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Alternative supports for catalysts preparation for low-temperature fuel cells using the alcohol reduction method

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Abstract

This work presents results with noble metal catalysts, Pt and Pt1Ru1 supported on Carbon Pearl with a high surface area of 1500m2g-1 and also in comparison with a comercial high surface area carbon powder Vulcan XC-72R and Vulcan XC72. The nanoparticles were synthesized following the Alcohol Reduction Method (Patent submitted-INPI-Brazil). X-ray Diffraction (XRD), Energy Dispersive Analysis by X-rays (EDAX) experiments were carried out to characterize the nanoparticles 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 the nanocatalysts.

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, platinum metallic is the most important electrocatalysts material employed. 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 (from

CABOT Company). According to CABOT Company, the only difference between the two materials is that the XC72 is in the pellets form, and XC72R is in powder form, but even this morphological difference can influence considerably the fuel cell performance. Because of the large surface area and the chemical stability, also the Carbon Pearl has been considered for several types of applications, including as a support material for electrocatalysts. In this study, the investigation results concerning electrochemical properties for electrocatalysts supported onto three different types of commercial supports: Vulcan XC72; Vulcan XC72R and Carbon Pearl are reported.

2. EXPERIMENTAL

2.1 Pt/C and Pt_1Ru_1/C electrocatalysts prepared by alcohol reduction process

The carbon supported electrocatalysts, Pt/C (20 wt%) and Pt_1Ru_1/C (20 wt%, Pt:Ru atomic ratio of 50:50) were prepared using the alcohol reduction method [13,14]. A mixture of the desirable metallic ions solution was used as precursor, where the ions were reduced to its metal forms, using ethylene glycol as solvent and reducing agent in the presence of the carbon support with high surface area, Carbon Vulcan XC-72R, Vulcan XC-72 and Carbon Pearl. 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 EDX DX-4 microanalyses. The XRD analyses were performed using a STOE STADI-P diffractometer with germanium monochromized Cu Kα radiation and a position-sensitive detector with 40 aperture in transmission mode. The catalysts were also examined by X-ray diffraction techniques (XDR) using a URD-6 Carl Zeiss-Jena diffractometer. The X-ray diffractograms were obtained with a scan rate of 1° min^{-1} and an incident wavelength of 1.5406 Å (KαCu). The XDR data were used to estimate the Pt lattice parameter and, using Scherrer's equation [8,9], the average crystallite size. Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [10-12]. An amount of 10mg of the electrocatalysts was added to 10 g of water. The mixture was submitted to an ultrasound bath for 5 min, where drops of a PTFE (Polytetrafluorethylen) suspension were added. Again, the mixture was submitted to an ultrasound bath for 5 min, filtered and transferred to the cavity (0.30mm deep and area with 0.36 cm^2) of the working electrode. By the cyclic voltammetry experiments, the current values (I) were expressed in amperes and were normalized per gram of platinum. The reference electrode was RHE (Reversible Hydrogen Electrode) and the counter electrode was a platinized Pt net with 4 cm^2. Electrochemical measurements were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a computer using the Microquimica Software. Cyclic voltammetry was performed in a 0.5 $molL^{-1}$ H_2SO_4 solution saturated with N_2. The evaluation of the 1 $molL^{-1}$ Methanol solution oxidation was performed at 25 °C in H_2SO_4 0.5 $molL^{-1}$. 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

The Pt:Ru atomic ratio of the obtained electrocatalysts using the EDX Analysis was very similar to that previously calculated before the preparation and the results are shown in Table 1. All of the electrocatalysts showed diffraction peaks at about $2\theta = 40$, 47, 67 and 82 o characteristic of the fcc structure of platinum and platinum alloys [15-17]. The broad peak at about $2\theta = 25$ o was associated with the carbon black used as support material. For Pt-Ru/C electrocatalysts, no other peaks of ruthenium hcp phase or ruthenium oxides were observed, Figure 2. The Pt:Ru atomic ratios of the electrocatalysts prepared by the alcohol reduction method were similar to the nominal atomic ratios. The average particle size may be estimated using the Scherrer equation applying the platinum peak (220) [9], the results are show in Table 1. The average particle sizes were in the range of 4.5 nm for Pt/C XC72, 4.9 nm for Pt/C XC72R and 5.6 nm for Carbon Pearl. These results show that the alcohol reduction method produces nanoparticles in the desirable size range for fuel cell applications.

Table 1

Pt:Ru atomic ratio (EDX analysis) and particles size (Scherrer Equation) of the prepared electrocatalysts

Electrocatalysts	Pt(wt.%)	Ru(wt.%)	Pt:Ru atomic ratio	Pt:Ru atomic ratio EDX	Particle size (nm) Scherrer*
Pt/Vulcan XC72 20%	20	-	-	-	4.5
Pt/Vulcan XC72R 20%	20	-	-	-	4.9
Pt/CarbonPearl 20%	20	-	-	-	5.6
Pt/C E-TEK 20%	20	-	-	-	2.8
Pt_1Ru_1/Vulcan XC72 20%	13.2	6.8	1:1	1:1	4.3
Pt_1Ru_1/Vulcan XC72R 20%	13.8	6.8	1:1	1:1	4.8
Pt_1Ru_1/CarbonPearl 20%	13.8	6.8	1:1	1:1.3	5.2
Pt_1Ru_1/C E-TEK 20%	13.8	6.8	1:1	1:1.1	1.5

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

Despite using XC72, XC72R or Carbon Pearl the results show a relatively high particle average size, around 5.6 nm. These results show also 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, showed in the table 1, 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 Figure 2.

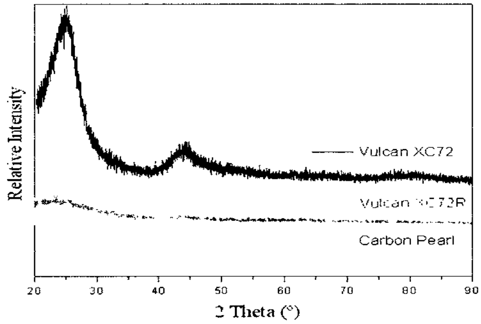
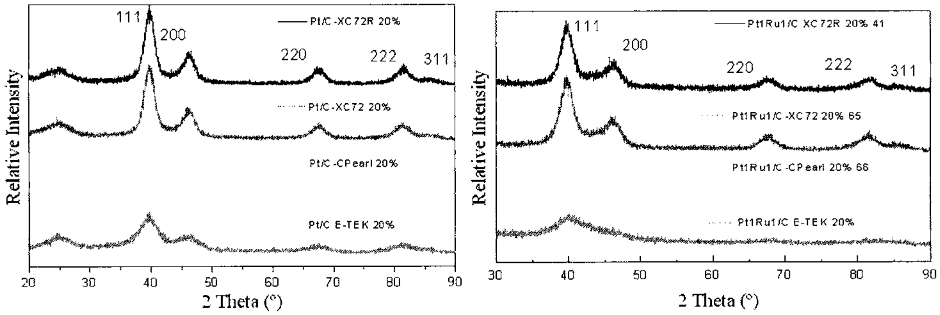


Figure 1: X-ray diffractograms of the different carbon support: Vulcan XC72, Vulcan XC72R and Carbon Pearl.

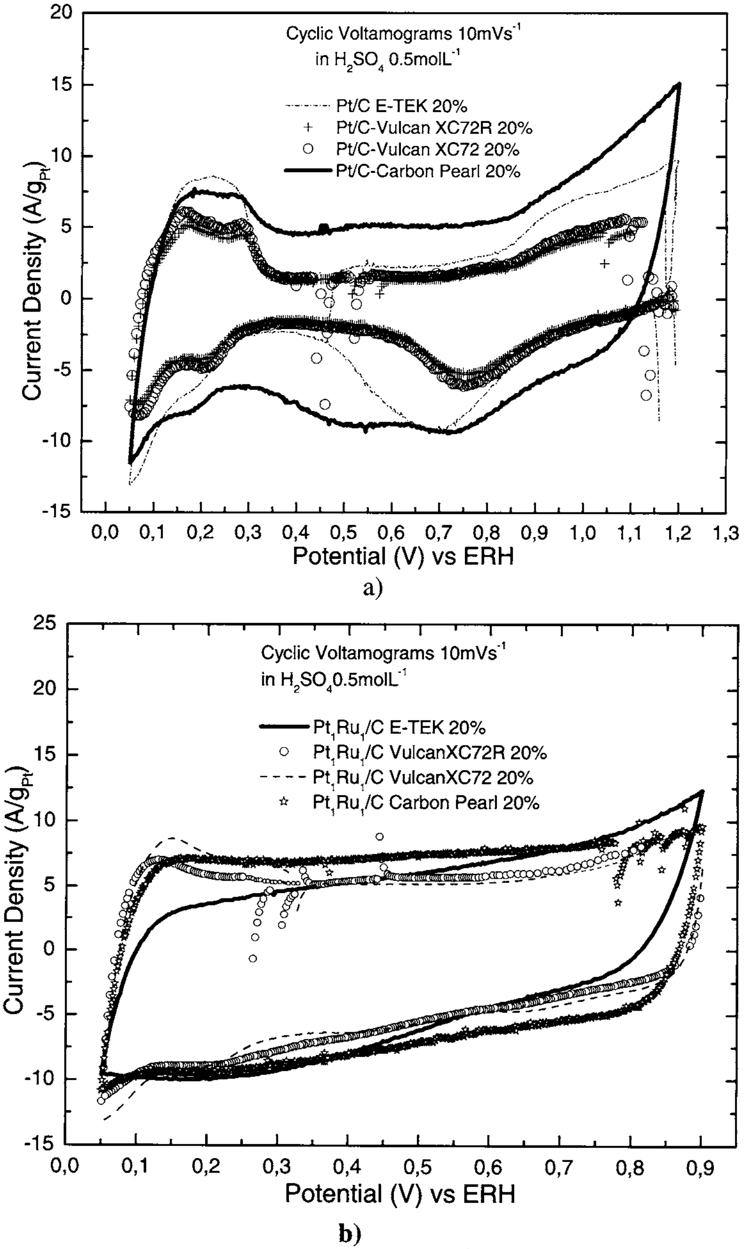


a) b)

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

3.2 Electrochemical results

The cyclic voltammograms (CV) performed in 0.5 mol L^{-1} H_2SO_4 of Pt/C 20 % and PtRu/C 20%, using different materials as support, are showed in figure 3. The cyclic voltammograms shows characteristics for each type of catalysts, Pt/C and PtRu/C [8]. The hydrogen UPD (Underpotential desorption) region (0.075 – 0.35 V vs RHE(Reversible Hydrogen Electrode)) in Pt catalysts is well defined, while for PtRu catalysts it is less defined, because the adsorption/desorption hydrogen peaks are not developed on Ru. The double layer region of the PtRu/C catalysts is larger than for Pt/C, both because of the presence of more oxygenated species and also of a larger surface area due to a smaller particle size. Furthermore, the performance of the PtRu/C catalysts, for methanol oxidation, shows a superior activity as compared to the Pt catalysts in the



a)

b)

Figure 3: Cyclic Voltammograms in H_2SO_4 0.5 mol L^{-1}, 10 mV s^{-1} for a) Pt and b) PtRu

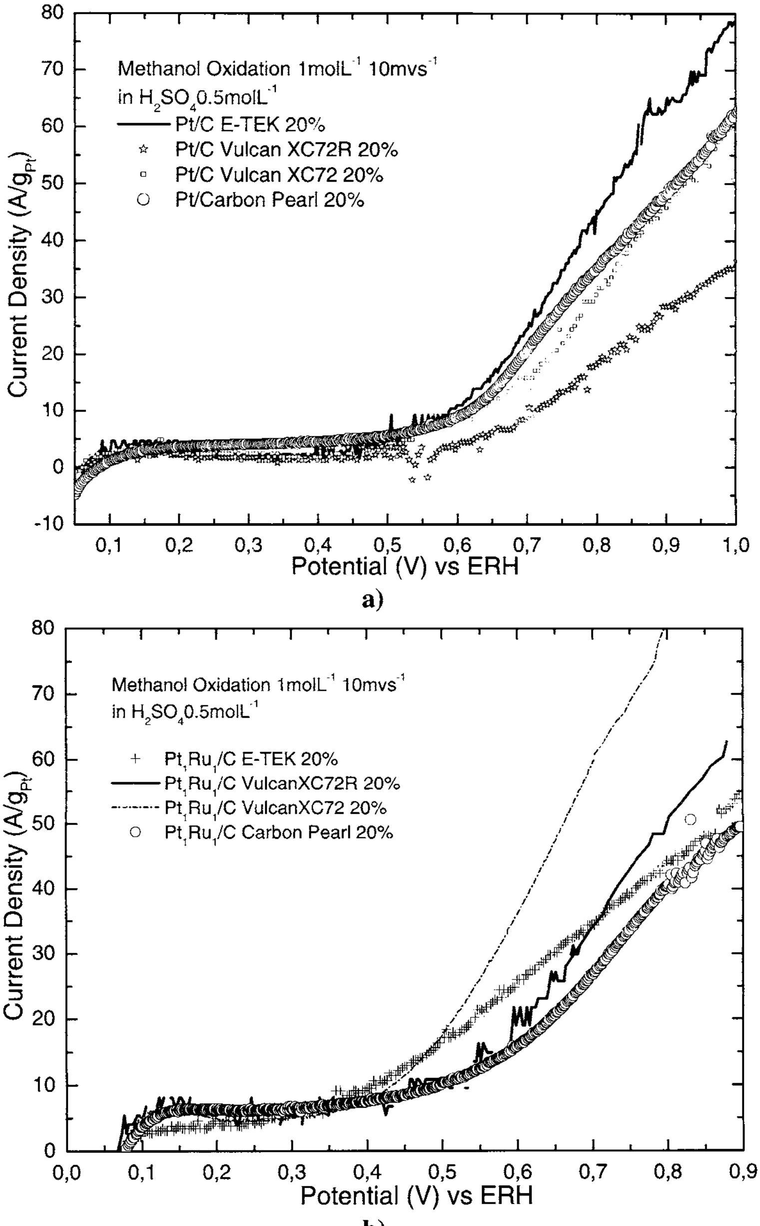


Figure 4: Anodic stripping for Methanol 1 mol L^{-1} oxidation in H_2SO_4 0.5 mol L^{-1} 10 mV s^{-1}, for a) Pt and b) PtRu

investigated potential range (between 0.4 and 0.55 V). This better performance of the PtRu-alloy catalysts was explained by a functional mechanism [19,20] for oxidation of CO-containing intermediates (referred to as CO_{ad}) on PtRu surfaces.

However, due to the higher affinity of Ru towards oxygen-containing species [21], sufficient amounts of OH_{ad}, to support reasonable CO oxidation rates, are formed at lower potencials (above=0.35 V) on Ru sites than on Pt sites (above 0.55 V). This effect leads to higher activities for the overall methanol oxidation process on PtRu compared to Pt. At higher potentials ($E \geq 0.55$ V), pure Pt becomes more active than PtRu, but this potential region is irrelevant for DMFC (Direct Methanol Fuel Cell) 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. Figure 4a shows also that the best result for methanol oxidation was obtained using the commercial material from E-TEK, and considering only the materials prepared upon Vulcan XC72, Vulcan XC72R, one can see that the best result was achieved using the Carbon Pearl support. Before this experiment was carried out, good results with Carbon Pearl were expected, because of its high surface area. However, the results showed here suggest that the Alcohol Reduction Method was not able to produce well dispersed nanoparticles onto the high surface area of the Carbon Pearl, or that the porous of the support is smaller than the metal ions, so the internal surface of the carbon support porous can not be achieved by the metal ions. Figure 4b showed in the range of 0.6 – 1.0 V, that the best result for methanol oxidation was obtained using the carbon support Vulcan XC72. Due to the high conductivity properties of the XC72, proved by the XDR measurements, Figure 1. The results showed that the Alcohol Reduction Method was suitable to be used for the PtRu catalyst, applied to this material as a support.

4. CONCLUSION

The work presented shows 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, 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 Suport, 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 CO_{ads} oxidation. At higher current densities, an increasing consumption of methanol is required, being this mass transport the determining step of the MOR.

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