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Enhanced activity observed for sulfuric acid and chlorosulfuric acid functionalized carbon black as PtRu and PtSn electrocatalyst support for DMFC and DEFC applications

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ABSTRACT

In this study, carbon black Vulcan XC72 was successfully functionalized in an autoclave with sulfuric acid (SA) and Chlorosulfuric acid (C-SA). The functionalized carbons were then used as supports to prepare PtRu/C and PtSn/C electrocatalysts by an alcohol-reduction process. Physical characterization was performed by BET, LS, XRD, EDX, and TEM. The electrochemical characterization showed that the catalysts supported on functionalized carbons exhibited better performance for alcohol oxidation if compared to those using unfunctionalized supports. The observed better performance can be mainly attributed to the easier access with protons (higher ionic transport), better wettability (higher water uptake), and better distribution of the nanoparticles over the support (higher platinum utilization); indicating that sulfonation is an efficient approach to functionalize, improve performance, and reduce costs of fuel cell catalysts.

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1. Introduction

Ethanol offers an attractive alternative as a fuel in low temperature fuel cells because of its lower toxicity than methanol [1]. Moreover, ethanol is produced in large quantities from agricultural products by fermenting biomass [2]. However, its complete oxidation to CO₂ is more difficult than that of methanol due to the difficulties in C–C bond breaking and the formation of intermediates that poison the platinum anode catalysts [3–5]. Hence, the search of novel

electrocatalysts there are more actives is still an essential goal in the current development of direct alcohol fuel cells. In recent years, PtRu nanoparticles deposited on a carbon black support have become a common catalysts for the electro-oxidation of methanol and carbon monoxide-containing hydrogen feeds for low temperature fuel cell applications [6–10]. Also, many studies have indicated that the modification of Pt catalysts by introducing Sn [3–5,11–17] can lower the onset potential for ethanol oxidation, compared to pure Pt. It is becoming a consensus in the literature that the best

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binary catalyst for the ethanol oxidation reaction (EOR) in acidic environment is not PtRu (as for methanol oxidation) but PtSn [3–5,11–17].

The enhancements of the carbon support properties have been also pursued and are considered to be crucial [18–20]. Previous studies have shown that Pt or PtRu supported on functionalized carbon blacks exhibit improved performance for the electrooxidation of methanol over that supported on standard carbon black (e.g., Vulcan XC-72) [18–26]. Nevertheless, further studies on the functionalization of carbon supports still need to be conducted, especially considering the fact that the impact of the chemical and physical properties of functionalized carbon supports on the fuel cell performance is not yet sufficiently understood. For instance, oxygen-containing surface groups can influence the wettability and adsorptive behavior of the carbon surface, which can directly affect the electrocatalytic properties of the carbon support [18,27,28]. The contact interface between the supported metal nanoparticles and the Nafion[®] ionomer micelles in the catalyst layer can be strongly affected by the carbon pore size and its distribution. As reported by Uchida et al. [29], the Nafion[®] ionomer has micelles of about 40 nm in size. Hence, if metal catalyst nanoparticles are deposited into carbon pores with diameters below 40 nm, the nanoparticles will have no contact to the Nafion[®] ionomer (to form a triple-phase boundary) and therefore they will not contribute to the total catalytic activity. Consequently, catalytic utilization of the metal nanoparticles is determined by electrochemical accessibility and not just by the carbon surface area. Recently, Rao et al. investigated the effect of carbon porosity on PtRu/C specific activity for methanol oxidation [30]. They have found that for carbon black with a large concentration of small diameter pores (pores < 20 nm and filled with metal nanoparticles); the contact between the Nafion[®] micelles and the metal nanoparticles can be very poor, resulting in a low methanol oxidation activity. They concluded that an increase in the carbon surface area did not increase the catalytic activity.

Several studies have also been focused on enhancing the catalyst utilization in the PEFC electrodes by extending the so-called triple-phase boundaries [20,31–36]. Among them, sulfonation of carbon materials [22,37–40] and its use as a support for catalysts as mixed electronic and protonic conductors has been demonstrated to be an efficient way to improve the structure of the triple-phase boundaries. In our previous work [20], we have already demonstrated that the grafting of carbon black with polystyrene sulfonic can enhance Pt utilization, increase proton conductivity, and overall improve the triple-phase boundary in the catalytic layer. It is also already observed that less Nafion[®] ionomer is required within the catalyst layers when a sulfonated support is used [41,42]. The compatibility between the Nafion[®] ionomer and the functionalized carbon support is anticipated to improve significantly, due to the presence of sulfonic groups grafted onto the carbon surface.

Nevertheless, it is still necessary to investigate if an easy one step method of carbon support sulfonation/functionalization would be efficient to produce the same effect in the triple-phase boundary of a catalyst for alcohol fuel cell applications. It is also worthy to investigate the use of

chlorosulfuric acid, which is a very powerful sulfonation agent [43], and see whether it could produce electrocatalysts with higher activities. In the present investigation we report how the performance for methanol or ethanol electrooxidation is improved using PtRu and PtSn nanoparticles deposited on a carbon black support pretreated with sulfuric acid (SA) or chlorosulfuric acid (C-SA).

2. Experimental

A commercial carbon black Vulcan XC72 (Cabot Co.) was chemically treated with concentrated sulfuric acid (H₂SO₄) or concentrated chlorosulfuric acid (HSO₃Cl) in a stainless steel autoclave reactor, with an internal PTFE case. The treatment was performed at 180 °C, for 24 h. The functionalized/sulfonated H₂SO₄ or HSO₃Cl carbon black was filtered, washed until pH neutral and dried at 110 °C overnight. Carbon black functionalized with H₂SO₄ or HSO₃Cl was labeled C-SA and C-CSA, respectively.

Carbon-supported electrocatalysts with 20 wt% metal loading were prepared by an alcohol-reduction process [44]. In a typical procedure, H₂PtCl₆·6H₂O (Aldrich) and RuCl₃·2H₂O (Aldrich) or SnCl₂·2H₂O (Aldrich) were dissolved in ethylene glycol:water (75:25) and the carbon support was added. The resulting mixtures were treated in an ultrasonic bath for 5 min and were refluxed for 3 h under open atmosphere. The mixtures were filtered and the solid was washed with water and dried at 70 °C for 2 h. PtRu/C (20 wt%, Pt:Ru atomic ratio of 1:1) and PtSn/C (20 wt%, Pt:Sn atomic ratio of 3:1) commercial electrocatalysts from BASF were used for comparative purposes.

A NOVA 300 Brunauer–Emmett–Teller (BET) analyzer was used to determine the specific surface area of the carbons. Prior to measurement, the carbon samples were purged with pure nitrogen gas overnight at 150 °C to remove any contaminants and moisture in the carbon material.

A Light Scattering LS230 Small Volume Module Plus – Coulter was used to estimate the average particle size of the carbon particles. Before measurement, 5 mg of the sample was dispersed in MilliQ water and ultrasonically dispersed for 48 h.

The Pt:Ru atomic ratios of the electrocatalysts were evaluated using a Philips XL30 scanning electron microscope coupled to an EDAX DX-4 microanalyser with a 20 keV electron beam.

The X-ray diffraction (XRD) analyses were performed using an STOE STADI-P diffractometer with germanium monochromized Cu K α radiation and position-sensitive detector with 40° aperture in transmission mode. The X-ray diffraction patterns were collected with a scan rate of 1 degree min⁻¹ and an incident wavelength of 1.5406 Å (CuK α). The average crystallite size was estimated using the XRD data and the Scherrer equation [45,46].

Transmission electron microscopy (TEM) investigations were carried out with a Jeol JEM-2100EX transmission electron microscope equipped with LaB₆ cathode operating at 200 kV acceleration voltage. Powder samples were prepared by dispersing the catalyst powders in isopropyl and depositing a drop of the dispersion onto a standard holey carbon film-

covered copper grid. Average particle sizes and particle size distributions were obtained for all samples using the software LINCE. At least 300 particles of each image were counted to obtain the average particle size.

Electrochemical studies of the electrocatalysts were carried out by using the thin porous coating technique [4]. An amount of 10 mg of the electrocatalysts was added to 20 g of water. The mixture was sonicated for 5 min, and three drops of a 6% PTFE (polytetrafluoroethylene) water suspension were added. Again, the mixture was sonicated for 5 min, filtered and transferred to the working electrode support cavity (0.30 mm deep and area of 0.36 cm²). In the cyclic voltammetry (CV) results, the current values were expressed in ampere and were normalized per gram of platinum (Ag_{Pt}^{-1}). The reference electrode was an SHE (standard hydrogen electrode) and the counter electrode was platinized Pt gauze with a geometric area of 4 cm². Electrochemical measurements were taken using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat and using the Microquimica Software. Cyclic voltammetry was performed in a 0.5 mol L⁻¹ H₂SO₄ solution saturated with N₂. The evaluation of the 1.0 mol L⁻¹ methanol and 1.0 mol L⁻¹ ethanol oxidation was performed at 25 °C in 0.5 mol L⁻¹ H₂SO₄.

Inks for the anode catalyst layers were typically prepared with a ratio of 75 wt% of the PtRu/C or PtSn/C catalyst and 25 wt % Nafion® solution (Aldrich, 5 wt% in lower aliphatic alcohols and water) and dispersed in a suitable solvent mixture. The typical anode solution consisted of 50.3 mg catalyst, 382.9 µL of Nafion® solution, and 3.0 ml of methanol. Inks were sonicated for 30 min then stirred with a micro stir bar for an additional 30 min. Inks for all cathodes were prepared with 20 wt% Pt/C BASF, 25 wt% Nafion®, dispersed in a 50:50 mixture of isopropyl alcohol and water. The inks were applied using the inkjet printing (IJP) technique [47] with a commercial printer Lexmark Z715. The Pt loading was 0.50 mg_{Pt} cm⁻² for all anodes and cathodes. Carbon paper (Toray) EC-TP1-060T was cut into 5 cm² squares and used as a gas diffusion layer (GDL). The fabricated electrodes were placed in an oven for final bake out at 180 °C for 1 h to dry any residual solvent.

Nafion® 117 (Dupont) membranes were cleaned using the following procedure: to remove organic impurities and to obtain the H⁺ form for use in the PEMFC, the membranes were pretreated by boiling in deionized water for 1 h, rinsing in cold deionized water for 30 min, boiling in 0.5 mol L⁻¹ H₂SO₄ solution for 30 min, and boiling twice in DI water for 30 min. The membranes were subsequently stored in DI water until ready for use.

The MEAs were made by hot pressing an anode, electrolyte membrane, and cathode in a heated press set at 125 °C for 2 min at a pressure of 5 tons. The MEAs were conditioned overnight until a steady state current was achieved at a potential of 0.6 V. In the polarization test, methanol/ethanol and oxygen at flow rates of 12 mL min⁻¹ and 200 SCCM, respectively, were fed to the anode and the cathode. Oxygen was passed through a humidifier (operated at 90 °C), before they entered the MEA. A single homemade cell with graphite serpentine channels was tested in a DMFC/DEFC test station. The polarization curves were plotted as cell voltage against steady state current. The temperature of the fuel cell was 80 °C.

Table 1 – Light scattering (LS) particle size and BET surface area analysis obtained for the carbons support.

Carbon black	LS particle size (µm)	BET area (m ² g ⁻¹)
Vulcan XC72	14.9	241
Vulcan XC72 + H ₂ SO ₄	12.06	175
Vulcan XC72 + HSO ₃ Cl	10.22	184

3. Results

The functionalization of carbon materials with sulfonic groups has previously been demonstrated and well characterized by other groups as already discussed above [34–36,41]. Using infra-red spectroscopy, these studies confirmed the nature and presence of sulfonic groups on the surface of the sulfonated carbon materials after sulfuric acid treatment. The FTIR absorption peaks were ascribed to the functional sulfonic groups on the surface of the carbon materials, which therefore verifies that they were successfully grafted using methods similar to the one described in this manuscript. The density of the SO₃H groups were already also estimated based on the sulfur content determined from elemental analyses, and the total amount of functional groups can be determined using conventional titration techniques [35,41].

X-ray photoelectron spectroscopy (XPS) analysis has also been conducted to verify the chemical state of sulfur in sulfonated carbon and it was already verified and observed to be denoted as SO₃H group [40]. Using TGA and/or DSC analysis for the sulfonated carbon materials, these studies also showed more significant weight losses over the raise in temperature, which can be ascribed to the loss of terminal groups such as –OH, CO, –COOH, and –SO₃H at the defective sites of the carbon surface, confirming the successful introduction the sulfonated groups. It is noteworthy that the functional groups should be stable up to around 150 °C, below fuel cell operating temperatures [48].

Table 1 shows the surface area results of the functionalized carbons. After H₂SO₄ and HSO₃Cl functionalization, it is shown that the surface area of the carbon black is reduced. We have shown previously [18,19] that oxidative chemical treatments significantly decrease the surface area of carbon black. Chen and Wu [49] have shown a reduction in the surface area of carbons after dilute HNO₃ treatment. They have also shown that organic acids with larger molecule sizes better penetrate the carbon structure, resulting in pore blockage. As also

Table 2 – Pt:Ru and Pt:Sn atomic ratio (EDX analysis), particles size (from DRX and TEM), for the prepared electrocatalysts.

Electrocatalysts	Pt:Ru/PtSn atomic ratio	Particle size (nm) XRD	Particle size (nm) TEM
PtRu/C E-TEK	50:50	<2	2.8
PtSn/C E-TEK	52:48	<2	2.9
PtRu/C-SA	52:48	3.5	3.7
PtRu/C-CSA	51:49	3.3	3.8
PtSn/C-SA	53:47	3.6	3.9
PtSn/C-CSA	52:48	3.3	3.2

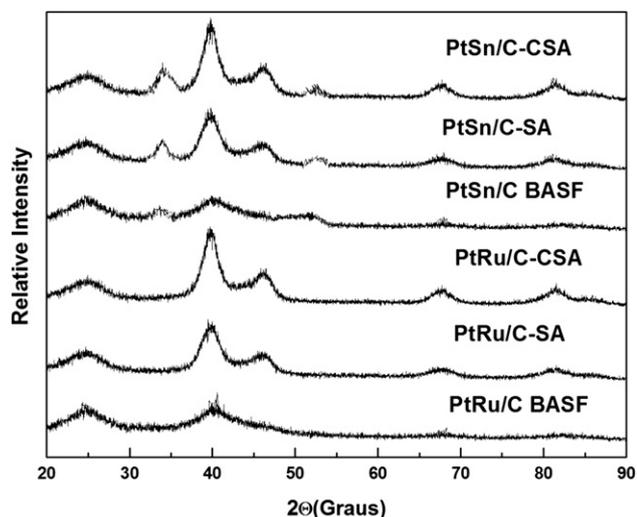


Fig. 1 – XRD patterns of PtRu/C-BASF, PtRu/C-SA, PtRu/C-CSA, PtSn/C-BASF, PtSn/C-SA and PtSn/C-CSA. Marcelo Carmo et al.

indicated in the literature [50–53], oxidation treatments produce a large amount of oxygenated groups (carboxylic, hydroxyl, lactones, etc.) on the carbon black surface. These groups are able to change the acid–base characteristics of the carbon black and can also modify its pore structure. Carbon micropores that are filled with metal catalyst are undesirable as they restrict the access of the fuel cell reactants to the catalysts active sites, resulting in waste of noble catalysts. Some authors [50–53] have reported similar restrictions for diffusion in micropores of carbon black after other chemical treatment. Thus, the decrease of the surface area after H_2SO_4 and HSO_3Cl functionalization could be attributed to the blockage of the micropores.

Table 1 shows the average of the carbon particle size in water media, determined by light scattering (LS). A reduction in the average particle size of carbon black dispersed in DI water is obtained. After functionalization, the carbon black became much more hydrophilic and consequently, the dispersion or the wettability of the carbon black in water is facilitated. The particle size of the functionalized carbon is significantly smaller than the carbon black without functionalization, thus indicating a beneficial behavior in terms of

electrocatalyst preparation, as well as for the final MEA preparation, using electrocatalyst inks. It is suggested, that the capability to keep the high moisture content is critical for proton conductivity of the in the triple-phase boundary in the catalyst layer. The LS results suggest that the water uptake of the functionalized carbon is significantly higher than the water uptake for the unfunctionalized sample. The higher water uptake is due to the sulfonic acid groups presented in the functionalized sample. We have also observed that, before sulfonation, the carbon black does not mix well with deionized water but it becomes more hydrophilic upon sulfonation.

The EDX results of the PtRu/C and PtSn/C electrocatalysts prepared by an alcohol-reduction process using the functionalized carbons as supports are shown in Table 2. The Pt:Ru and Pt:Sn atomic ratios of the electrocatalysts are very close to the desired nominal values. For the prepared catalysts, at the end of the preparation and separation of the solids (PtRu/C and PtSn/C electrocatalysts) by filtration, the reaction media became colorless suggesting that Pt (IV), Ru (III) and Sn (II) ions were completely reduced. To confirm this assumption, a qualitative test using potassium iodide [54] did not detect Pt ions in the filtrates, which suggest that all Pt (IV) ions were reduced to its metallic form. Since Pt ions were not detected in the filtrates and the obtained Pt:Ru and Pt:Sn atomic ratios were similar to the nominal ones (Table 2), it was considered that all electrocatalysts were obtained with 20 wt% of metal loading.

Fig. 1 shows the X-ray diffraction patterns for the prepared catalysts. In all cases, the broad peak at about $2\theta = 25^\circ$ is associated with the carbon support material. For PtRu/C and PtSn/C electrocatalysts were observed in the diffractograms (four peaks at approximately $2\theta = 40^\circ, 47^\circ, 67^\circ$ and 82°) which are associated with the Pt (111), (200), (220) and (311) planes, respectively, characteristic of a Pt face-centered cubic (fcc) structure [36,37]. No peaks of metallic Ru or Ru oxides were observed for the prepared PtRu/C electrocatalysts. However, the presence of these phases should not be ruled out. On the other hand, the diffractograms of the PtSn/C electrocatalysts show two peaks at $2\theta = 34^\circ$ and 52° that were identified as a SnO_2 phase. The average particle size, can be estimated from the Scherrer equation, using the platinum peak (220) [45]. The XRD results show that alcohol-reduction process produces nanoparticles (around 3 nm) in the desirable size range for fuel cell applications (Table 2). Recently, Xin et al. [32] described the preparation of SnO_2 nanoparticles by heating ethylene

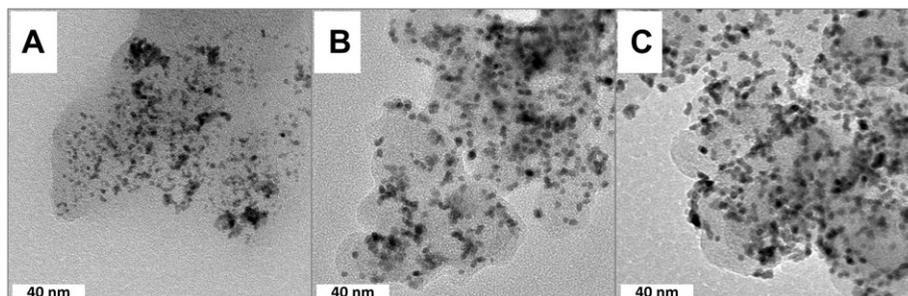


Fig. 2 – TEM micrographs for A) PtRu/C-BASF, B) PtRu/C-SA and C) PtRu/C-CSA. Marcelo Carmo et al.

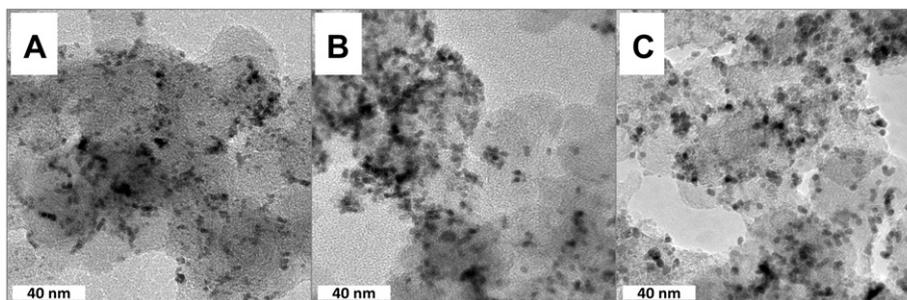


Fig. 3 – TEM micrographs for A) PtSn/C-BASF, B) PtSn/C-SA and C) PtSn/C-CSA. Marcelo Carmo et al.

glycol solutions containing SnCl_2 . Our synthesis method is similar to the procedures used by Xin et al. and yielded comparable particle sizes ca. 3 nm (Table 2). The PtRu/C and PtSn/C from BASF have a smaller crystallite size compared to the synthesized PtRu/C and PtSn/C electrocatalysts. The TEM micrographs of the PtRu/C and PtSn/C electrocatalysts are shown in Figs. 2 and 3, respectively. The micrograph of the commercial PtRu/C-BASF (Fig. 2a) revealed many agglomerates and a non-uniform particle distribution. For PtRu/C-SA (Fig. 2b) and PtRu/C-CSA (Fig. 2c) electrocatalysts the micrographs revealed a more homogenous and uniform particle distribution. The micrograph of the commercial PtSn/C-BASF (Fig. 3a) also reveals many agglomerates and a non-uniform particle distribution. A relatively homogenous and uniform particle distribution were also observed for PtSn/C-SA (Fig. 3b) and for PtSn/C-CSA (Fig. 3c) electrocatalysts.

Figs. 4–10 present the electrochemical characterization for all prepared catalysts. Our previous work have indicated that, PtRu and PtSn supported on Vulcan XC72 and prepared using the same method used for this manuscript, have presented similar results compared to commercial PtRu/C-BASF and PtSn/C-BASF [44,55]. This excludes the necessity to discriminate between the effect of the synthetic method and the effect obtained from the functionalization. In this case we can assure that only one parameter (the nature of the carbon support) has changed. Fig. 4 shows the voltammograms in 0.5 mol L^{-1} sulfuric acid and Fig. 5 shows the linear sweep voltammograms for 1.0 mol L^{-1} methanol oxidation in

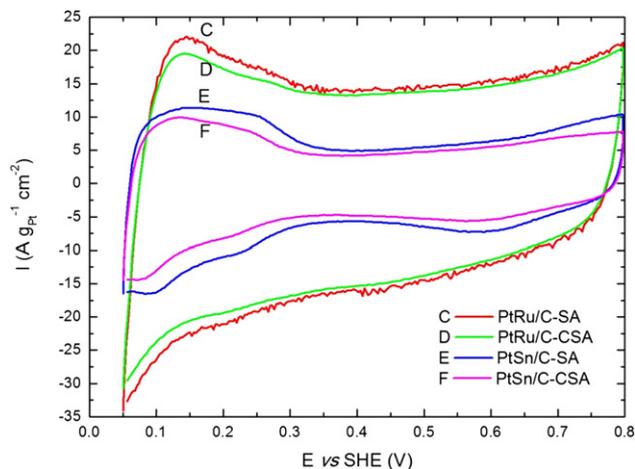


Fig. 4 – Cyclic voltammograms in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, scan rate: 20 mV s^{-1} . Marcelo Carmo et al.

0.5 mol L^{-1} sulfuric acid for PtRu/C-BASF, PtRu/C-SA and PtRu/C-CSA catalysts. The voltammograms (Fig. 4) of the PtRu and PtSn electrodes show that although the double layer was relatively thick due to Ru or Sn content, hydrogen adsorption and desorption peaks were clearly shown between 0.05 and 0.4 V. A distinct point is that electrochemical surface area (ECSA) using the hydrogen desorption potential region (UPD) cannot be measured for PtRu or PtSn. This is attributed to the fact that hydrogen does not adsorb on oxygenated saturated Ru or Sn atoms at this UPD potential region (0.05–0.4 V) [9]. As can be seen from the anodic scans in Fig. 5, the shape of the oxidation curves for the catalysts supported on functionalized carbon black is different from that of the PtRu/C-BASF. The onset potential for the methanol oxidation reaction was (in order of increasing onset potential) PtRu/C-SA < PtRu/C-CSA < PtRu/C-BASF. For the PtRu/C-SA and PtRu/C-CSA catalysts, the j/E curve slowly increases up to 0.5 V, then a fast increase takes place. For the PtRu/C, instead, a slow increase of the j/E curve occurs up to ca. 0.5 V, then a slower increase can be observed up to 0.8 V. For potentials up to 0.8 V, the current density of methanol oxidation on the PtRu/C-SA catalyst was the highest. The PtRu/C electrocatalyst performances for methanol oxidation were also evaluated by chronoamperometry in 1.0 mol L^{-1} of methanol in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at a given anodic potential of 0.5 V vs. SHE (Fig. 6). The current values were normalized per gram of platinum,

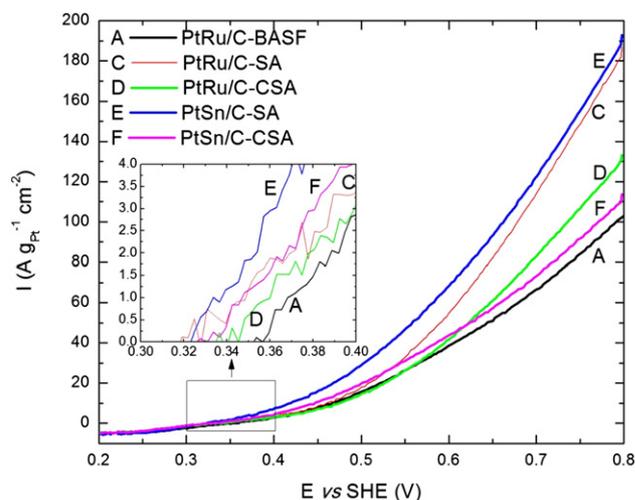


Fig. 5 – Linear sweep voltammograms for 1.0 mol L^{-1} methanol oxidation in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, scan rate: 20 mV s^{-1} . Marcelo Carmo et al.

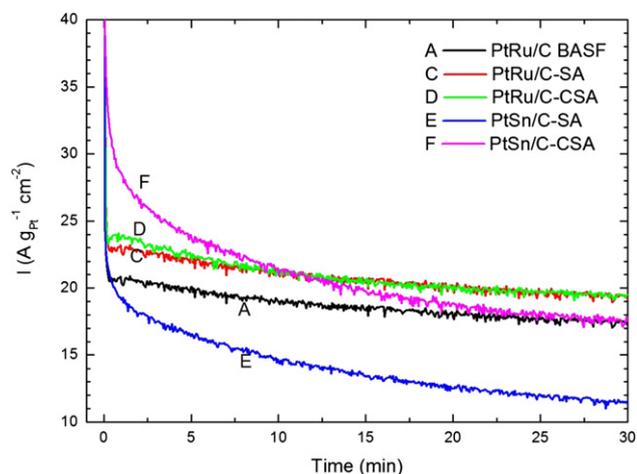


Fig. 6 – Chronoamperometry profiles for 1.0 mol L^{-1} methanol oxidation in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Marcelo Carmo et al.

considering that methanol adsorption and dehydrogenation occur only on platinum sites at room temperature [4]. In all current–time curves there was an initial current drop in the first minute (possibly due to the changing current), followed by a slower decay. The current values obtained for PtSn/C-CSA electrocatalysts were higher up to 10 min. After 10 min the PtRu/C-SA and PtRu/C-CSA present higher current activities than those obtained with the other electrocatalysts.

Cyclic voltammograms (anodic scans) of ethanol electro-oxidation on PtRu and PtSn electrocatalysts supported on the functionalized carbon blacks are shown in Fig. 7. Hydrogen adsorption (0–200 mV vs. SHE) was inhibited due to the adsorption of ethanol. The ethanol oxidation current increased slowly in the double layer regime (200–600 mV vs. SHE). The oxidation current peak occurred at 800 mV (vs. SHE). After 800 mV, the current decreases, which is due to the oxidation of Pt on the surface leading to the decrease in the number of active sites. This behavior can be explained by the

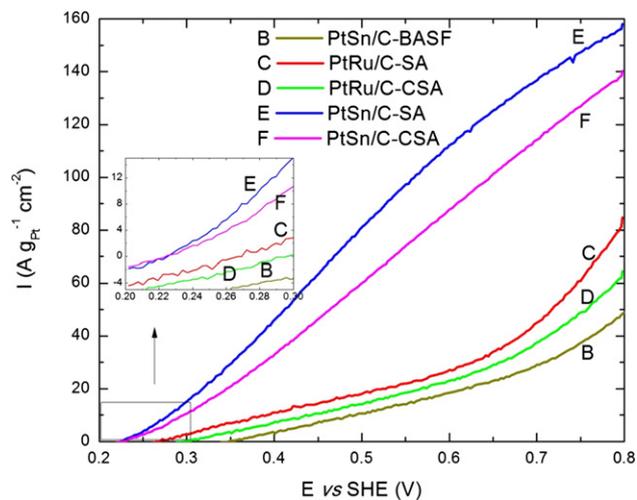


Fig. 7 – Linear sweep voltammograms for 1.0 mol L^{-1} ethanol oxidation in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, scan rate: 20 mV s^{-1} . Marcelo Carmo et al.

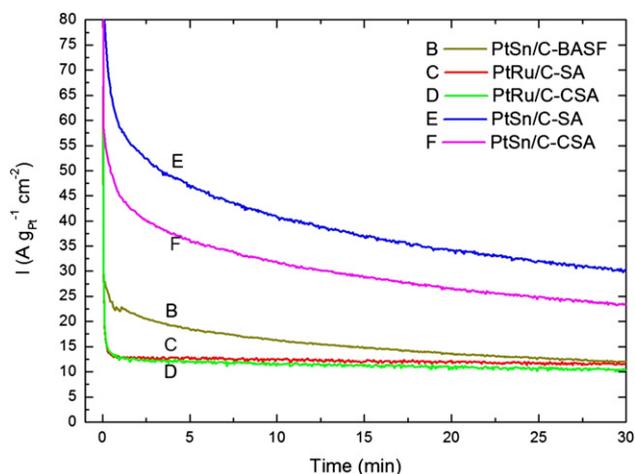


Fig. 8 – Chronoamperometry profiles for 1.0 mol L^{-1} ethanol oxidation in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Marcelo Carmo et al.

fact that the ethanol oxidation reaction could occur on the surface of Pt oxide at such a high potential. In the negative scan, the active sites recovered due to the reduction of Pt oxide on the surface to produce the oxidation current peak. However, we present just the potential where the oxidation begins up to the current peak (anodic sweep) for clear presentation purposes. From Fig. 7, the ethanol oxidation reaction started at 235 mV for PtSn/C-SA and PtSn/C-CSA, at 280 mV for PtRu/C-SA, at 300 mV for PtRu/C-CSA and at 350 mV for PtSn/C-BASF. Fig. 7 also shows higher current activities for PtSn/C-SA and PtSn/C-CSA in the whole swept range, indicating that the best catalysts for ethanol oxidation reaction were PtSn/C-SA and PtSn/C-CSA. To compare the potentiostatic behavior of the prepared catalysts, chronoamperometry measurements for ethanol oxidation at 0.5 V were carried out at room temperature and the results are shown in Fig. 8. It can be seen that the currents for ethanol oxidation on the PtRu catalysts dropped rapidly at first and then became relatively stable. For the PtSn catalysts the drop is also fast, but the results also show that the steady state

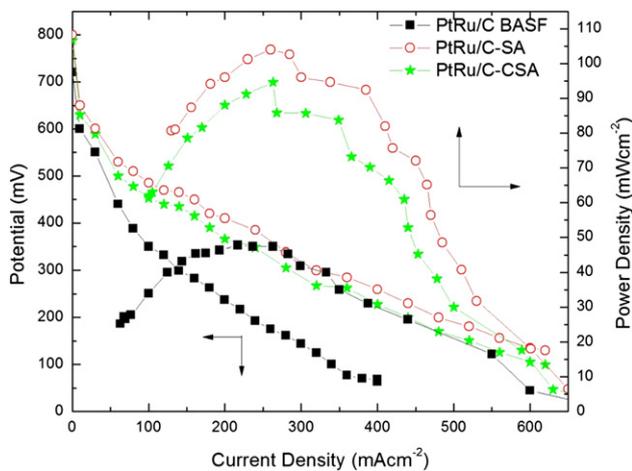


Fig. 9 – Polarization curves of the prepared MEAs working with methanol/ O_2 . Marcelo Carmo et al.

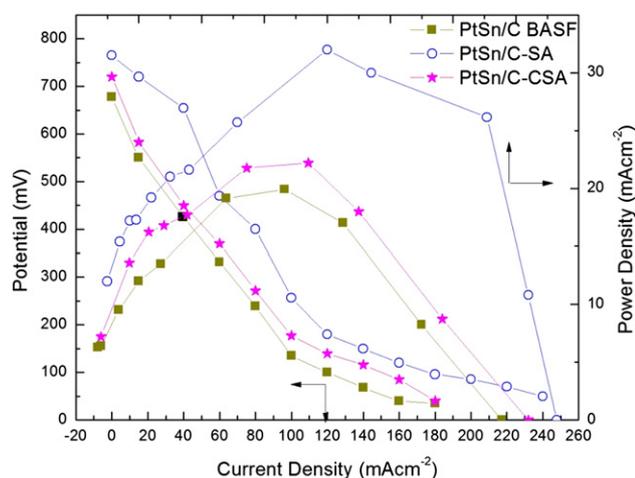


Fig. 10 – Polarization curves of the prepared MEAs working with ethanol/O₂. Marcelo Carmo et al.

current density for the ethanol oxidation reaction on binary PtSn is considerably larger than those on binary PtRu catalysts. The superior performance regarded to the use of PtSn alloys for ethanol oxidation is attributed to the synergic effect of Sn as a water activator (bifunctional mechanism), and because Sn is generally recognized as a good catalyst for C–C cleavage [12,14]. The decrease in the ethanol oxidation reaction activity over time could be ascribed to the decrease of the lattice parameter, as discussed by Antolini et al. [17].

Fig. 9 shows a series of cell polarization curves using 1.0 mol L⁻¹ methanol solution as fuel and oxygen as oxidant. As can be seen from Fig. 9, the polarization curves exhibit better performances for PtRu/C-CSA and PtRu/C-SA. The maximum power density of the cell reaches 110 mW cm⁻² at a voltage of 0.250 V. The PEMFC polarization curves and power density curves, working with ethanol and oxygen are shown in Fig. 10. The PtSn/C-SA achieves a maximum power density of 33 mW cm⁻² g_{metal}⁻¹. The PtSn/C-CSA catalyst achieves 25 mW cm⁻² g_{metal}⁻¹. The PtSn/C-BASF achieves 20 mW cm⁻² g_{metal}⁻¹. The polarization curves in Figs. 9 and 10 reveal improved performance of the electrocatalyst supported on functionalized carbon black.

The polarization curves (Figs. 9 and 10) also reveal improved performance of the electrocatalyst supported on sulfonated carbon black in the region dominated by ohmic drop. The slope of the polarization curves for the catalysts supported on the functionalized carbon is significantly lower (DMFC) than that recorded for the MEA based on commercial catalyst. This can be attributed to better proton transfer compared to that for the non-functionalized material.

Overall, the increase in the current density, stability, and fuel cell performance for the particles supported on the functionalized carbons can be ascribed to a better structural arrangement of the triple-phase boundary (nanoparticles, carbon, and ionomer) in the catalytic layer. The characteristics of the triple-phase boundary are improved. In other words, these results suggest that the functionalized catalysts have better catalytic activity due to better particle distribution (higher platinum utilization), higher water uptake (wettability), better proton transport, less platinum agglomeration

(stabilization of the particles by the functional groups), and higher resistance to poisoning. However, at this stage, it is difficult to conclude why sulfuric acid functionalization seems to give better results compared to chlorosulfuric acid functionalization, and further studies might still be necessary to clarify this question. The chemical stability of the oxygenated groups on the carbon black surface over longer periods of time (fuel cell durability studies) is also an important issue that still needs to be considered and is suggested for further investigations.

4. Conclusions

BET results show that the specific surface area of the carbon support after functionalization is reduced. The TEM images reveal a more homogeneous and uniform particle distribution for PtRu or PtSn supported on the functionalized materials. The improvement in electrocatalytic activity of PtRu and PtSn supported on the functionalized carbon blacks could be attributed to a better particle distribution (higher platinum utilization), higher water uptake (wettability), better proton transport, less platinum agglomeration (stabilization of the particles by the functional groups), and higher resistance to poisoning; indicating that sulfonation is an efficient approach to functionalize, improve performance, and reduce costs of fuel cell catalysts. The experiments in DMFC and DEFC showed that the prepared PtRu/C and PtSn/C electrocatalysts with functionalized supports were more active compared to catalysts supported on conventional carbon black for methanol and ethanol oxidation, respectively.

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