

Physical and electrochemical evaluation of commercial carbon black as electrocatalysts supports for DMFC applications

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Abstract

This work presents results with noble metal catalysts, Pt and PtRu supported on Black Pearl with a higher surface area in comparison with carbon black Vulcan XC-72R and Vulcan XC72. The nanoparticles were synthesized following the alcohol reduction method. Brunauer–Emmet–Teller (BET) surface area analysis, X-ray diffraction (XRD), energy dispersive analysis by X-rays (EDAX), and high resolution transmission electronic microscopy (TEM) experiments were carried out to characterize the materials obtained. Cyclic voltammograms (CV) of catalysts using the porous thin layer electrode technique were obtained for the catalysts surface evaluation and for methanol oxidation to check the electrocatalytic behavior of these nanocatalyst systems.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) are suitable for portable, mobile and stationary applications due to their inherent advantages, such as high-power density, reduced system weight, simple construction and quick startup, even at low operating temperatures, producing low (or no) emissions [1–3]. For such applications, in order to provide the best performance, metallic platinum is the most important electrocatalysts material employed for several kinds of electrochemical reactions; in particular of those occurring in PEMFC gas diffusion electrodes. The performance of the noble metal catalysts in the form of nanoparticles supported on high surface area carbon will depend strongly on the support material characteristics like: chemical/electrochemical stability, good electrical conductance, high surface area, suitable pore-size area distribution and low impurity or surface group contents. The most used carbon support for catalysts preparation is the commercial material Vulcan XC72

and VulcanXC72R (Cabot). According to Cabot Company, the only difference between the two materials is that the XC72 is in the form of pellets, whereas XC72R is in powder form, but even this morphological difference might influence considerably the fuel cell performance.

Because of the large surface area and its chemical stability, Black Pearl 2000 (Cabot) has also been considered for several types of applications, including as a support material for electrocatalysts.

In this study, the investigative results concerning electrochemical properties for electrocatalysts supported onto three different types of commercial supports – Vulcan XC72; Vulcan XC72R and Black Pearl – are reported.

2. Experimental

2.1. Pt/C and PtRu/C electrocatalysts prepared by alcohol reduction process

The carbon supported electrocatalysts were prepared using the alcohol reduction method [4,5]. A mixture of the desirable metallic ions solution was used as precursor, where the ions were

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reduced to their metal forms, using ethylene glycol as solvent and reducing agent in the presence of the carbon support.

Pt/C (20 wt.%) and PtRu/C (20 wt.%, Pt:Ru atomic ratio of 1:1) were prepared using ethylene glycol (Merck) as solvent and reducing agent, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{RuCl}_3 \cdot 2\text{H}_2\text{O}$ (Aldrich) as metal sources and high surface area Carbon Vulcan XC-72R, Vulcan XC-72 and Black Pearl 2000 as supports. In this procedure the salts were added to the carbon support, followed by an ethylene glycol solution (75:25—ethylene glycol:water). The system was ultrasonically treated for 15 min. After that, it was refluxed heated at 160°C for 1 h. The resulting powder was filtered, washed and dried at 110°C overnight [6–9]. Pt/C 20 wt.% and PtRu/C (20 wt.%, Pt:Ru atomic ratio of 1:1) commercial electrocatalysts from E-TEK were used for comparative purposes.

The Pt:Ru atomic ratios of the electrocatalysts were obtained using a scanning electron microscope Philips XL30 with a 20 keV electron beam and equipped with EDAX DX-4 microanalyses. The X-ray diffraction (XRD) analyses were performed using a STOE STADI-P diffractometer with germanium monochromized Cu $K\alpha$ radiation and a position-sensitive detector with 40 apertures in transmission mode. The X-ray diffractograms were obtained with a scan rate of 1 min^{-1} and an incident wavelength of 1.5406 \AA (Cu $K\alpha$). The average crystallite size was estimated with the XRD data [10,11]. The transmission electron microscopy (TEM) characterization were obtained using a JEM-1200EX JEOL microscopy, and the average particle size histograms were calculated using Image Tool Software with one TEM micrograph for each catalyst.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [12–14]. An amount of 10 mg of the electrocatalysts was added to 10 g of water, and this weight was determined with a precision of 0.0001 g, indicating that the nominal precision of the balance used was 0.0001 g. The mixture was submitted to an ultrasound bath for 5 min, where two drops of a Polytetrafluorethylen (PTFE) suspension 6% were added. Again, the mixture was submitted to an ultrasound bath for 5 min, filtered and transferred to the cavity (0.30 mm deep and area with 0.36 cm^2) of the working electrode. The quantity of the electrocatalysts in the working electrode was determined with a precision of 0.0001 g. By the cyclic voltammetry experiments, the current values (I) were expressed in amperes and were normalized per gram of platinum. The reference electrode was an reversible hydrogen electrode (RHE) and the counter electrode was a platinized Pt net with 4 cm^2 . Electrochemical measurements were taken using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a computer using the Microquimica Software. Cyclic voltammetry was performed in a $0.5\text{ mol L}^{-1}\text{ H}_2\text{SO}_4$ solution saturated with N_2 . The hydrogen adsorption charge was measured (Eq. (1)) and the well established relationship of $210\text{ }\mu\text{C cm}^{-2}\text{ Pt}$ [15,16] from solid, planar polycrystalline platinum electrodes was employed, together with the assayed platinum content of the electrode, to calculate the electrochemical area (ECA) of the catalyst (Eq. (2)).



Table 1
BET analysis obtained for the carbons support

Type of carbon support	BET area ($\text{m}^2\text{ g}^{-1}$)
Vulcan XC72	232
Vulcan XC72R	241
Black Pearl	1485

$$\text{ECA} (\text{cm}^2\text{ Pt g}^{-1}\text{ Pt}) = \frac{\text{charge} (\mu\text{C cm}^{-2})}{[210 (\mu\text{C cm}^{-2}\text{ Pt}) \times \text{electrode loading} (\text{g Pt cm}^{-2})]} \quad (2)$$

The evaluation of the 1 mol L^{-1} methanol solution oxidation was performed at 25°C in $\text{H}_2\text{SO}_4\text{ }0.5\text{ mol L}^{-1}$. For comparative purposes a commercial carbon supported Pt and PtRu catalysts from E-TEK (20 wt.%; Pt:Ru molar ratio 1:1).

3. Results and discussion

3.1. Brunauer–Emmet–Teller (BET) surface area results

BET surface area measurements were taken from the catalysts supports to first evaluate the surface area of the carbon supports used. The results are presented in Table 1.

The support material Black Pearl presented the highest surface area, about $1400\text{ m}^2\text{ g}^{-1}$, and the results obtained with the Vulcan materials were very similar. These results show that the difference between the Vulcan materials (XC72 and XC72R) is not related with the surface area, but with other characteristics that will be discussed later.

3.2. XRD and EDX results

The disperse energy of X-ray analysis (EDX) and the mean particle sizes of the electrocatalysts are shown in Table 2. The Pt:Ru atomic ratio of the obtained electrocatalysts using the disperse energy of X-ray analysis was very close to the nominal composition, calculated from the masses of the metallic components used in preparation.

The XRD data for the carbon black supports are shown in Fig. 1, the Vulcan XC72 material is the most crystalline material with higher intensity peaks compared with the other materials.

All of the electrocatalysts showed diffraction peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ$ and 82° , Fig. 2, characteristic of the fcc structure of platinum and platinum alloys [17–19]. The broad peak at about $2\theta = 25^\circ$ was associated with the carbon black used as support material. For PtRu/C electrocatalysts, no other peaks of ruthenium hcp phase or ruthenium oxides were observed.

The Pt:Ru measured composition was very close to the nominal composition (calculated from the masses of the metallic components used in catalysts preparation).

The average particle size, L , may be estimated from the parameters listed in Table 2 according to the Scherrer equation

Table 2
Pt:Ru atomic ratio (EDX analysis), particles size (Scherrer equation) and electrochemical surface areas (cyclic voltammetry) of the prepared electrocatalysts

Electrocatalysts	Pt (wt.%)	Ru (wt.%)	Pt:Ru atomic ratio	Pt:Ru atomic ratio EDX	Particle size (nm) Scherrer ^a	Particle size (nm) TEM	Electrochemical surface areas (cm ² g ⁻¹ Pt)
Pt/Vulcan XC72 20%	20	—	—	—	4.5	—	348
Pt/Vulcan XC72R 20%	20	—	—	—	4.9	—	323
Pt/Black Pearl 20%	20	—	—	—	5.6	—	121
Pt/C E-TEK 20%	20	—	—	—	2.8	—	540
PtRu/Vulcan XC72 20%	13.2	6.8	1:1	1:1	4.3	4.1	—
PtRu/Vulcan XC72R 20%	13.8	6.8	1:1	1:1	4.8	4.5	—
PtRu/Black Pearl 20%	13.8	6.8	1:1	1:1.3	5.2	4.7	—
PtRu/C E-TEK 20%	13.8	6.8	1:1	1:1.1	1.5	2.8	—

^a Mean particle size calculated from X-ray diffraction data using the Scherrer equation.

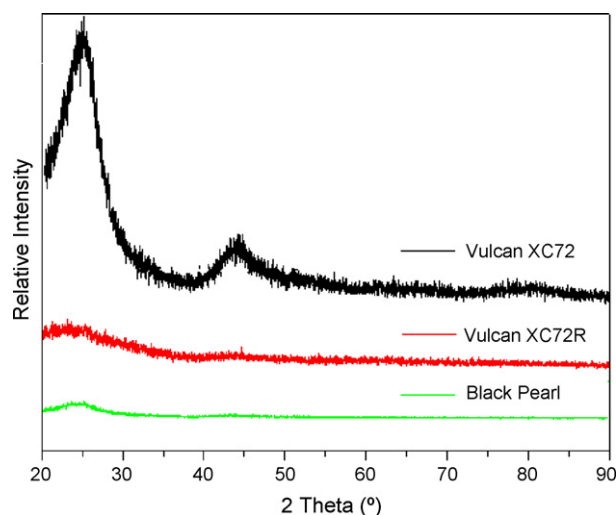


Fig. 1. X-ray diffractograms of the different carbon support: Vulcan XC72, Vulcan XC72R and Black Pearl.

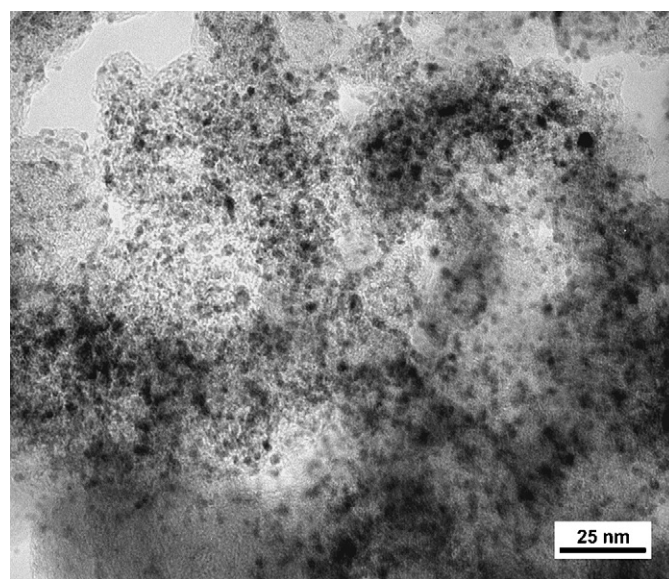


Fig. 3. TEM micrograph for the PtRu/C ETEK material.

using the platinum peak (2 2 0) [11].

$$L = \frac{0.9\lambda_{k\alpha 1}}{B_{(2\theta)} \cos \theta_{\max}} \quad (3)$$

where $\lambda_{k\alpha 1}$ is 1.54056 Å, and $B_{(2\theta)}$ is in radians.

The XRD average particle sizes compared with the TEM average particle size were very similar, showing that both techniques are very efficient in estimating the particle size. The

values of the average particle size are presented in Table 2. These results show that the alcohol reduction method produces nanoparticles in the desirable size range for fuel cell applications.

The same particle size, around 5.6 nm, was seen for all three carbon supports, despite their differences in BET area. Therefore, high support surface area alone is not sufficient to

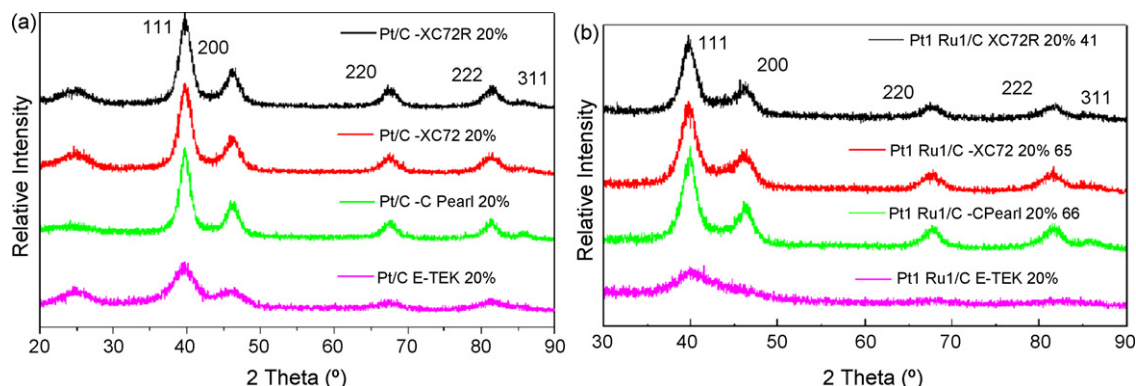


Fig. 2. X-ray diffractograms of the different (a) Pt and (b) PtRu carbon supported catalysts prepared in Vulcan XC72, Vulcan XC72R, Black Pearl and commercial catalyst from E-TEK.

ensure a small Pt particle size. These results also show that using carbon support with higher superficial area does not mean that in this case the nanoparticles size will be smaller. It is supposed that by using the alcohol reduction method the homogeneity of the electrocatalyst on the carbon surface was affected or even that the carbon porous was not accessible by the ions. The particle size values for the Pt/C E-TEK, shown in Table 2, indicate that the support used and/or the method used to produce the electrocatalysts is able to produce nanoparticles with an average size of 2.8 nm. The same discussion is valid for the PtRu/C results with different supports. The diffractograms of the electrocatalysts are shown in Fig. 2.

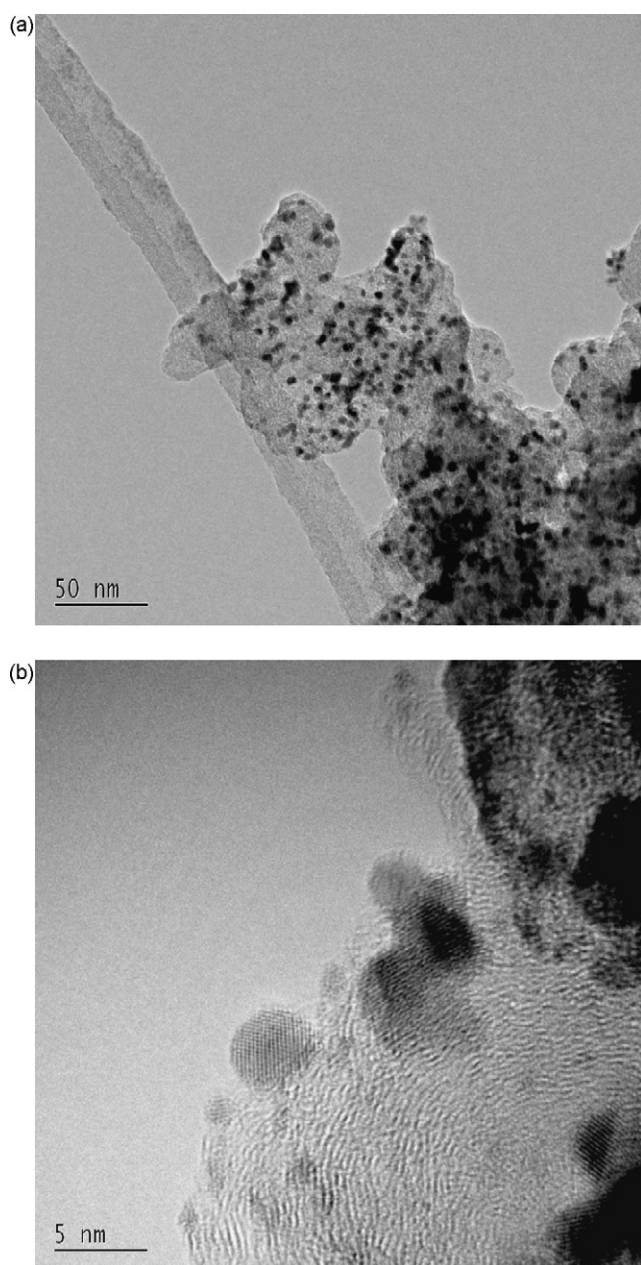


Fig. 4. Micrographs for the PtRu/XC72R material (a) TEM and (b) HRTEM.

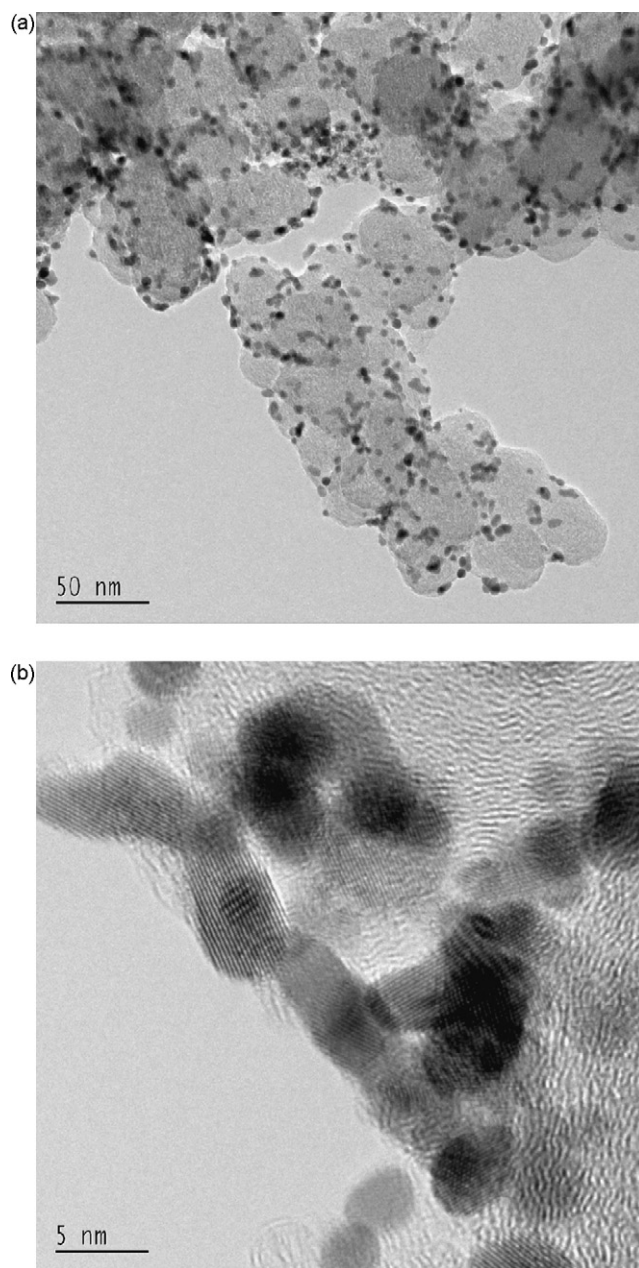


Fig. 5. Micrographs for the PtRu/XC72 material (a) TEM and (b) HRTEM.

3.3. Transmission electron microscopy

The TEM images in Figs. 3–6 reveal a very homogenous and uniform particle distribution for the material PtRu/C Vulcan XC72, and a less homogeneous distribution for the material PtRu/C Vulcan XC72R. For the materials PtRu/C Black Pearl, the results were a material with a lot of agglomerates and no uniform particle distribution. The TEM particle size histograms are presented in Fig. 7 and the average particle size in Table 2. The TEM results of particle size are in agreement with the XRD particle size results. Looking at the histograms, the materials supported in Vulcan XC72 are more homogeneous than other materials. Also compared with the commercial material PtRu/C ETEK, the electrocatalysts supported in Vulcan XC72 present

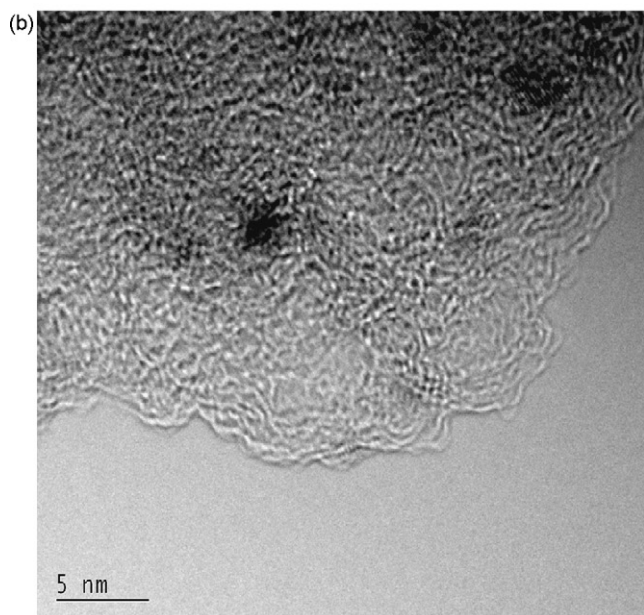
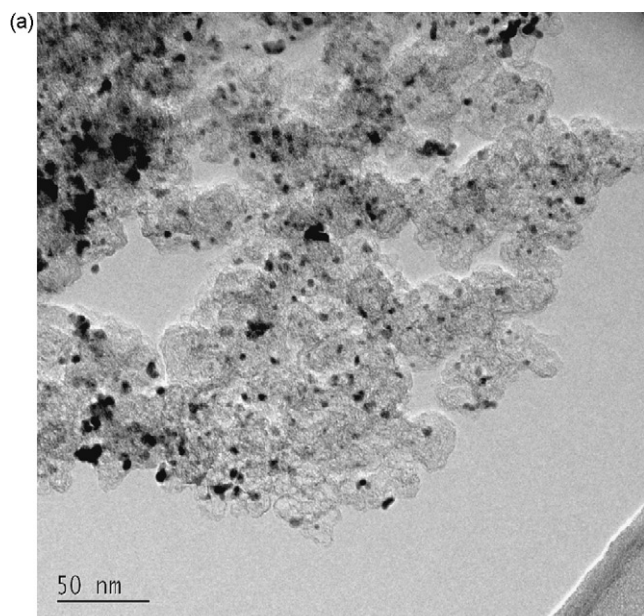


Fig. 6. Micrographs for the PtRu/Black Pearl material (a) TEM and (b) HRTEM.

more homogeneous distribution. In the commercial material, particles in the average range (2–3 nm) correspond to no more than 40% of the particles, while for the Vulcan XC72 material, in the average range (3–5 nm), the particles correspond to about 70%.

3.4. Electrochemical results

The cyclic voltammograms (CV) of Pt/C 20% performed in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and PtRu/C 20%, using different materials as support are shown in Fig. 8. The cyclic voltammograms show characteristics for each type of catalysts, Pt/C and PtRu/C [10]. The hydrogen underpotential desorption (UPD) region (0.075–0.35 V) vs. reversible hydrogen electrode (RHE) in Pt catalysts is well defined, while for PtRu catalysts it is less

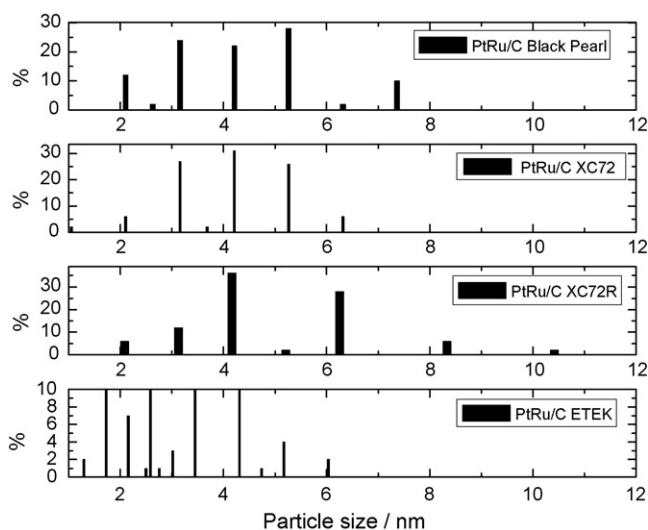


Fig. 7. TEM particles size histograms for the different electrocatalyst systems prepared.

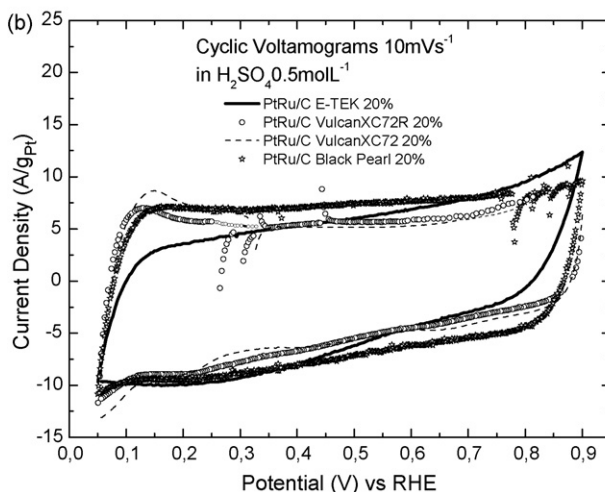
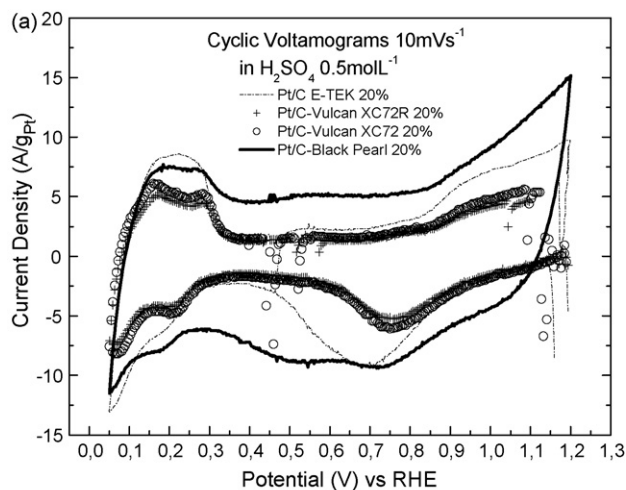


Fig. 8. Cyclic voltammograms in H_2SO_4 0.5 mol L^{-1} , 10 mV s^{-1} for (a) Pt and (b) PtRu.

defined, because the adsorption/desorption hydrogen peaks are not developed on Ru. Some differences are apparent between the materials. The PtRu/C Black Pearl and PtRu/C XC72 have a more characteristic hydrogen region and lower currents in the double layer region, which are probably due to the different preparation methods.

The electrochemical surface area of the platinum supported materials prepared and obtained from the hydrogen adsorption region in the voltammetric cycles in H_2SO_4 0.5 mol L^{-1} is presented in Table 2. The results are in agreement with the particle size results. The Pt/C ETEK material with a smaller particle size will consequently present a greater surface area, as shown in the results.

The performance of the PtRu/C catalysts, for methanol oxidation, shows a superior activity as compared to the Pt catalysts in the investigated potential range (between 0.4 and 0.55 V). This enhanced performance of the PtRu catalysts was explained by a functional mechanism [20,21] for oxidation of CO-containing intermediates (referred to as COad) on PtRu surfaces. Due to the high affinity of Ru towards oxygen-containing species [22], sufficient amounts of OHad are formed at lower potentials (above = 0.35 V) on Ru sites than on Pt sites (above 0.55 V)

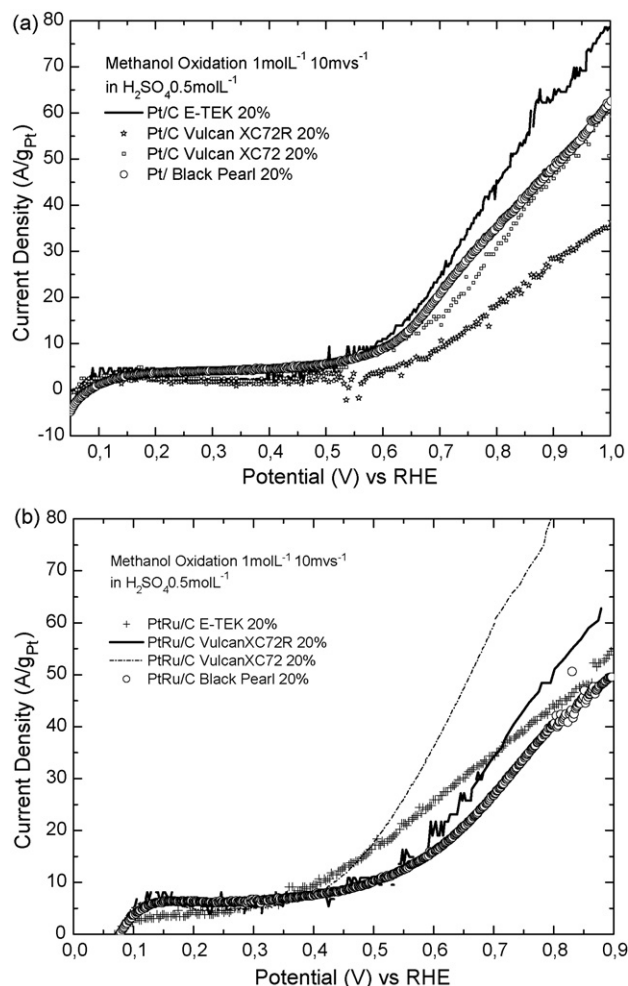


Fig. 9. Anodic stripping for methanol 1 mol L^{-1} oxidation in H_2SO_4 0.5 mol L^{-1} 10 mV s^{-1} , for (a) Pt and (b) PtRu.

to support reasonable CO oxidation rates. This effect leads to higher activities for the overall methanol oxidation process on PtRu compared to Pt. At higher potentials ($E \geq 0.55 \text{ V}$), pure Pt becomes more active than PtRu, but this potential region is irrelevant for direct methanol fuel cell (DMFC) applications, where the anode potential is much lower than 0.5 V.

This high activity on Pt at high potentials can be understood by the formation of strongly bonded surface oxides, which occur at more negative potentials on Ru and PtRu surfaces than on pure Pt. Fig. 9a shows also that the best result for methanol oxidation on Pt was obtained using the commercial material from E-TEK, and considering only the materials prepared upon Vulcan XC72, Vulcan XC72R, the best result was achieved using the Black Pearl support. Before this experiment was carried out, good results with Black Pearl were expected, because of its high surface area. However, the results shown here suggest that the alcohol reduction method was not able to produce well dispersed Pt nanoparticles over the high surface area of the Black Pearl support. This is perhaps due to the fact that much of the porosity of the support is smaller than the hydrated metal ions, thus meaning that much of the internal surface of the carbon cannot be accessed by the metal ions.

Fig. 9b shows that, in the range of 0.6–1.0 V, the best result for methanol oxidation on PtRu was obtained using the carbon support Vulcan XC72. Due to the high conductivity properties of the XC72, proved by the XDR measurements.

4. Conclusion

The results presented show that an increase of the electrocatalytic activity can be obtained, if a suitable method for the catalyst synthesis is employed. In this sense, the alcohol reduction method showed a positive effect for PtRu supported materials, probably due to the good particle dispersion at the carbon surface and the suitable particle size distribution that this method produces. For the methanol oxidation results, an increase in the cell potential by PtRu/C electrocatalyst on Vulcan XC72 system was observed compared to the PtRu/C E-TEK formulation. This can be explained due to the better conductivity of this carbon support, enhancing the speed of the electron transference in the methanol oxidation reaction (MOR). These results can also be attributed to the good particle distribution at the carbon surface and suitable particle size distribution of the PtRu catalyst. Indeed, at low and intermediate current densities a low amount of methanol is required for the cell operation. The methanol adsorption/dehydrogenation reactions can proceed more readily, and the rate of the MOR is determined by the rate of the COads oxidation. At higher current densities, an increased consumption of methanol is required, with this mass transport being the determining step of the MOR.

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