GRAFT POLYMERIZATION OF SULFONATED STYRENE FROM CARBON BLACK SURFACE AND ITS USE AS ELECTROCATALYSTS SUPPORT FOR PEMFC AND DMFC APPLICATIONS

Marcelo Carmo[a,b,*], João Guilherme Rocha Poco[a], Marcelo Linardi[b]

[a]Technological Research Institute of São Paulo State - IPT, São Paulo,05508-901,Brazil
[b]Energetic and Nuclear Research Institute – IPEN, São Paulo,05508-000,Brazil

*Corresponding author: +00551137674922, marcelocarmo1@gmail.com

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Abstract

The objective of this study is to graft the carbon support surface by chemically introducing polymer chains (Nafion® like) with proton conducting properties. It enables a better interaction of the proton-conducting phase with the metallic catalyst particles, hinders posterior support particle agglomeration and prevents loss of active surface. The proton conduction between the active electrocatalyst site and the Nafion® ionomer membrane enhances thus diminishes the ohmic drop in the polymer electrolyte membrane fuel cell. PtRu nanoparticles are anchored on the carbon support by the impregnation method and direct reduction with ethylene glycol and characterized using amongst others FTIR, XRD and TEM. The screen printing technique is used to produce membrane electrode assemblies (MEA) for single cell tests in H_2/air (PEMFC) and methanol operation (DMFC). The PEMFC measurements indicate that PtRu supported on grafted carbon has a power density of 550 $mWcm^{-2}gmetal^{-1}$, which compared to the power density of commercial PtRu/C ETEK (305 $mWcm^{-2}gmetal^{-1}$), has at least a 78% improvement in performance. The DMFC results of the grafted electrocatalyst achieve a 100 % improvement with a power density of 70 $mWcm^{-2}gmetal^{-1}$ (36 $mWcm^{-2}gmetal^{-1}$ for the standard). The polarization curves clearly explain the reduction in ohmic drop caused by the grafted polymer.

1. Introduction

Carbon black is frequently used as a catalyst support in polymer electrolyte membrane fuel cells (PEMFCs), because of its stability in both acid and basic media, good electronic conductivity and high specific surface area. The support material has a strong influence on the properties of the catalysts, such as metal particle size, electrochemical active area and size distribution. Furthermore, degree of alloying, stability, mass transport and electronic conductivity of the catalyst layer are also affected by the chosen support material. Hence, development of novel carbon supports plays an important role for the future PEMFC technology. The support should be properly selected, with a suitable specific surface area, porosity, morphology, surface functional groups and electronic conductivity. Corrosion resistance is also a crucial parameter to be considered, while developing an active commercial catalyst. Most of these parameters are affected by the process used to prepare the carbon black. Some parameters such as, surface area, which is accessible and sufficiently large for maximum catalyst dispersion, pore size, pore distribution and surface functional groups of carbon blacks are being discussed as essential for optimized carbon supports. These parameters also affect the preparation and performance of carbon black used in a fuel cell electrode. Carbon black still reveals inadequacies for this purpose.[1, 2] For example, in a conventional impregnation process, some of the metal nanoparticles could sink into the micropores of carbon black or strongly attach to its impurities. The electrochemical activity could be reduced or hindered due to reactant inaccessibility to the metal nanoparticles inside the micropores or adsorbed at the impurities. This is the main reason, why some catalysts prepared by the impregnation method have not shown high activities even when the metal loading was very high.

In the electrocatalysis process, in a polymer electrolyte membrane fuel cell (PEMFC), operating with H_2/O_2, the hydrogen molecules must be first distributed in the porous gas diffusion electrode and there rapidly reach the nanoparticulate metal surfaces, providing the

catalytic active sites. The species must electrochemically adsorb on the metal and be oxidized, releasing thereby an electron to the metal and to the carbon particles, which finally enters the external circuit. The protons formed in this process have to be transported from the catalytic site to the electrolyte membrane, mostly Nafion®, then cross the membrane and react with the O_2 molecule at the cathode side to produce H_2O as a final product. To get a more efficient H^+ conduction from the catalytic site to the membrane, a certain amount of dispersed Nafion® ionomer in the porous gas diffusion electrode is usually used to enhance platinum utilization. The contact between the metal nanoparticles and the Nafion® ionomer micelles in the catalytic layer of the gas diffusion electrode is crucial and is also affected by the carbon pore size and its distribution. As reported by Uchida et al. [3], the Nafion® ionomer has micelles of about 40 nm in size. The nanoparticles, which sink into the carbon pores with diameters below 40 nm, have no access to the Nafion® ionomer and thus do not contribute to the total catalytic activity. Consequently, catalytic utilization of the metal nanoparticles is determined by electrochemical accessibility and not by the carbon surface area. Recently, Rao et al. [4] investigated the effect of carbon porosity on PtRu/C specific activity for methanol oxidation. They found that for carbon black with a large concentration of small diameter pores (< 20 nm), which were filled with metal nanoparticles, the contact between the Nafion® micelles and the metal nanoparticles was very poor, resulting in a low methanol oxidation activity. These authors reported that 20 % of PtRu supported on a specific Sibunit carbon black (Sib-19P; S_{BET}=72 m^2g^{-1}) showed an activity of 180 $mAmg_{(metal)}^{-1}$ at 500 mV in a half cell test (DMFC). This performance was six times higher compared to another Sibunit carbon (PtRu/Sib-619P; S_{BET}=415 m^2g^{-1}). Hence these authors concluded that an increase in the carbon surface area did not increase the catalytic activity.

On the basis of these facts, three distinct interfaces have been identified, which are responsible for improving or deteriorating the catalytic performance of a PEMFC: 1- Metal-C Interface, 2- Metal-Nafion® Interface and 3- C-Nafion® Interface. Consequently, the

development of electrocatalysts with improved performance for H_2 oxidation as well as for methanol oxidation has to look out for new materials with optimized physical and chemical conditions at these interfaces. One approach would be the chemical modification of the surface of the carbon black support used to anchor the nanoparticles of the electrocatalysts. In this case, the modifications at the micro(nano)scopic level could be done by linking simple organic compounds and eventually growing macromolecules. Chemical reactions could be applied to encapsulate, protect and change the hydrophobic/hydrophilic character of the materials. By this means, the reactivity can be changed, catalytic properties modified as well as composites created and polarities changed (zeta potential).[5-8]

The grafting of polymers onto and from carbon black surfaces has been widely investigated. There are two ways to attach polymers to carbon materials; *graft-onto* and *graft-from*. Graft-onto requires the attachment of separately prepared polymer to carbon black and graft-from involves the growth of the desired polymer directly from the carbon surface using previously attached initiators, via several polymerization intermediates.[9-11] In general, polymer is grafted onto the surface during polymerization in the presence of carbon black, but the percentage of grafting is very low. It is well known that carbon black itself has unpaired electrons,[12] but these unpaired electrons have no ability to initiate the radical polymerization of vinyl monomers, because the unpaired electrons are stabilized by the polycondensed aromatic rings of carbon black and therefore the introduction of active radical groups onto the carbon black surface is required. To prepare the polymer grafted carbon black with a higher percentage of grafting, it is necessary to initiate the graft polymerization from active sites on the carbon black surface.[13] There are other ways to get carbon black grafted. For example: using radical,[14, 15] anionic [16] or cationic [17] initiators, by cationic grafting from acylium perchlorate groups on carbon black,[13, 18] by graft polymerization from carbon black initiated with a redox system, consisting of ceric ions and alcoholic hydroxyl groups introduced onto the surface [19] and by reacting azo groups onto the carbon black surface [20].

The objectives of this study were the cationic grafting of styrene sulphonic from carbon black surface using ACPA (4,4'-azobis(4-cyanopentanoic acid) as initiator, followed by the physical, chemical and electrochemical characterization of the innovative support that was produced and the characterization of prepared PtRu electrocatalysts supported on the new grafted support for PEMFC and DMFC applications.

2. Experimental

2.1. Grafting of poly(styrene sulphonic) from carbon black surface[1]

2.1.1. Introduction of carboxyl groups onto carbon black.

$$\text{C (1)} \xrightarrow{HNO3} \text{C-COOH (2)} \qquad (1)$$

The introduction of carboxyl groups onto carbon black (2) was achieved by treatment of carbon black (1) with nitric acid. Into a glass thermostatized reactor, 15g of carbon black and 300 mL of concentrated nitric acid were charged. The mixture was stirred for 24 hours at 80 ºC. The resulting carbon was filtered, thoroughly washed with Milli-Q water until nitrate removal and dried with air in an oven at 110 º for 2 hours. The sample was labeled C-COOH.

2.1.2. Introduction of acyl chloride groups onto Carbon black.

$$\text{C-COOH (2)} \xrightarrow{SOCl2} \text{C-COCl (3)} \qquad (2)$$

Carbon black having acyl chloride groups (3) was prepared by the reaction of carboxylic functionalized carbon black (2) with thionyl chloride. In a suspension of vacuum dried carbon black (5g) in 50 mL of absolute benzene. A large excess (15 mL) of $SOCl_2$ was added and the mixture was refluxed with stirring for 50 hours. After the reaction, benzene and unreacted $SOCl_2$ were distilled under reduced pressure and then the resulting carbon black was dried at 110 ºC in vacuum. The treated carbon black was stored in vacuum in the dark. The sample was labeled C-COCl.

2.1.3. Introduction of azo groups onto carbon black.

$$\text{C-COCl (3)} \xrightarrow{HOOC-R-N\approx N-R-COOH\,(ACV)} \text{C-COO-R-N=N-R-COOH (5)} \qquad (3)$$

To a pre-dissolved 4,4'-azobis(4-cyanovaleric acid) (4) (500 mg) in 60 mL chloroform, 500 mg of carbon black with acyl chloride groups (3) was added and the mixture was stirred for 24 hours at 25 ºC. After the reaction, the resulting carbon black (5) was filtered and repeatedly washed with chloroform and dried in vacuum at room temperature. The treated carbon black was stored in the dark below 0 ºC. The sample was labeled C-azo.

2.1.4. Polymerization of styrene sulphonic sodium salt monomer from carbon black surface.

$$\text{C-COO-R-N=N-R-COOH} \xrightarrow{\textit{Styrenesulphonatesodiumsalt}} \text{C-PSSO}_3^-\text{Na}^+ \qquad (4)$$

$$\text{C-PSSO}_3^-\text{Na}^+ \xrightarrow{H2SO4} \text{C-PSSO}_3^-\text{H}^+ \qquad (5)$$

To pre-dissolved styrene sulphonic sodium salt monomer (1.5 g) in 100 mL Mili Q H_2O, 500 mg of carbon black with azo groups was added and the mixture was stirred for 1 hour at 80 ºC, (4). After the reaction, 100 mL of sulfuric acid 0.5 $molL^{-1}$ was added and mechanically stirred for 1 hour at 80 ºC in order to change the cation in the sulfuric group of the polymer, from Na^+ to H^+, to make the polymer proton conductive (5). The resulting carbon black was filtered and repeatedly washed with water and dried at 100 ºC. The final product was labeled C-PSSH.

2.2. Preparation of Electrocatalysts

The carbon-supported electrocatalysts were prepared using the impregnation method and subsequent reduction with an alcohol. A mixture of the desirable metallic ions in solution was used as precursor. The ions in the solution were reduced to their metallic form, using ethylene glycol (Merck) as solvent and a reducing agent in the presence of the carbon support. PtRu/C (20 wt%, Pt:Ru atomic ratio of 1:1) was prepared using this procedure. $H_2PtCl_6{\cdot}6H_2O$ (Aldrich) and $RuCl_3{\cdot}2H_2O$ (Aldrich) were used as metal sources. High surface area carbon black Vulcan XC-72 in the as-received condition and grafted carbon black Vulcan XC-72 were used as supports. In this procedure the salts were first added to the carbon support, followed by an ethylene glycol solution (75:25 - ethylene glycol:water). The system was ultrasonically treated for 15 minutes. It was then refluxed and heated at 160ºC for one hour.

The resulting powder was filtered, washed and dried overnight at 110ºC. Commercial electrocatalysts PtRu/C (20 wt%, Pt:Ru atomic ratio of 1:1) from E-TEK and HISPEC were used for comparison.

2.3. Characterization of physical properties

2.3.1. Potentiometric titration

The titration method was used to determine the quantity of H^+ and consequently, the quantity of polymers grafted on the carbon surface. The potentiometric titration method was performed using standard NaOH that had previously been degassed with N_2 and the carbon grafted material to be titrated was previously stirred in CO_2 degassed Mili Q H_2O for 24 hours. During data acquisition, each curve point was registered after one hour of stabilization.

2.3.2. Infra red spectrometry analysis

The infrared spectra were registered on a Nicolet FTIR-8100 spectrometer in KBr matrix. The KBr was previously heat treated at 400^{o}C for 2 hours in air and was kept inside a desiccator with $CaCl_2$.

2.3.3. Brunauer-Emmet-Teller (BET) surface area analysis

A NOVA 300 BET (Brunauer-Emmet-Teller) 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^{o}C to remove contaminants and moisture that could be in the carbons.

2.3.4. Laser scattering analysis (LS)

A Laser Scattering (LS) LS230 Small Volume Module Plus – Coulter was used to estimate the average particle size of the carbons. Before measurement, 5 mg of the sample was dispersed in water and ultrasonically dispersed for at least 48 hours.

2.3.5. Thermogravimetric (TGA) analysis

A Thermal Analysis System STAR TGA/SDTA851^{e} Module from Mettler Toledo with Star-e version SW 8.01 software was used for thermo gravimetric analysis (TGA). A heating rate of 10^{o}C min^{-1} and a nitrogen flux of 50 mL.min^{-1} were used.

2.3.6. EDX and X – Ray Diffraction (XRD)

The Pt:Ru atomic ratios of the electrocatalysts were obtained by using a Philips XL30 scanning electron microscope coupled to an EDAX DX-4 microanalyzer with a 20 keV electron beam. The X-ray Diffraction (XRD) analyses were performed using a STOE STADI-P diffractometer with germanium monochromized Cu Kα radiation and position-sensitive detector with 40 aperture in transmission mode. The X-ray diffractograms were obtained with a scan rate of 1ºmin^{-1} and an incident wavelength of 1.5406 Å (CuKα). The average crystallite size was estimated using the XRD data and the Scherrer equation.

2.3.7. Transmission Electron Microscopy – TEM

The transmission electron microscopy (TEM) characterization was done using a JEOL JEM-1200EX microscope and the average particle size was calculated using the Image Tool Software with one TEM micrograph for each catalyst.

2.4. Electrochemical Characterization

To prepare the MEA´s, water and a desired amount of the conducting polymer solution (Nafion®) were added to the catalyst powder. The system was emulsified with a ultra-turrax system for 10 minutes and stirred at 90º C, until the loss of water was sufficient, resulting in an optimum paste to be applied by the sieve printing technique. The amount of catalytic material (metal loading) was controlled after the printing process. After sieve printing, heat treatment was carried out at 135°C for 30 minutes. The membrane was treated with 5wt. % nitric acid at 100°C and then washed in hot Milli-Q water, followed by cold Milli-Q water. The MEA were placed in the single cell, using as gas diffusion layer Toray paper (TGP-H-060) in the anode and Sigracet 10CC in the cathode. The experimental conditions for PEMFC were: test cell: HIAT FC25/125; contact pressure on electrochemically active area: 1 Nmm^{-2};

cathode - air: 1.5 $NLmin^{-1}$ (100% humidity); anode - H_2 0.8 $mL.min^{-1}$; cell temp. 70°C; GDLs: anode Toray TGP-H-060, cathode Sigracet 10CC. The experimental conditions for DMFC were: test cell: HIAT FC25/125; contact pressure on electrochemically active area: 1 Nmm^{-2}; air: 1.5 $NL.min^{-1}$ (100% humidity); CH_3OH 3.5%, 15 $mL.min^{-1}$; cell temp. 70°C; GDLs: anode – 0.6 $mg_{PtRu}cm^{-2}$, Toray paper TGP-H-060, cathode – 1.5 $mg_{Pt}cm^{-2}$, Toray paper Sigracet 10CC; Nafion® membrane 117.

3. Results

3.1 Physico-chemical characterization of the poly(styrene sulphonic) grafted carbon black

3.1.1. Fourier transform infrared spectroscopy - FTIR

Figure 1 presents the infrared spectroscopy results of commercial carbon black, carbon black after functionalization with HNO_3, after $SOCl_2$ funcionalization, after azo agent functionalization and the carbon black grafted with poly(styrene sulphonic). **Figure 1** presents also the infrared spectroscopy results for the azo agent. **Figure 2** compares the grafted carbon black, the pure poly(styrene sulphonic) polymer, the styrene sulphonic sodium salt monomer and the commercial Nafion® membrane. The wavelenght and the intensity of the characteristic absorption bands of the functional groups in the respective spectra were compared. In sample 1, carbon black functionalized with nitric acid (shown in the spectra in **Figure 1**), the peaks in the region of 1860-1650 cm^{-1} (1) are attributed to the stretching of C=O related to the cabonyl and carboxyl groups.[21, 22] The spectra also shows peaks at 1740 cm^{-1} (2), that could be associated to the lactones groups.[21, 22] Data [23] are available in literature about C=O streching/vibration from carboxylic groups near aromatic rings and these generally present peaks between 1700-1680 cm^{-1}. The wave number is affected by the different peripheric groups [23]. The peak at 1580 cm^{-1} (3), that appears in the original sample and in the HNO_3 oxidized sample has been observed by many authors and associated to the aromatic ring streching, coupled to the carbonyl group and moreover, to the increase in the C=O bond

streching [22]. The peak at 1460 cm^{-1} (4), could be associated to O-H vibration deformation in the carboxylic groups and also to the C-H vibrations.[22-25] The peaks in the region between 1400-1380 cm^{-1} (5) can be attributed to carboxyl-carbonate structure [5, 22] or to the aromatic bond C=C and also to several aromatic ring substitutions.[22] Peaks between 1200-1000 cm^{-1} (6) are difficult to identify, because of the large number of overlapping peaks and therefore cannot be attributed to functional groups or chemical bonds.[22] Peaks below 950 cm^{-1} (7) are characteristic of vibration deformation of the C-H group plane in the aromatic structures.[5, 22, 26] Gómez-Serrano et al. [27] also showed the presence of N-O and -NO_2 groups that take the place of hydrogen in the carbon structure. Salame and Bandosz [28] also discussed the presence of peaks related to nitrogenated groups between 1540 cm^{-1} and 1350 cm^{-1}. Barkauskas and Dervinyte [29] reported that by carbon functionalized with nitric acid, the carboxylic groups was introduced to greater extent and phenols and lactones groups to lesser extent. For sample 2, carbon black functionalized by thionyl chloride, (shown in the spectra of **Figure 1**), there is no information about the incorporation of chloride groups in the carbon black surface. FTIR spectroscopy is probably not sensitive enough to detect the chloride groups. For sample 3, carbon black functionalized with the ACPA based (or derived) azo component (or coupling agent) groups, (shown in **Figure 1**), the peaks at 1500-1200 cm^{-1} can be attributed to the azo groups strechings on the carbon surface. For sample 4, grafted carbon black with poly(styrene sulphonic), peaks in the region at 1200-1000 cm^{-1} (8), in **Figure 1**, can be attributed to the sulphonic groups stretching. In **Figure 2**, the same peaks related to the sulphonic groups in all samples can be seen. Qualitatively, the FTIR spectroscopy revealed that the synthesis route to graft carbon black was very successful.

3.1.2 Brunauer-Emmet-Teller (BET) surface area results

Table 1 shows the specific surface area results of the carbons. After grafting, it can be seen that the surface area of the carbon was reduced by 85 %, which indicates that the treatment caused changes in the carbon structure. Chen and Wu [30] showed a slight reduction

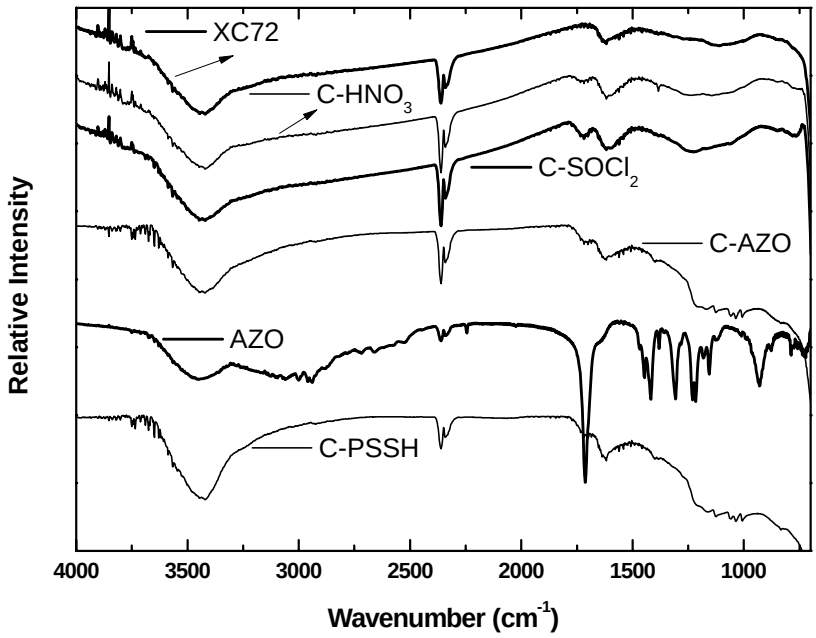


Figure 1. FTIR spectra for Vulcan XC72, C-HNO_3, C-$SOCl_2$, C-AZO e C-PSSH

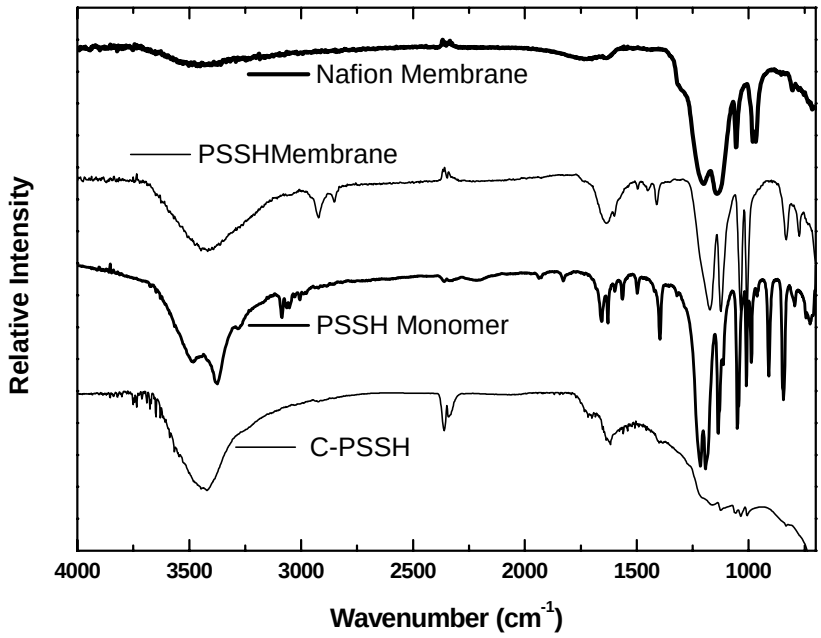


Figure 2. FTIR spectra for C-PSSH and poly(styrene sulphonic)

in the surface area of carbons, after dilute HNO_3 treatment and showed also that organic acids with higher molecular size could better penetrate the carbon structure, resulting in pore

blockage. This behavior was also noted by Gómez-Serrano et al.[27] As indicated in the literature,[24, 31-33] oxidation treatments produce a large amount of oxygenated groups (carboxylic, hydroxyl, lactones, etc.) on the carbon surface. These groups are responsible for changing not only the acid-basic character of the carbon black, but also the pore structure. The pore structure of carbon black is of great importance in the development of support material for DMFC applications, as discussed in the introduction. Carbon micropores filled with metal catalysts are undesirable as they restrict the access of the reactants to the active sites, resulting in waste of noble catalysts. It has been suggested that the oxygen surface groups fixed at the entrance of micropores after carbon functionalization. It is especially true with the grafting of polymeric chains, which were introduced in the carbon structure, block the diffusion of species into the micropores. Some authors [24, 31-33] reported similar restrictions for diffusion in micropores of carbon black after other chemical treatment. In this study, the blocking of micropores can be clearly seen from the BET results. The model of the carbon pore structure, before and after the grafting, is shown in **Figure 3**.

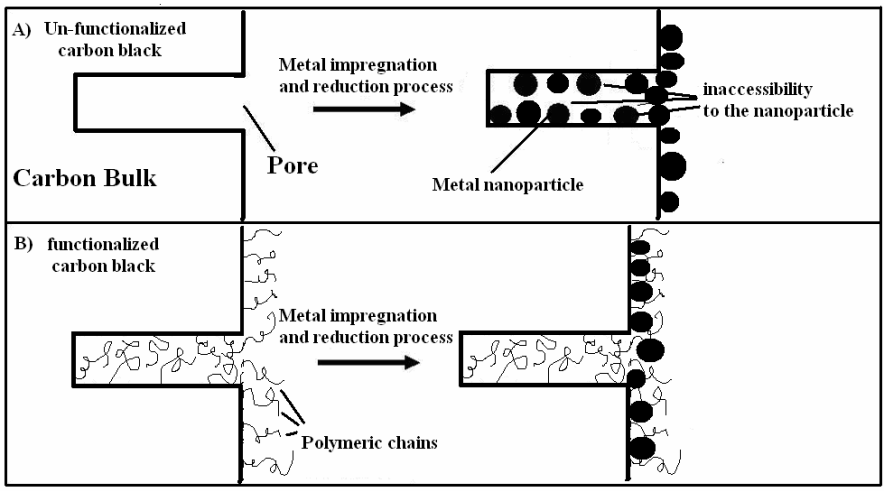


Figure 3. Model of the carbon pore blockage before and after the grafting.

3.1.3 Laser scattering (LS) results

Table 1 shows the carbon particle size average in water media, as determined with a laser scattering technique. A reduction in the average particle size of carbon black can be seen. After grafting, the carbon black became much more hydrophilic and consequently, the

dispersion of the carbon black in water was facilitated. The particle size of grafted carbon black dispersed in water is significantly smaller than the carbon black without grafting, thus indicating a beneficial behavior in terms of electrocatalyst preparation, as well as for the final MEA preparation, using electrocatalyst inks (**Figure 4**). As shown in **Figure 5**, a much more carbon particle stabilizated dispersion (in water) was obtained after grafting. The system was placed for decantation for five months and no obvious sedimentation was observed.

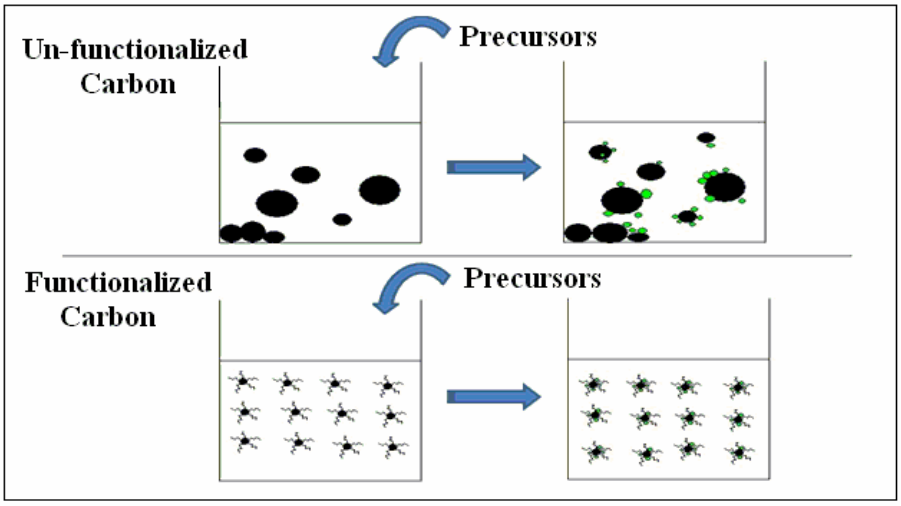


Figure 4. Model of the grafted carbon black stabilization in water media, in the PEM fuel cell electrocatalysts preparation

Figure 5. Solubility photo of carbon black (left) and grafted carbon black (right) in water

3.1.4 Thermogravimetric analysis (TGA) results

The relative content of poly(styrene sulphonic) grafted carbon black compared to commercial carbon black was determined from thermogravimetric analysis. The grafted

carbon black showed a gradual mass loss of about 10% from 25 to 110 ^{o}C, mainly loss of water. The presence of water in the grafted carbon black can be attributed to its hydrophilic nature. In the range 150 – 1000 ^{o}C the polymer decomposed and the content of polymer grafted from the carbon black was 20 %, as intended. In **Figure 6**, at 140 ^{o}C the melting point of polymer in the grafted carbon black surface can be observed.

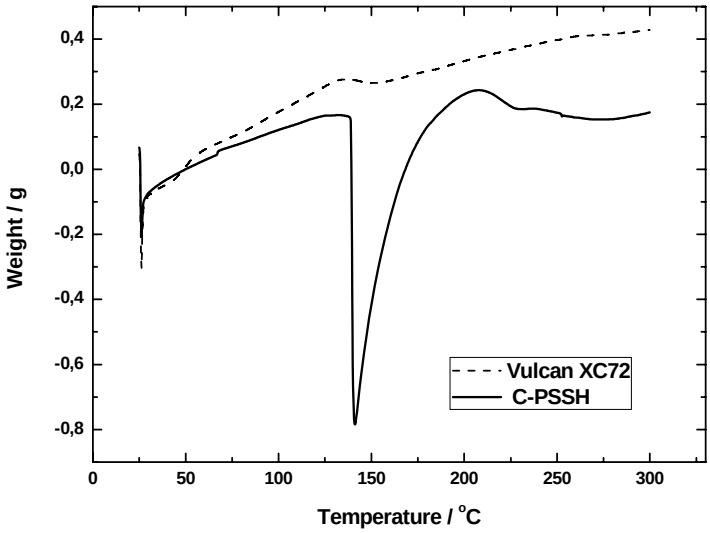


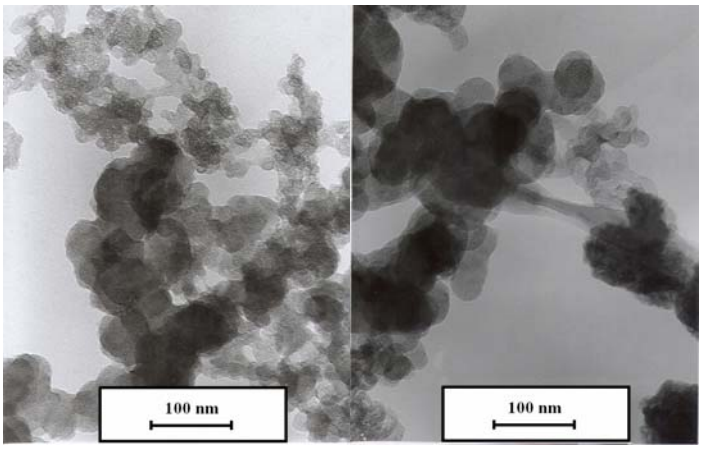
Figure 6. DSC curve of poly(styrene sulphonic) grafted carbon black.

3.1.5 Transmission Electron Microscopy – TEM

TEM analyses of the carbon black and grafted carbon black samples were carried out. It is difficult to perform TEM measurements on polymeric materials, due to destruction of the polymer chains by the electron beam. Hence, the polymer staining, by the reaction (reaction 1) of the sulphonic groups in the polymeric chains with barium chloride was necessary.[34]

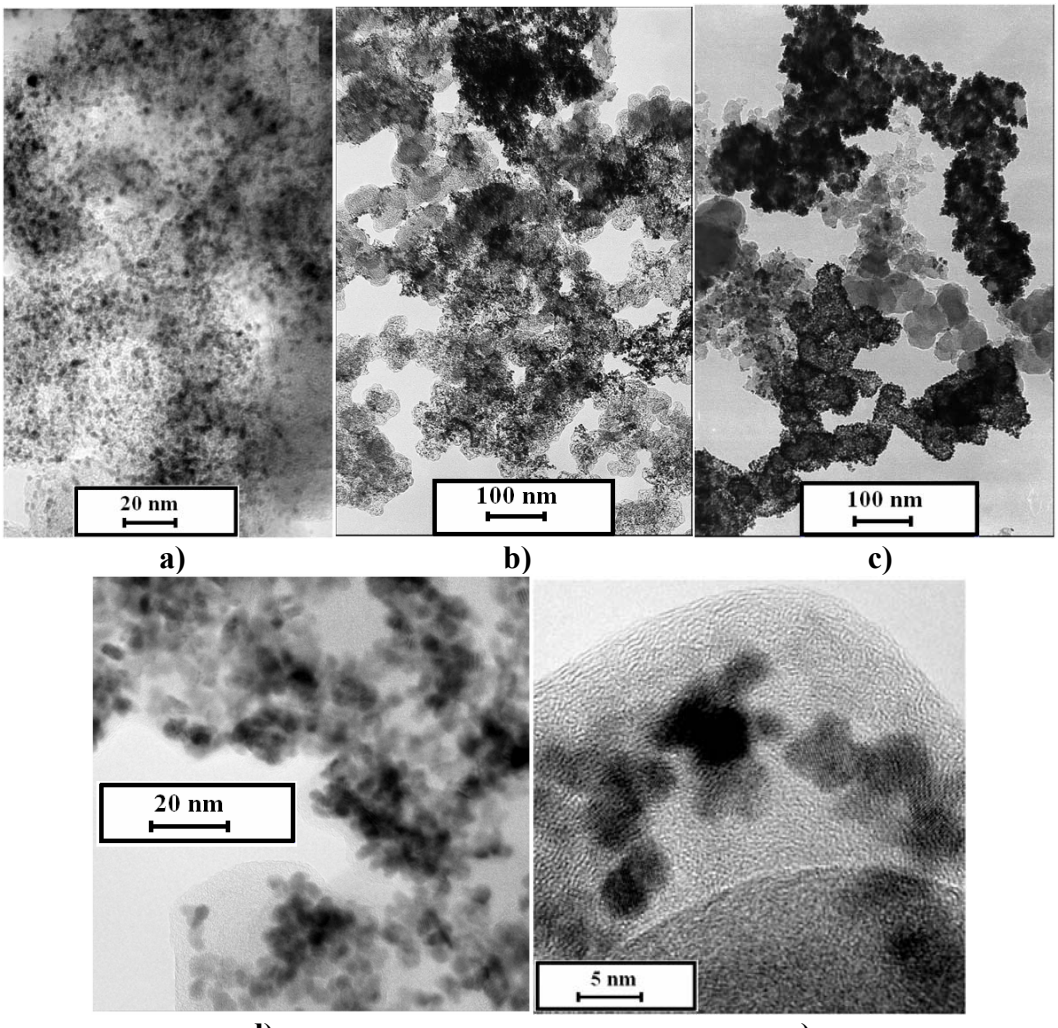
$$2\text{-}SO_3H + BaCl_2 \longrightarrow (R\text{-}SO_3)_2Ba + 2HCl \quad (1)$$

Figure 7a shows the TEM micrograph without barium and **9b** with barium. In **Figure 7b**, it is possible to observe the particles at regions where the polymeric chains were grafted. Also from the hydrophilic character of the grafted particles, it is possible to observe the hydrophilic and hydrophobic agglomerates.



a) b)

Figure 7. Transmission electron micrographs for a) grafted carbon black b) grafted carbon black with barium marker



a) b) c)

d) e)

Figure 8. TEM micrographs for a)PtRu/C Etek, b)PtRu/C Hispec, c)PtRu/C, d)PtRu/C-PSSH and e)PtRu/C-PSSH (another sample)

3.2 Physico-chemical characterization of the PtRu electrocatalyst supported on poly(styrene sulphonic) grafted carbon black.

3.2.1. Energy dispersive analysis of X-rays (EDX), X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM) results

The Pt:Ru atomic ratios of the electrocatalysts, which were determined by EDX, were very close to the nominal composition, calculated from the mass of the metallic components, which were used. All the electrocatalysts showed diffraction peaks at about 2θ = 40, 47, 67 and 82°, characteristic of the FCC structure of platinum and platinum alloys.[35, 36] The broad peak at about 2θ = 25° was associated with the carbon black used as support material, as discussed before. For the PtRu/C electrocatalysts, no other peaks of the HCP phase of ruthenium or ruthenium oxides were observed. The average particle size, L, could be estimated from the Scherrer equation, equation (2), using the platinum peak (220).[36]

$$L = \frac{0.9\lambda_{k_{\alpha 1}}}{B_{(2\theta)} \cos \theta_{\max}} \qquad (2)$$

where the wavelength $\lambda_{k\alpha L}$ is 1.54056Å and the full width half maximum $B_{(2\Theta)}$ is in radians.

The XRD results show that alcohol reduction produces nanoparticles in the desirable size range for fuel cell applications (Table 2).

Table 1. BET surface area and LS particle size results

	Surface area (m^2g^{-1})	**Particle size (µm)**
Vulcan XC72	232	14,9
Vulcan XC72-PSSH	39	0,06

The PtRu/C catalysts from E-TEK had a smaller crystallite size compared to the PtRu/C catalyst. However the crystallite size of the polymer grafted carbon was smaller than that of the ungrafted carbon.

Table 2. XRD and TEM particle size results for the PtRu/C electrocatalysts

	Diameter (nm)XRD	Diameter (nm)TEM
PtRu/C-PSSH	3,7	3,2
PtRu/C	4,3	4,7
PtRu/C ETEK	< 2	2,8
PtRu/C Hispec	--	3,9

The TEM images in **Figures 8a to 8e** reveal a very homogenous and uniform particle distribution for PtRu/ETEK (**fig. 8a**) and for PtRu/C with grafted polymer (**fig. 8d**). The materials PtRu/C HISPEC (**fig. 8b**) and PtRu/C without treatment (**fig. 8c**) revealed many agglomerates and a non-uniform particle distribution.

3.2.2. Fuel cell operation results

The PEMFC polarization curves and power density curves, working with hydrogen and air, are shown in **Figure 9**. The cathode was set as standard, using commercially available Pt/C HISPEC and Pt/C E-TEK. The PtRu/C-PSSH achieved a maximum power density of 535 $mWcm^{-2}gmetal^{-1}$, the PtRu/C catalyst without treatment: 305 $mWcm^{-2}gmetal^{-1}$, PtRu/C E-TEK: 35 $mWcm^{-2}gmetal^{-1}$ and PtRu/C E-TEK with the HISPEC cathode 200 $mWcm^{-2}gmetal^{-1}$. The performance of the functionalized material was at least 78% better compared to the commercial materials. The polarization curve in **Figure 9** reveals improved performance of the electrocatalyst supported on grafted carbon black in the region dominated by ohmic drop. This can be attributed to better proton transfer and fuel transport compared to that in other non-grafted materials. The DMFC polarization curves and power density curves, working with methanol at approx. 1.0 $molL^{-1}$ (3.5wt %) and air, are shown in **Figure 10**. The PtRu/C-PSSH electrocatalyst achieved a maximum power density of 70 $mWcm^{-2}gmetal^{-1}$, PtRu/C E-TEK: 35 $mWcm^{-2}gmetal^{-1}$ and PtRu/C E-TEK with the HISPEC cathode 16 $mWcm^{-2}gmetal^{-1}$.

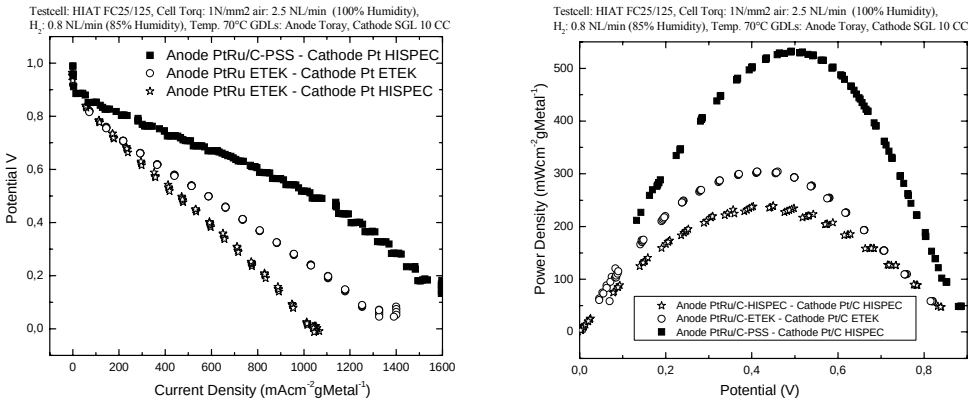


Figure 9. a) Polarization curves working with H_2/air. operational conditions: test cell: HIAT FC25/125, cell pressure: 1,0 Nmm^{-2}, air: 2.5 $NLmin^{-1}$ (100% humidity), H_2: 0.8 $NLmin^{-1}$ (85% humidity), cell temp.: 70°C GDLs: anode toray, cathode SGL 10 CC. and b) power density versus potential curves, working with H_2/air, operational conditions: test cell: HIAT FC25/125, cell pressure: 1Nmm^{-2}, air: 2.5 $NLmin^{-1}$ (100% humidity), H_2: 0.8 $NLmin^{-1}$ (85% humidity), cell temp.: 70°C GDLs: anode toray, cathode SGL 10 CC.

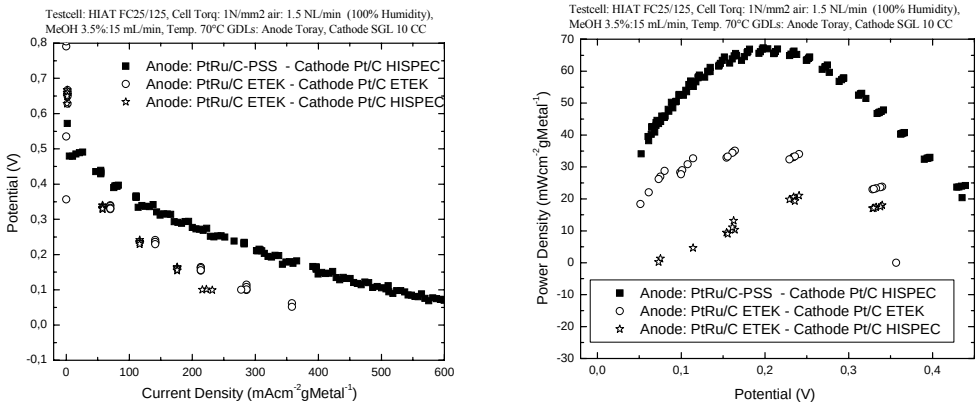


Figure 10. a) Polarization curves, working with methanol/air, operational conditions: and the experimental conditions for DMFC were: test cell: HIAT FC25/125, cell pression: 1Nmm^{-2} air: 1.5 $NLmin^{-1}$ (100% humidity), CH_3OH 3.5%:15 $mLmin^{-1}$, cell temp. 70°C GDLs: anode toray, cathode SGL 10 CC. b) power density vs. potential curves, working with methanol/air, operational conditions: and the experimental conditions for DMFC were: test cell: HIAT FC25/125, cell torch: 1Nmm^{-2} air: 1.5 $NLmin^{-1}$ (100% humidity), CH_3OH 3.5%:15 $mLmin^{-1}$, cell temp. 70°C GDLs: anode toray, cathode SGL 10 CC.

The performance of the grafted material was at least 100% better compared to the commercial materials. Summarizing, the results presented the following performance order: PtRu/C-PSSH > PtRu/C ETEK with ETEK cathode > PtRu/C ETEK with HISPEC cathode.

4. Conclusions

BET results showed that the specific surface area of the carbon support after functionalization is reduced by 85 %, indicating that the treatment used changed the carbon pore structure markedly. It was suggested that the oxygen surface groups produced by the HNO_3 treatment and the grafted polymeric chains were fixed at the entrance of the micropores, blocking the diffusion of species into the micropores. The TEM images revealed a very homogeneous and uniform particle distribution for the PtRu/C-PSSH material and a less homogeneous distribution for the PtRu/C material. A decrease in the ohmic drop polarization region and/or an increase in proton transfer by the grafted polymeric chains introduced on the carbon black pore structure were observed. This beneficial behavior resulted in remarkable improved performance, 78%, for PEMFC and 100%, for DMFC, indicating that this might be a promising novel support for fuel cell applications. These results open a new investigation field, the specific functionalization of the carbon/electrolyte or carbon/electrocatalyst surfaces for PEMFC and DMFC applications.

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