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ORIGINAL PAPER

Mesoporous carbons as low temperature fuel cell platinum catalyst supports

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Abstract Platinum catalysts supported on ordered mesoporous carbons (OMC) are described. The mesoporous carbon support, CMK3 type, was synthesised as an inverse replica of a SBA-15 silica template. The platinum catalysts (i.e. Pt 20 wt% and Pt 10 wt%, respectively), obtained through a conventional wet impregnation method, have been investigated to determine their structural characteristics and electrochemical behaviour. The electro-catalytic performance towards the oxygen reduction reaction (ORR) was compared to those of commercial Pt/C-Vulcan XTC72R (E-Tek) catalysts with the same Pt wt%, under the same experimental conditions. The two catalyst samples have allowed the effect of the variation of both the Pt to Nafion and Pt to the supporting carbon ratios to be studied. Electrochemical tests have been carried out in three different systems: a catalyst ink deposited on a glassy carbon rotating disk electrode (RDE), a gas diffusion electrode (GDE) in a three-electrode cell with H_2SO_4 as the electrolyte and a complete PEM single fuel cell. The first results indicate that the OMC performs slightly less well than commercial carbon supports, mainly in the complete fuel cell system. The data from the cell tests indicate a less effective distribution of Nafion on the OMC surface which, probably, decreases the platinum utilisation and the proton conductivity.

Keywords Mesoporous carbon · Platinum catalysts · PEMFC · Oxygen reduction

1 Introduction

Among the various types of fuel cells, low temperature systems are particularly promising because they are free from the technical complications due to high temperature management. On the other hand, low temperature fuel cells need good water management and an efficient catalyst. In low temperature fuel cell catalysts, the carbon supports the metal nanoparticle dispersion and provides an electrical connection among them. Fuel cell catalysts are usually made of platinum supported on carbon Vulcan XTC72, and the specific surface area of such a carbon type is one of the most important features of such catalysts [1].

Recently, ordered mesoporous carbons (OMC) have attracted considerable attention as catalyst supports because of their high surface areas and their regular structure, which might be useful to disperse metal particles. The OMC structure is based on periodic arrays of carbon nanorods connected by carbon spacers with uniform mesopores among them [2]. Mesoporous carbons are characterised by a surface area of up to 2,000 $m^2\ g^{-1}$, uniform pore diameters of 2–10 μm, and high thermal, chemical and mechanical stability. Three different pore types are responsible for the porosity of a carbon material [3]: micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) and, in fuel cell electrodes, the transport

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of the reactants and products through the pore system can be very difficult when the pore size is less than 10 nm. Nevertheless, micropores are always present in the carbons commercially available today that are used for catalytic applications in fuel cells.

Generally, it is accepted that the catalytic activity of a fuel cell catalyst based on platinum is related to the dispersion and the size distribution of the metal particles [4–6]. An increase in the metal particle dispersion on the carbon support should lead to an enhancement of the kinetics, particularly of the oxygen reduction reaction (ORR), whose rate is an important limiting factor in fuel cell performances [4]. Moreover, it is necessary to ensure simultaneous contact between the reactant fuel, the catalyst and the polymer electrolyte, for the electrochemical fuel cell reactions to take place. As a consequence, the membrane electrode assembly (MEA) preparation and performance become critical for catalysts that are different from commercial ones such as Pt/C Vulcan XTC72. It is possible to prepare samples with different mesoporosities by changing the molar ratio of the silica to the carbon precursor [7] in order to optimise the behaviour of Pt catalyst supports. High mesoporosity could also enhance the diffusion of Nafion ionomer during MEA preparation. Finally, it has been reported [8] that the functionalisation of OMCs can improve the dispersion and anchoring of platinum particles, even though it has been reported [8] that the functionalisation of mesoporous carbons can also lead to the collapse of their ordered structure. In order to perform a simple and low cost catalysts synthesis, functionalisation of the carbon support has not been considered in this work but it will be taken into account in future studies.

The present work aims at obtaining a deeper insight into the preparation of Pt/OMC electrocatalysts giving enhanced oxygen reduction kinetics (ORR) in low temperature fuel cells. Structural and morphological characterisation of Pt/OMC catalysts is also presented.

The mesoporous catalyst support is a CMK3 type of carbon derived from a SBA-15 silica template. The electrochemical evaluation of the catalyst activity was performed by cyclic voltammetry and polarisations in acidic media. In this case, it was possible to determine the "true" electrochemical active area by cyclic voltammetry when the catalyst ink is deposited onto the surface of a glassy carbon rotating disc electrode. Evaluation of the catalyst activity towards the ORR was also carried out in a three-electrode cell in sulphuric acid. The catalyst ink was deposited onto a gas diffusion layer to obtain a gas diffusion electrode (GDE). Finally, preliminary tests of membrane electrode assemblies (MEA), containing the Pt/OMC at the cathode, were carried out in a single 5 cm^2 PEMFC. A comparison between Pt/OMC and commercial Pt/Vulcan XTC72 catalysts was made.

2 Experimental

2.1 Catalysts preparation

The catalysts were obtained by a simple low cost preparation, based on the synthesis of a silica template (SBA-15), the template conversion into the carbon replica (CMK3) and, finally, the insertion of the metal (Platinum) particles by wet impregnation. The SBA-15 was synthesised through the classical hydrothermal method reported by Zhao et al. [9]. Yields were about 95% based on silicon as reported in the literature [9, 10]. One gram of calcined SBA-15 was used to synthesize the CMK3 carbon replica [11]. The calcined silica was mixed with a solution containing 1.25 g of sucrose (Aldrich), 0.14 g of sulphuric acid (98 wt% Aldrich) and 5.0 g of distilled water. In order to carbonise the sucrose, the slurry was heated in an oven at 373 K for 6 h, and then at 433 K for 6 h. The acidic environment catalysed the carbonisation process. It was necessary to repeat this procedure twice to assure complete carbonisation of the material; moreover during the second treatment, the solution contained 0.8 g of sucrose, 0.09 g of sulphuric acid and 5.0 g of distilled water, respectively. Carbonisation was completed by pyrolysis at 1,173 K under nitrogen flow. After pyrolysis, a carbon-silica composite was obtained. To remove the silica walls from the carbon replica, a solution of HF (Aldrich) 3 wt% in ethanol was added drop by drop and stirred for 3 h. The dark brown powder was then filtered, washed with ethanol and water and oven dried at approximately 323 K. Dispersion of the catalytic metal on the mesoporous carbon was achieved by a wet impregnation technique. A solution of chloroplatinic acid hexahydrated (H_2PtCl_6, Aldrich) in acetone was added drop by drop to the carbon powder and stirred for 5 h. The slurry was then heated at approximately 333 K, with continuous stirring, in order to evaporate excess acetone. The amount of acid in the solution depended on the desired platinum content in the catalyst [6]. The sample was then treated under H_2 flow, under high vacuum, at 573 K for 3 h, in order to reduce the $PtCl_6^{2-}$ ions to platinum.

The characterisation of two Pt/OMC catalysts is reported in the paper: the first, which contains Pt 20 wt%, is hereafter reported as CMK3Pt-20 and the second, with a lower Pt weight percentage (around 10 wt%), as CMK3Pt-10.

2.2 Gas diffusion electrode (GDE) and membrane electrode assembly (MEA) preparation

The gas diffusion electrodes consisted of a hydrophobic layer (a commercial LT 1200-W ELAT GDL E-TEK) on which the catalyst ink (the hydrophilic layer) was deposited by painting. The catalyst ink was a mixture of carbon supported catalyst, Nafion (5 wt%, Electrochem Inc.), bi-distilled water and isopropanol (Aldrich). The amount of each component in the ink was chosen in order to have 0.5 mg cm^{-2} of platinum on the electrode surface (1 cm^2). The ratio of pure Nafion to supported catalyst was 1:2 and that of pure Nafion to water was 1:8.5. The same ratio was also maintained between pure Nafion and isopropanol. The ink was stirred at room temperature for 3 h, left 1 h in an ultrasonic bath, painted on the LT 1200-W ELAT E-TEK gas diffusion layer (GDL) surface, and finally oven dried at 333 K.

Membrane electrode assemblies, containing the Pt/OMC catalysts at the cathode and Pt20%/C Vulcan XTC72R (E-TEK) at the anode, were prepared by painting the catalyst inks on the LT 1200-W ELAT E-TEK gas diffusion layers. The platinum load for both electrodes was 0.5 mg cm^{-2}. In both inks the ratio of pure Nafion to supported catalyst was 1:2; those of pure Nafion to water and pure Nafion to isopropanol were kept at 1:8.5. The catalyst inks were stirred for 3 h at room temperature and kept 1 h in the ultrasonic bath.

The catalysts used in the GDE and in the MEA cathodic electrode were CMK3Pt-20, CMK3Pt-10. Pt 20%/C Vulcan XTC72R and Pt 10%/C Vulcan XTC72R were used for comparison. Therefore, for a given Pt loading, the inks prepared from Pt 10% samples contain a quantity of carbon and Nafion ionomer double than that of the Pt 20% samples.

Nafion 115 (DuPont) membranes purchased from Ion Power Inc. were employed and the electrodes were hot pressed to the membranes at 3.5 MPa and 393 K for 2 min by a DGTS press PM20 04799C.

2.3 Structural and morphological characterisation of the electrocatalysts

Once synthesised, the SBA-15 silica templates and their corresponding carbon replicas CMK3 were characterised by low angle X-ray powder diffraction. The XRPD diffraction patterns of the samples were collected in the 2θ-range between 0.8° and 4° with an acquisition step of 0.02° and a time per step of 10 s. The instrument was a Philips X-Pert MPD powder diffractometer, equipped with a Cu Kα radiation ($V = 40$ kV, $I = 30$ mA) and a curved graphite secondary monochromator.

The platinum to carbon weight percentage in the catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a Varian Liberty 100 instrument. Prior to analysis, the samples were digested in hot concentrated $HCl:HNO_3 = 3:1$ mixture.

Specific surface areas (SSA) of the catalysts and their precursors were determined using the Brunauer, Emmett, Teller (BET) method on a ASAP 2010 Micrometrics instrument. Prior to adsorption, approximately 50.0 mg of the sample were placed in the cell and evacuated at 623 K for 5 h.

High resolution transmission electron microscopy (HRTEM) on the catalysts was performed by a JEOL 2000× instrument operated at 200 kV, top entry stage. HRTEM analysis was carried out on the catalyst powders and on the MEA and GDE materials, both at the beginning and at the end of their testing periods.

2.4 EAS determination by cyclic voltammetry on glassy carbon rotating disk electrode in 1 M sulphuric acid

Five microlitres of the catalyst ink were deposited on a glassy carbon rotating disk electrode (RDE) (geometrical area: 0.03 cm^2). The electrochemical active surface (EAS) was determined through the evaluation of the Coulombic charge (Q_H) for hydrogen desorption as defined in reference [12]:

$$EAS = Q_H/([Pt] \times 210)$$

where [Pt] was the platinum load on the electrode (mg cm^{-2}), Q_H the charge for hydrogen desorption (mC cm^{-2}) and 210 μC cm^{-2} represented the charge required to oxidise a monolayer of hydrogen on bright platinum [13, 14].

Cyclic voltammetry was carried out in 1 M sulphuric acid at room temperature at 10 mV s^{-1} between ±0.7 V vs. Hg/Hg_2SO_4 (std.). The rotation speed of the RDE electrode was set at 900 rpm. The cell was purged with Argon for 1 h prior to the measurements. The evaluation of the EAS was carried out on the 50th cycle for each tested catalyst. A VoltaLab PGZ301 Radiometer Analytical was employed to run the measurements.

2.5 Electrochemical testing of the electrodes

A VoltaLab PGZ301 Radiometer Analytical was employed to run the polarisation curves of the gas diffusion electrodes. From these measurements the catalyst activity for the oxygen reduction reaction can be evaluated. A gas diffusion electrode (1 cm^2 of geometrical area) was placed in a Plexiglass cell filled with 1 M sulphuric acid. The counter electrode was a platinum foil of large area and a Hg/Hg_2SO_4 (std.) reference electrode was placed externally to the cell and connected to the main compartment through a Lugging capillary whose tip was placed close to the working electrode surface. Pure oxygen (5–7 ml min^{-1}) was continuously fed to the backside of the gas diffusion layer and diffused from the hydrophobic layer towards the catalyst ink, the latter being in contact with the electrolyte. The Plexiglass cell was used to trace polarisation curves of the gas diffusion electrode at 0.2 mV s^{-1} from the open circuit potential towards cathodic potential values (−0.35 V vs. Hg/Hg_2SO_4 (std.) reference electrode) where the oxygen reduction reaction (ORR) took place.

The catalysts activity was tested in a single 5 cm^2 PEMFC Electrochem (code number E3974) fed by pure hydrogen and oxygen at 343 K; the fuels were humidified to a relative humidity (RH) of 80%; the stoichiometry was 4. Polarisation curves of the membrane electrode assemblies (MEAs) were traced by using a PC driven ET electronic load model ELP/SL400. The current was modified at a rate of 10 mA s^{-1} until a cell potential of 0.3 V was reached.

The Ohmic resistance of the fuel cells was obtained by applying the current interrupt technique by the use of an AMEL5000 potentiostat [15]. The ohmic resistance, R_Ω, of the cell is evaluated as the quotient of the instantaneous change in voltage and the cell current density i (A cm^{-2}) just prior to the interruption event, $R_\Omega = \Delta V/i$. All the R_Ω measurements were carried out at $i = 0.1$ A cm^{-2} with acquisition steps of 10 or 40 μs.

3 Results and discussion

3.1 Material characterisation

3.1.1 Textural characterisation of the catalysts and their precursors

Mesoporous silica templates and the corresponding carbon replicas show the typical XRPD diffraction pattern of mesoporous systems, Fig. 1. The calcined SBA-15 sample (a) shows three well-resolved peaks: the (100), (110) and (200) reflections associated with $p6\,mm$ hexagonal symmetry. The ordered arrangement of the carbon replica gives rise to the well resolved XRD peaks shown in Fig. 1b. Again, the (100), (110) and (200) reflections can be assigned to the 2d hexagonal space group similar to that of the calcined SBA-15. The carbon product, obtained by pyrolysis at 1,173 K, retains the same structural order with full cross linking of the carbon frameworks [11], since the main mesoporous channels in SBA-15 are interconnected through micropores inside the walls of the main channels.

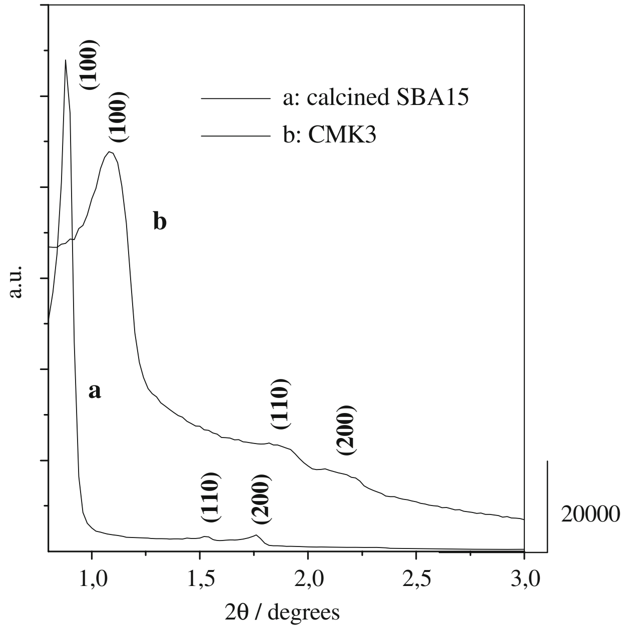

Fig. 1 XRPD pattern of the parent SBA15 after calcination (**a**) and its carbon replica CMK3 (**b**) collected in the 2θ-range between 0.8° and 4° with an acquisition step of 0.02° and a time per step of 10 s

Table 1 reports the samples textural properties, as the BET (Brunauer, Emmett and Teller) specific surface area (SSA) and the BJH (Barret-Joyner-Halenda) average pore diameter of the silica material (SBA-15), of the carbon replica (CMK3) and of the catalysts (CMK3Pt). SSAs of the synthesised mesoporous carbons ranged between 961 and 1,081 m^2 g^{-1}. Commercial carbons exhibited SSAs of 254 m^2 g^{-1} for the Vulcan XTC72R (Cabot) and of 82 m^2 g^{-1} for the Shawinigan Black AB50 (Chevron) [16].

XRD, BET and BJH data indicate that the carbon supports are mostly mesoporous since the pore distribution is centred on 3 nm, while BJH values of the template silica materials are centred on 6 nm.

Specific surface areas of the catalysts decrease if compared to those of the mesoporous carbon supports due to the insertion of the platinum particles in the CMK3 structure.

Representative N_2 adsorption/desorption isotherms at 77 K of the two catalysts are reported in Fig. 2, for the CMK3Pt-10 catalyst containing 8.74 wt% of Pt and for the CMK3Pt-20 containing 20.07 wt% of Pt. Three well-distinguished regions of the adsorption isotherm can be observed: a monolayer multilayer adsorption, a capillary condensation, and a multilayer adsorption on the outer particle surface [17]. A clear H1-type hysteresis loop is observed, which is typical of mesoporous materials with one-dimensional cylindrical channels [9, 18] and capillary condensation occurs at a higher relative pressure ($p/p_0 = 0.4$–0.5). The adsorption at very low relative pressure, p/p_0, is due to monolayer adsorption of N_2 on the walls of the mesopores. The sharp inflection in this

Table 1 Textural characteristics (BET, BJH and Pt weight percentage by ICP-AES analysis) of the catalysts CMK3Pt-10 and CMK3Pt-20 and their precursors

Sample	BET (m^2 g^{-1})	BJH (nm)	ICP (Pt wt.%)
SBA-15	927	6.243	
CMK3	961	3.504	
CMK3Pt-10	853	3.280	8.74
SBA-15	1,070	6.081	
CMK3	1,081	3.120	
CMK3Pt-20	754	3.062	20.07

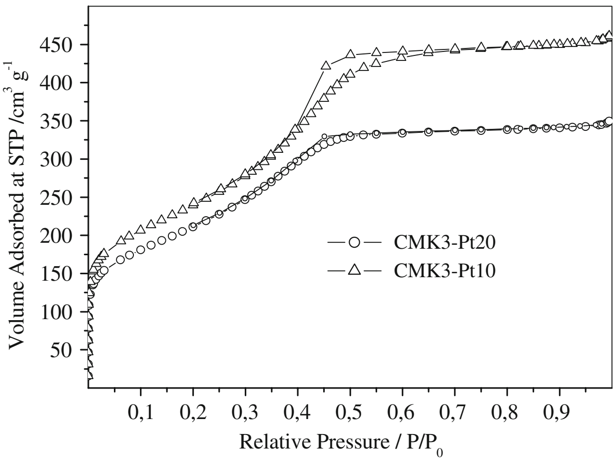

Fig. 2 Adsorption/desorption isotherms of N_2 at 77 K of the CMK3Pt-10 containing Pt 8.74 wt% (triangles) and CMK3Pt-20 containing 20.07 wt% (circles)

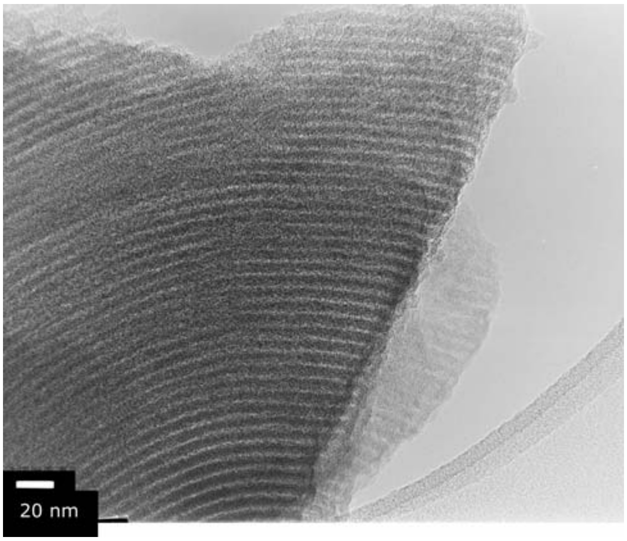

Fig. 3 Typical HRTEM image of an ordered mesoporous carbon CMK3, original magnification ×2,500,000 (marker: 20 nm)

isotherm corresponds to capillary condensation within uniform mesopores, reflecting the uniform pore size in this material. Larger pores are filled at higher p/p_0.

The amount of physisorbed nitrogen decreases with increasing platinum weight percentage in the catalyst. The hysteresis loop, which is not pronounced for the CMK3Pt-10 sample and is nearly absent in the CMK3Pt-20, is probably related to the pore shape since some conical or close-end pore geometries can yield isotherms without pronounced hysteresis [19, 20]. The mass considered in the evaluation of the catalyst BET area was the total mass including the platinum weight percentage.

3.1.2 *Morphological characterisation of the catalysts and of the carbon support CMK3*

The HRTEM image of a carbon replica CMK3 viewed along the direction parallel to the carbon rods is shown in Fig. 3. The structure of CMK3 consists of cylindrical mesoporous tubes randomly interconnected by micropores in the pore walls [11].

The insertion of platinum particles on the CMK3 carbon support does not modify its structure as shown in Fig. 4a, b, where the sample CMK3Pt-10 is viewed along both directions perpendicular (Fig. 4a) and parallel (Fig. 4b) to the carbon rods. Both catalysts have homogeneous dispersion of platinum particles. The sample CMK3Pt-20 (Fig. 5) showed a higher density of platinum clusters with particle dimensions slightly lower than those observed in the CMK3Pt-10 catalyst, whose platinum to carbon weight percentage is 8.74%. A quantitative determination of the particle size of the samples is reported in Fig. 6a and b. In the case of CMK3Pt-10 the distribution appears centred around a mean value of approximately 2.0 nm. For the CMK3Pt-20 catalyst the average particle diameter is set around 1.7 nm. These values are not far from the average particle diameters of both Pt 20%/C Vulcan XTC72R and Pt 10%/C Vulcan XTC72R catalysts which have been evaluated around 2.0 nm, according to HRTEM analyses carried out in our laboratory, the ETEK website and literature [21].

For the CMK3 samples, an unexpected decrease in the grain dimension occurs, passing from the lower to the higher Pt % sample, since in many cases, the particle dimension increases with increase in metal weight percentage. The particle diameter distribution in Fig. 6a is much more dispersed than in Fig. 6b and two maxima at 1.5 and 3 nm can be detected.

3.2 Electrochemical characterisation

3.2.1 *Evaluation of the electrochemical active surface (EAS)*

The EAS of the catalysts were determined by evaluating the atomic hydrogen desorption charge during cyclic voltammetry in acidic media.

When a catalyst ink is used, the measured EAS might be lower than the real values as a consequence of the electrode preparation [2, 12,]. Figure 7 reports, as an example, the cyclic voltammetry feature of the CMK3Pt-20 catalyst at 10 mV s^{-1} in 1 M H_2SO_4 at room temperature.

The effect of the Nafion ionomer, which is one of the components of the catalyst ink, as well as the inaccessibility of the protons towards the platinum particles supported on carbon, are some of the possible causes of surface losses. In order to minimise such effects in the

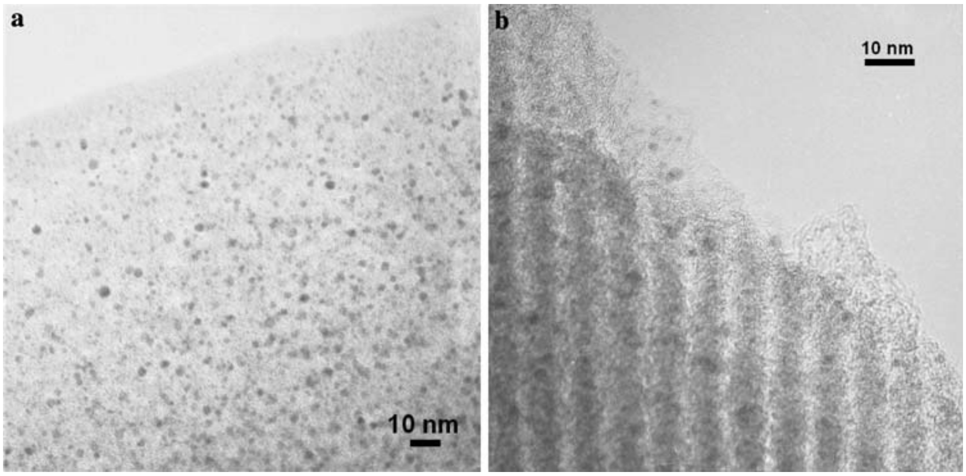

Fig. 4 HRTEM images of the CMK3Pt-10 catalyst, containing Pt 8.74 wt%, original magnification ×600,000 for both images. (**a**) The sample is viewed along the perpendicular direction to the carbon rods; (**b**) the sample is viewed along the parallel direction to the carbon rods

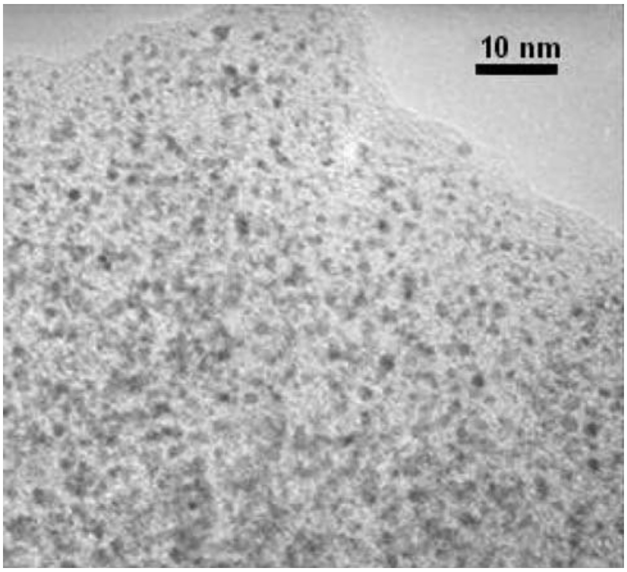

Fig. 5 HRTEM images of the CMK3Pt-20 catalyst, containing Pt 20.07 wt%, original magnification ×600,000

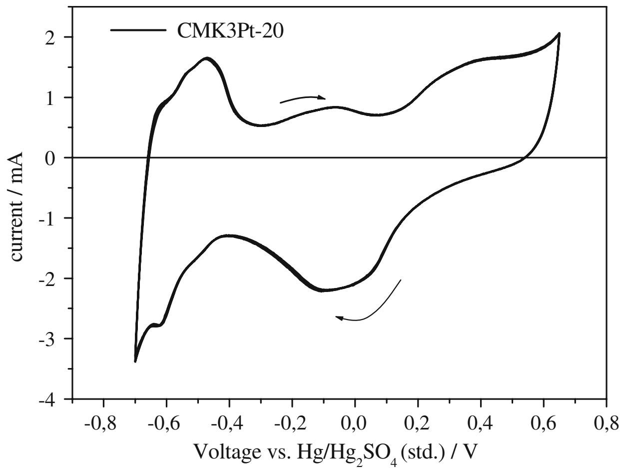

Fig. 7 Cyclic voltammetry of the CMK3Pt-20 catalyst at 10 mV s^{-1} in 1 M H_2SO_4 at room temperature

evaluation of the active area, we chose to simply deposit the catalyst ink on the surface of a glassy carbon rotating disk electrode, with a low geometrical area (0.03 cm^2) to guarantee a perfect adhesion. The amount of ink to be deposited is also critical [12]: it must not be too high to reduce the platinum utilisation and not too low so that part of the electrode surface is uncovered. In both cases the evaluation of the EAS would be underestimated.

Table 2 reports the catalysts loads (mg cm^{-2}) present on the electrode surface and the corresponding Q_H and EAS values obtained as described in [12]. By considering the EAS values, both mesoporous and commercial catalysts have similar EAS values, indicating that the Pt/OMC have

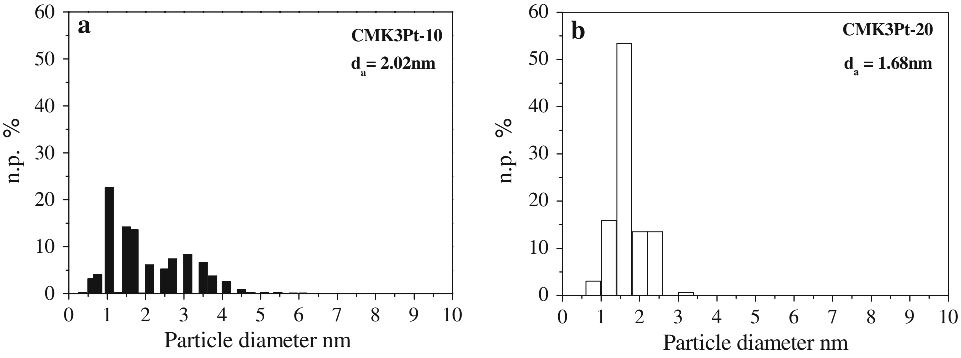

Fig. 6 Distribution of the platinum particles diameters in the two catalysts: CMK3Pt-10 (**a**) and CMK3Pt-20 (**b**) containing Pt 8.74 wt% and Pt 20.07 wt%, respectively

Table 2 Q_H, Pt loading, EAS and TS values obtained by means of cyclic voltammetric measurements (scan rate 10 mV s^{-1} between ±0.7 V vs. Hg/Hg_2SO_4 (std.) in 1 M H_2SO_4)

Sample	Q_H (mC cm^{-2})	[Pt] (mg cm^{-2})	EAS (m^2 g)−1)	TS (m^2 g^{-1})
Pt/C 10%	44.8	0.4	53.3	69.4
Pt/C 20%	86.8	0.8	51.4	63.7
CMK3Pt-10	35.9	0.3	56.7	70.1
CMK3Pt-20	87.4	0.8	51.9	82.5

comparable electrochemical activity to standard catalysts. The slight decrease in EAS value with increase in Pt weight percentage in the Pt/C catalysts is not significant due to the reproducibility of the measurements. Nevertheless, the EAS values obtained for the Pt/OMC catalysts were close to those reported [4] for similar Platinum supported catalysts.

The last column of Table 2 reports the specific theoretical surface (TS) values. TS, which is the maximum ideal value of a Pt active surface, was obtained as the product, referred to the unity of Pt mass, of n_g (number of Pt grains having a certain diameter value) and s_g (surface area of one grain). These terms have been obtained from the average diameter values (reported for the samples considered in the previous section) and from the Pt density (21.4 g cm^{-2}).

In our experimental conditions and by comparing the EAS and TS values, most of the surface available for the reaction is really active. Moreover, a 20% loss in the specific surface area from TS to EAS is observed, a result which was expected when considering the theoretical feature of the TS values. The mesoporous catalyst CMK3Pt-20, with the highest TS values and the best metal dispersion, showed a 35% loss in the specific surface area from TS to EAS.

Our experience suggests that the loss of active surface area, due to the blocking and anchoring of the Nafion on the metal surface [2], is more extended as the grain dimensions decrease.

3.2.2 *Half cell tests with gas diffusion electrodes*

Gas diffusion electrodes containing either the Pt/OMC catalysts or the commercial Pt/C Vulcan XTC72R were prepared and tested in 1 M sulphuric acid. As the platinum load on the GDE was fixed at 0.5 mg cm^{-2} for all the tested catalysts, an electrode prepared with a catalyst powder containing 10 wt% of Pt was loaded with twice the carbon and Nafion with respect to a powder with 20 wt% of Pt.

Figure 8 shows the polarisation curves at 0.2 mV s^{-1}, in the range of potential where the oxygen reduction reaction (ORR) takes place. In the same experimental conditions, the Pt/OMC catalysts and the standard catalysts tested show similar behaviour. The best performing sample is the commercial Pt/C 20%, in contrast to the EAS values that are nonetheless very near, while the performances of CMK3Pt-10 and commercial Pt/C 10% are almost equal. CMK3Pt-20 shows a lower catalytic activity than CMK3Pt-10, which is in agreement with the EAS values (see Table 2).

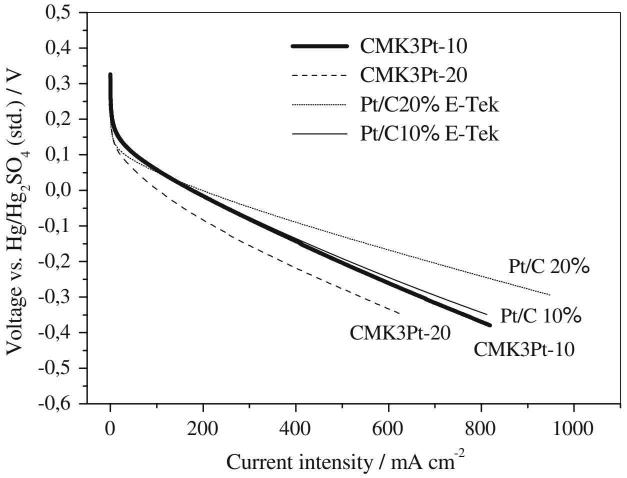

Fig. 8 Polarisation curves traced at 0.2 mV s^{-1} in 1 M H_2SO_4 at room temperature. Oxygen flows on the backside of the electrode at 5–6 ml min^{-1}. The gas diffusion electrodes (working electrode) were prepared with: CMK3Pt-10 (thick solid line), CMK3Pt-20 (dashed line), Pt/C 20% (dotted line) and Pt/C 10% (solid line) respectively

Impedance measurements were performed to extend the electrochemical characterisation of mesoporous carbon supports. The cell for impedance measurements is described in the experimental section. The impedance spectra were obtained in the frequency range 100 kHz–10 mHz in 1 M H_2SO_4 under continuous oxygen flow (5 ml min^{-1}). Figure 9 shows an example of impedance spectra, reported as a Nyquist plot, determined at 0.0 V (vs. Hg/Hg_2SO_4).

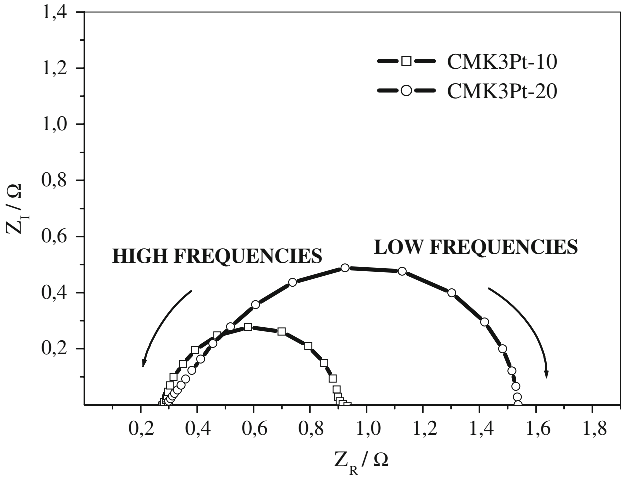

Fig. 9 Nyquist plots of the gas diffusion electrodes prepared with: CMK3Pt-10 (open squares), CMK3Pt-20 (open circles). The spectra were obtained in the frequency range: 100 kHz–10 mHz, at 0 V vs. Hg/Hg_2SO_4 (std)

Table 3 Transfer resistance values obtained by the Nyquist plots of the gas diffusion electrodes prepared with: CMK3Pt-10, CMK3Pt-20and the commercial catalysts

Sample	R_T (Ω cm^2)
Pt/C 10%	0.58
Pt/C 20%	0.30
CMK3Pt-10	0.63
CMK3Pt-20	1.25

The spectra were obtained in the frequency range: 100 kHz ÷ 10 mHz, at room temperature and at 0 V vs. Hg/Hg_2SO_4 (std.) in 1 M Hg_2SO_4

From this plot a resistance value can be obtained as the difference between the low frequency and the high frequency values on the real axis. This resistance can be interpreted as the charge transfer resistance R_t for the ORR. Due to the porous nature of the electrode, the interpretation of the impedance response by a simple charge transfer resistance at low frequency is over simplified. On the other hand, these values can be used for a qualitative description of the electrode behaviour. The results of charge transfer resistance are indicated in Table 3. These results agree fairly well with the polarisation curves with GDE electrodes (see Fig. 8). A higher charge transfer resistance value corresponds to a higher activation overvoltage on the polarisation curve.

3.2.3 Electrochemical characterisation of the catalysts in the 5 cm^2 single PEMFC

Table 4 Ohmic resistance values, obtained by the current interrupt method at 0.1 A cm^{-2}, for the MEAs whose performances are reported in Fig. 10

Sample	$R_Ω$ (mΩ cm^2)
Pt/C 10%	≅96.00
Pt/C 20%	≅96.00
CMK3Pt-10	145.4
CMK3Pt-20	329.2

Figure 10 reports the polarisation curves. As for the Pt/OMC catalysts, the performances of CMK3Pt-10 were better than CMK3Pt-20. The performances of the two commercial catalysts were quite similar and their current densities were higher than for the Pt/OMC samples.

These results should be discussed by taking into account the cell resistance values, reported in Table 4, which were measured by the current interrupt method. Such values are very high for the Pt/OMC catalysts, in particular, for the CMK3Pt-20 sample, while they are lower and similar for the commercial samples.

Therefore, the performance can be related to the cell resistance values and, as the equipment used for cell testing was the same in all cases, to the lower conductivity of the mesoporous carbon support and less effective action of proton transfer of the Nafion ionomer in the OMC samples. Another important feature is the increase in performance of CMK3Pt-10 with respect to CMK3Pt-20. As the ratios OMC support to Pt and Nafion ionomer to Pt, respectively, for the CMK3Pt-10 are double that of CMK3Pt-20, this most probably indicates that a further increase in such ratios leads to an increase in performance by decreasing the cell resistance.

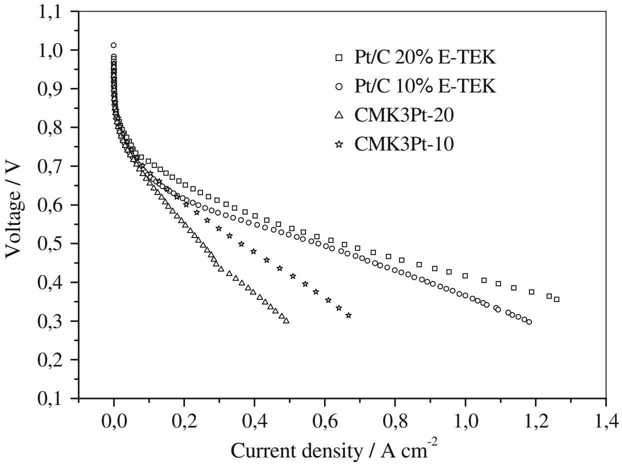

Fig. 10 Polarisation curves of a 5 cm^2 PEMFC, T cell = 343 K, RH = 80%. MEAs were prepared with: Pt/C 20% (squares), Pt/C 10% (circles), CMK3Pt-10 (stars), CMK3Pt-20 (triangles) at the cathode, being the platinum load equal to 0.5 mg cm^{-2} for all the tested MEAs. The current was modified at a rate of 10 mA s^{-1} until a cell potential of 0.3 V was reached

4 Conclusions

The results of the considered Pt/OMC catalysts, compared to those obtained under the same experimental conditions with standard catalysts, suggest that:

- High surface areas and an accessible mesoporosity exert a more limited influence than expected on the distribution of platinum particles. The catalyst ink samples show just slightly higher EAS values for the OMC samples.
- The distribution of the Pt particle dimensions changes markedly with the platinum weight percentage. This appears to be related to the concentration of H_2PtCl_6 used to add Pt to the OMC surface which, as the volume of solution is constant, is double for the 20% compared to the 10% sample.
- Electrochemical tests on gas diffusion electrodes showed that an increase in the OMC to Pt ratio and/or Nafion to Pt ratio is beneficial to the performance of

the OMC samples, which becomes similar to that of the commercial samples.

- In the PEMFC tests, the OMC catalysts showed a particularly unsatisfactory behaviour which has been related, on the basis of the cell resistance values, to the lower conductivity of the support and the ineffective action of the proton transport of the Nafion ionomer. This last characteristic is particularly important in a system where Nafion inside the ink acts not only as a binder but also as a proton conductor. A possible explanation which, at this stage, is only a hypothesis, is that the Nafion ionomer diffuses thoroughly in the OMC pores even when no Pt particles are present and therefore partially disperses unproductively inside the material.

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