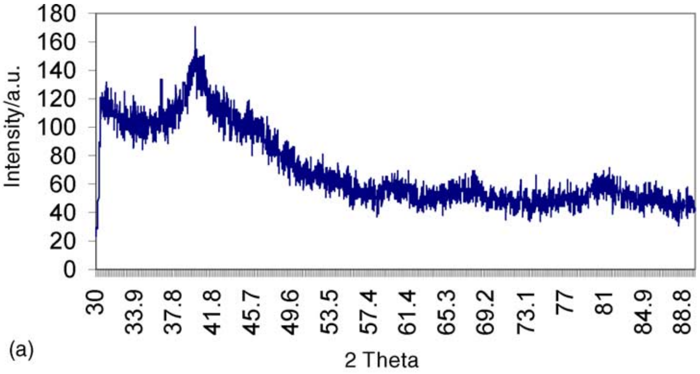
Among MEAs with Pt/F-CNFs as anode (Fig. 5a), electrocatalytic performance was the highest with 20 wt% platinum loading (F20). At a 0.325 V of cell potential, the current densities of the samples (F5, F20 and F40) with increasing Pt content (5, 20, 40 wt%) are 16, 60 and 32 mA/cm^2, respectively. The corresponding maximum power densities of 5.41, 19.50 and 10.53 mW/cm^2 could be calculated. This clearly evidences that there is a maximum in the cell performances for an intermediate Pt loading on these Pt/F-CNFs electrodes.

On the contrary, the electrocatalytic performances of Pt/C-CNFs based MEAs (e.g. derived from Cloth-type microfibers instead of Felt-type microfibers as those in Fig. 5a) decrease when the Pt loading increases from 5 to 20 wt%—C5 and C20 (Fig. 5b). The cell performance was 80 mA/cm^2 and 22.72 mW/cm^2 at 0.284 V with 5 wt% Pt loading deposited on C-CNFs electrode used as anode. At higher potential 0.423 V with a Pt loading of 20 wt% on C-CNFs, the current density was 10 mA/cm^2 and the power density was 4.23 mW/cm^2.

Potential versus current density curve for MEA prepared using commercial gas diffusion electrode (E-TEK Inc.) having 20% wt Pt loading (0.4–0.6 mg/cm^2) for both anode and cathode is reported in Fig. 6a. It may be noted a relatively fast initial decay of the cell potential increasing the current density, but above a current density of about 10 mA/cm^2 a significant reduction in the slope is observed, differently from what observed in Pt/CNFs based MEAs (Fig. 5).

The commercial MEA of E-TEK (Fig. 6a) is based on Pt deposited on graphitic carbon black, which was then deposited on the carbon Cloth gas diffusion membrane (GDM). The same carbon cloth GDM of E-TEK was used to analyze the performances of Pt nanoclusters, which were deposited directly on the carbon Cloth GDM instead of the preliminary deposition on the carbon black in the commercial method (see Section 2). The performances of this electrode (Pt_{nano}/CC based MEA) are reported in Fig. 6b. It should be mentioned that the Pt density (about 0.4 mg/cm^2) is the same in the two electrodes reported in Fig. 6a (commercial) and b (Pt_{nano}/CC based MEA).

Pt_{nano}/CC based MEA shows significantly better electrocatalytic performance with respect to the commercial sample. The current density was 160 mA/cm^2 at 0.365 V and at the same potential the power density was 58.40 mW/cm^2. With respect to the commercial sample, it may be noted that the change of the slope of the cell potential versus current density curves occurs nearly at the same current density value (about 10 mA/cm^2), but the loss of cell potential is about 50% for the commercial sample, while only about 10–15% for the Pt_{nano}/CC based MEA.



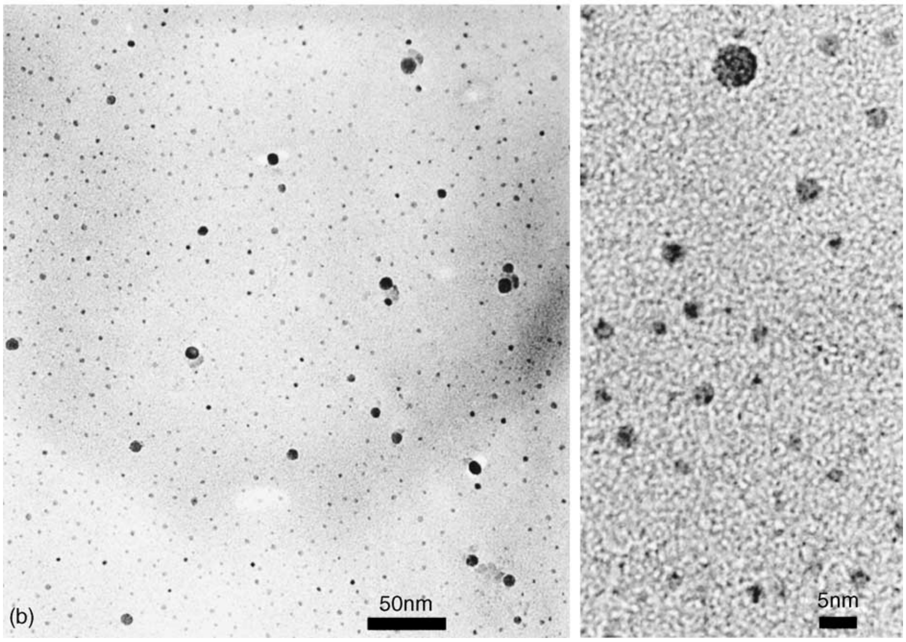


Fig. 4. XRD pattern (a) and TEM image (b) of the Pt nanoclusters.

It should be noted that all the polarization curves obtained in this study were comparable each other, being obtained under strict comparable reaction conditions. However, in comparing these results with literature data, attention should be given to the conditions of temperature and pressure in which the electrocatalytic tests were carried out and to the geometry of the fuel cell used for the electrochemical measurements, because these factors significantly influence the shape of the *I–V* curves. Fig. 7 summarizes the *I–V* curves obtained for the different classes of materials which represent the anode of the MEA (Pt_{nano}/CC, $Pt_{5\ wt\%}$/C-CNFs, $Pt_{20\ wt\%}$/F-CNFs and $Pt_{20\ wt\%}$ commercial/E-TEK GDM).

The reversible potential of the electrochemical reactions in a fuel cell is 1.23 V at standard conditions, but the actual voltage of an operational fuel cell is lower than this value due to irreversible losses. These losses are due to three types of polarization effects: activation, ohmic and concentration polarizations. It should be noted that the highest open circuit voltage (OCV) is about 0.9 V using Pt_{nano}/CC as the anode, while about 0.8 V with all the other materials. The sharp voltage drop of the first region (from about 0 to 10 mA/cm^2) is related to the activation energy barriers of the electrochemical reactions. Activation losses are sharper for the commercial sample than the others, meaning that activation energy of hydrogen oxidation is lower for $Pt_{5\ wt\%}$/C-CNFs (C5), $Pt_{20\ wt\%}$/F-CNFs (F20) and even more for Pt_{nano}/CC. Although further studies are necessary to better clarify this aspect, it is reasonable to consider that the Pt/carbon interface is the dominant factor determining this effect. In Pt nanoclusters, the contact interface is maximized and therefore the voltage drop is minimized. On the other hand, the carbon characteristics should influence this interface contact, in terms of both electrical contact and stabilization of different Pt crystal shapes and dimensions. This explains the different performances of the nano/micro carbon fibers composites derived from Felt and Cloth and the different effect of Pt loading on these two classes of materials. A characterization study is in progress in order to better understand these aspects.

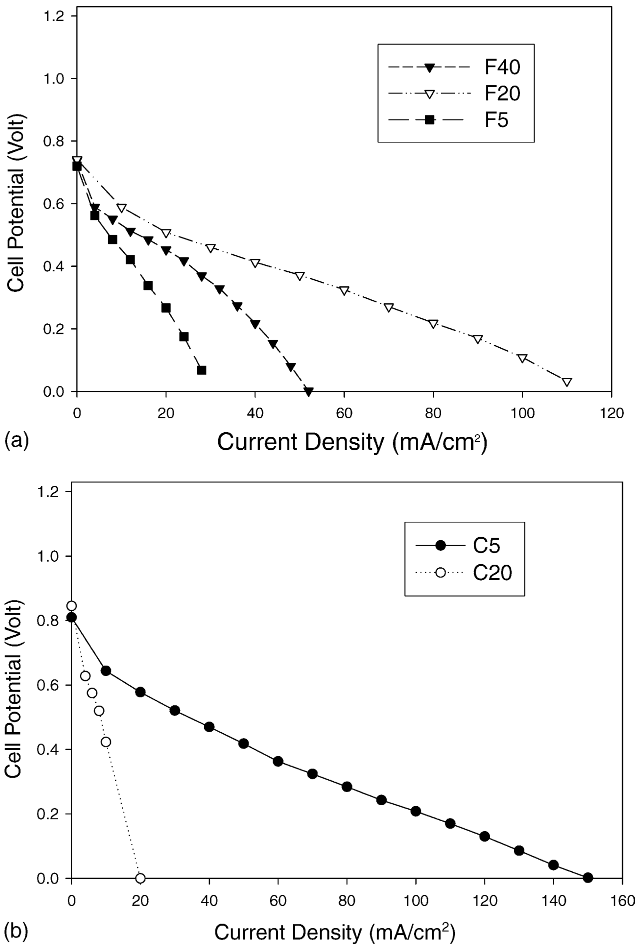


Fig. 5. Polarization curves for the different electrodes with different platinum loadings (a) Pt/Felt-CNFs and (b) Pt/Cloth-CNFs.

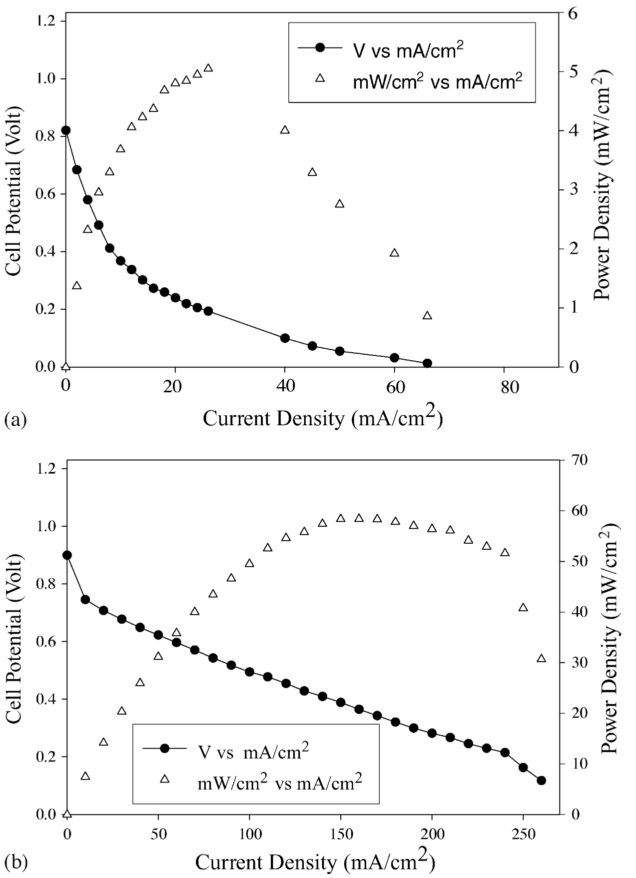


Fig. 6. Dependence of cell voltage and power density on current density for the different MEAs composed of (a) commercial E-TEK electrode (Pt 20%, w/w) on both side and (b) Pt nanoclusters (20%, w/w) based electrode at the anode.

The gradual drop in voltage of the second region (above 10 mA/cm^2 and up to a value which depends from sample to sample, about 240 mA/cm^2 for Pt nanoclusters and about 100 mA/cm^2 for F20 sample, e.g., when a further change in the *I–V* curve slope is detected) is related to ohmic resistance of cell components such as the electric and contact resistances of electrodes, membrane and current collecting components. Ohmic losses are the lowest with Pt$_{nano}$/CC due to the high Pt dispersion, as confirmed by TEM analysis. Moreover, Pt nanoclusters favour electron transfer from catalytic sites to the conductive carbon electrode possibly due to their high surface electron density. However, also the contact between the various components are important factors and therefore unique conclusions cannot be derived. It may be noted, however, that repeating the preparation of the electrodes, analogous results were obtained. Tests with larger electrodes surfaces are in progress, because cell geometry can be also an important factor to optimize the performances of the cell in this region.

Finally, the sharp voltage drop of the third region (above the threshold in current density indicated above) is associated with mass transport resistance of proton through the membrane, and of the gas phase, through the porous structure of the electrodes. The lowest mass transport losses were observed for MEAs constituted from CNFs composites possibly in relation with the high absorption capacity of hydrogen on carbon nanofibers.

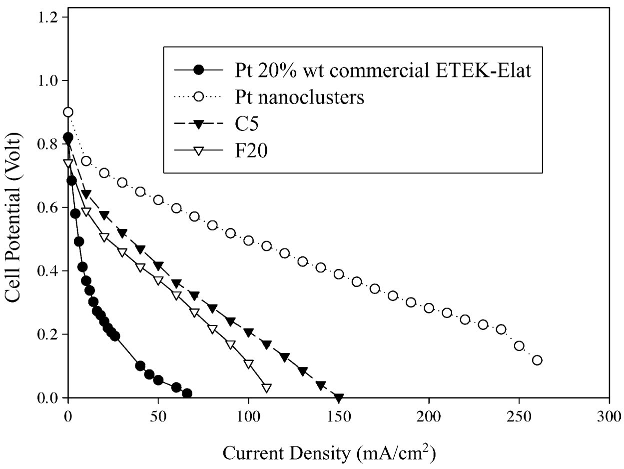


Fig. 7. Summary of the *I–V* curves for the different classes of electrodes.

4. Conclusions

The aim of the work reported here was to evaluate the electrocatalytic performance of new nanostructured platinum–carbon materials. The experimental data indicate that (i) nanostructured Pt–C materials are better electrocatalysts than commercial ones in a 1 cm^2 fuel cell operating at room temperature and (ii) Pt nanoclusters give the lowest ohmic losses while Pt/CNFs materials give the lowest mass transfer losses. Although MEA engineering needs to be improved leading possibly to further increases in the performances, present data pointed out that new materials based both on Pt nanoclusters and carbon nanostructures (nano/micro carbon fibers composites) could be very interesting for fuel cells applications. Data also indicate that the Pt/carbon interface (depending on the nature of Pt particles and the effect of carbon support on their stabilization), electron transport properties and mass transport resistance are the dominant factors determining cell performances (cell potential versus current density curves). The use of new nano/micro structured carbon supports together with the use of Pt nanoclusters are a relevant opportunity to improve all these factors.

References

[1] M.M. Hallman, M. Steinberg, Greenhouse Gas CO_2 Mitigation, CRC Press, Boca Raton, FL, USA, 1999.

[2] S. Ichikawa, R. Doi, Catal. Today 27 (1996) 271.

[3] T. Salama, R. Ohnishi, T. Shido, M. Ichikawa, J. Catal. 162 (1996) 169.

[4] G. Centi, S. Perathoner, Z.S. Rak, Science and Technology in Catalysis 2002, Studies in Surface Sciences and Catalysis, vol. 145, Kodansha Ltd./Elsevier Science, Tokyo/Amsterdam, 2003, p. 283.

[5] Proceedings at 1996 Fuel Cell Seminar, Orlando, 17–20 November 1996.

[6] T. Maoka, Electrochim. Acta 33 (1988) 379.

[7] Proceedings of Second International Fuel Cell Conference, Kobe, 5–8 February 1996.

[8] P. Costamagna, S. Scrinivason, J. Power Sources 102 (2001) 242.

[9] J.D. Aiken III, R.G. Finke, J. Mol. Cat. A: Chem. 145 (1999) 1.

[10] J.S. Yu, S. Kang, S.B. Yoon, G. Chai, J. Am. Chem. Soc. 124 (2002) 9382.

[11] R.H. Baughman, A.A. Zakhidov, W.A. Heer, Science 297 (2002) 787.

[12] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A: Gen. 253 (2003) 337.

[13] C. Pham-Huu, R. Vieira, M.J. Ledoux, L.J. Charbonniere, R. Ziessel, French Patent Application No. 0115178, assigné à SiCat, (2001).