

Enhancing Pt electrocatalytic activity by surface functionalization of carbon support with aromatic sulphonic groups

A.Capelo*, M.A. Esteves, A.I. de Sá and C.M. Rangel*

LNEG, Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal

(*)anabela.capelo@lneg.pt, carmen.rangel@lneg.pt

Abstract

Preliminary results are presented for Pt deposited on 4-aminobenzenesulphonic acid-functionalized carbon, **Pt/C_ABSA**. Vulcan XC-72R was functionalized with the objective of influencing the dispersion of catalyst nanoparticles and to decrease the resistance of three phase boundaries, by introducing sulphonic groups. Electrochemical characterization of the supported catalyst was done in a 0.5 M sulphuric acid solution with added chloride and also using methanol demonstrating well defined features and stable voltammograms after 30 cycles, with apparent higher currents when compared with commercial catalyst. The structure sensitive adsorption of anions on platinum is confirmed by the blocking effect of chloride ions in the hydrogen adsorption-desorption region as well as by the consequent dissolution of platinum, evident in both anodic and cathodic features of the voltammograms regarding surface oxide formation and reduction. The partial reversibility of the effect of chloride ions is discussed. Research is in progress in order to accomplish a comprehensive characterization of the synthesized catalyst and to ascertain the effect of the sulphonic groups.

Keywords: Pt electrocatalysts, chemically modified carbon, sulphonic groups, methanol oxidation, Pt dissolution, chloride

1 Introduction

Carbon blacks are commonly used as supports for catalysts of low temperature fuel cells [1]. The main requirements are high surface area, good electrical conductivity, suitable porosity and high stability in fuel cell environment.

In the last few years the need for an increase in electrochemical activity and stability of fuel cell catalysts has led to the study of new carbon materials. The modification of the surface chemistry of more commonly used carbon supports has received a great deal of attention, focusing on the influence of functional groups that might increase catalyst utilization. Carbon blacks submitted to chemical activation exhibit an increase in the number of anchoring sites for metal catalysts and consequently in metal loading and dispersion [2,3].

Reference is also been made to organics molecules, also used to modify the surface of carbon materials, as an efficient way to immobilize catalyst particles and retain essential characteristics, such as dispersion and stability [4,5]

In this work the strategy used for carbon functionalization consisted, first, on the introduction of oxygenated groups at the surface by chemical oxidation and then the reaction of these groups with an aminobenzenesulphonic acid. The objective of this kind of functionalization is to improve the dispersion of catalyst nanoparticles and the resistance of the three phase boundary layer by diminishing the amount of nafion ionomers in the catalyst layer and also to modify the

acid/base properties of the support. Better catalyst utilization is envisaged.

Preliminary results obtained with Pt deposited on 4-aminobenzenesulphonic acid-functionalized carbon are reported.

2 Experimental

The chemicals were of analytical reagent grade, used without further purification. FTIR spectra were recorded on a Perkin-Elmer Spectrum BX v5.3.1 spectrometer. **Vulcan-COOH** [6], **Vulcan-COOCI** and 4-aminobenzenesulphonic acid-functionalized carbon, **C_ABSA** [7] were prepared following published procedures. The synthesis of catalyst, **Pt/C_ABSA** was performed by a formate ion reduction method previously described [8].

The physical characterization of the catalysts was performed by SEM and EDX analysis using a JEOL 8500F Field Emission Gun, EDX (SSD type) instrument.

The voltammetric experiments were carried out with a PAR wave form generator, model 273, controlled by a PC (software "Corrware") using a Greene cell with a three electrode configuration. The auxiliary electrode was a platinum rod and the reference electrode was a commercial Ag/AgCl electrode, placed in a separate compartment, connected to the electrochemical cell by a salt bridge. All the potentials in this work are quoted to this reference electrode. The working electrode was prepared by depositing 20 μ L of a catalyst ink on the surface of glassy carbon specimens of 7 mm diameter. The ink was prepared by mixing 10 mg of catalyst, 500 μ L of isopropanol and 10 μ L of a

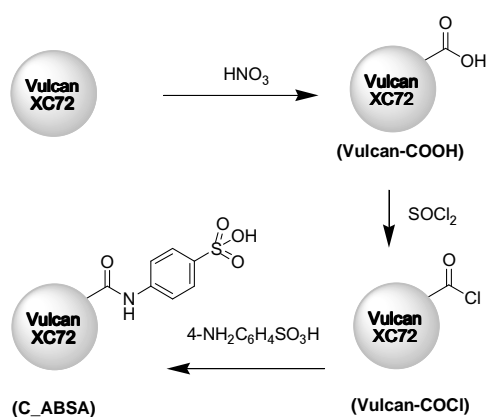
Nafion solution (5 %, Aldrich) and finally the mixture was sonicated by 30 min. After deposition, the ink was dried at 50 °C for 2 h. The specimens were also weighted before and after the deposition, and also during the drying operation, in order to estimate the catalyst load. The catalyst loadings were 1.0 and 1.3 mgcm⁻², for the study of effect of the chloride and methanol respectively. The electrochemical active surface area (ESCA) of the catalyst was estimated from voltammograms carried out within the potential range from -0.2 to 1 V, run at a scan rate of 50 mVs⁻¹ in 0.5 M H₂SO₄ solution. Before running the experiments the solution was purged with N₂ for 30 min, in order to remove any oxygen present. During the experiments the gas purging was maintained above the solution. The methanol oxidation reactivity was measured in a solution of 0.5 M H₂SO₄ + 1 M CH₃OH after N₂ purging for 30 min, at a sweep rate of 50 mVs⁻¹. All measurements were carried out at 25 °C. All voltammograms are normalized regarding geometrical area and catalyst loading.

3 Results

3.1 Catalyst synthesis

The synthesis of the 4-aminobenzenesulphonic acid functionalized carbon, **C_ABSA**, used in the preparation of Pt catalyst, **Pt/C_ABSA**, was accomplished by the synthetic procedure described in Scheme 1.

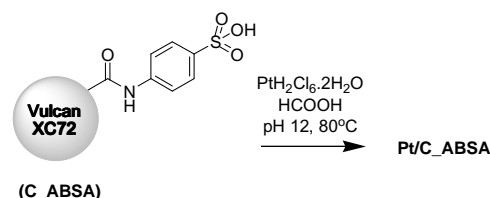
The first step consisted in the chemical oxidation of Vulcan carbon with nitric acid in order to introduce carboxylic groups at the surface (**Vulcan-COOH**). The second step proceeded with the introduction of acyl chloride groups (**Vulcan-COCl**). The latter compound is more reactive than **Vulcan-COOH**. **Vulcan-COCl** was coupled with the **ABSA**, 4-aminobenzenesulphonic acid in toluene reflux.



Scheme 1. Synthesis of **C_ABSA** functionalized carbon.

The **C_ABSA** was characterized by FTIR and the carbon material by elemental analysis.

The **Pt/C_ABSA** catalyst with a nominal metal loading of 20% platinum was obtained by the formate ions reduction method (Scheme 2). The carbon material, **C_ABSA** was dispersed in a solution of 2 M formic acid, basified at pH 12 and mixed with a solution of platinum chloride salts at 80 °C in order to obtain catalyst **Pt/C_ABSA**.



Scheme 2. Synthesis of **Pt/C_ABSA** catalyst.

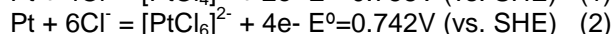
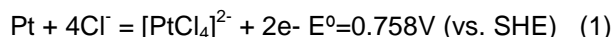
3.2 Electrochemical characterization

The electrochemical characterization of the catalyst proceeded in acid medium with the assessment of the separate effects of added chloride and methanol.

Fig. 1a) shows the cyclic voltammogram of **Pt/C_ABSA** in 0.5 M sulphuric at 50 mVs⁻¹ acid exhibiting typical features of Pt, with well defined peaks in the regions of hydrogen adsorption-desorption and Pt surface oxidation region. Also well defined is the double layer region.

The addition of chloride affected the voltammogram as a result of chloride structure sensitive adsorption in the H_{upd} region. The activity of the supported Pt can be correlated with the blocking effect of chloride ions on specific crystal planes, namely (100) facets. The capacitive region is shown to be extended due to the suppression of the formation of Pt oxide followed by a quasi linear current increase, adjudicated to platinum dissolution (see Fig.1b). This is in agreement with the decrease of the charge associated to the oxide reduction peak located at ~-0.5V (see Fig.1), as evidenced in the cathodic sweep.

The dissolution of Pt has been put forward by some authors [9] by means of the formation of the soluble chloride complexes:



The effect of chloride is found to be partially reversible as indicated when the electrode was removed from the chloride medium and placed in a fresh H₂SO₄ solution. Fig. 1c) shows that the voltammetric profile is recovered, even though with less electrochemical surface area. After 30 voltammetric cycles in the presence of chloride the ESCA has reduced in 31.60 %. Initial ESCA value was estimated in 41.75 m²g⁻¹_{Pt}.

Commercial Pt/C with Vulcan XC-72R was tested in the same experimental conditions and used as reference for comparative purposes. Preliminary results show that **Pt/C_ABSA** exhibits larger current densities. Furthermore, the loss associated to the chloride effect appears to be smaller with **Pt/C_ABSA** when comparing with the commercial catalyst. Results will be discussed.

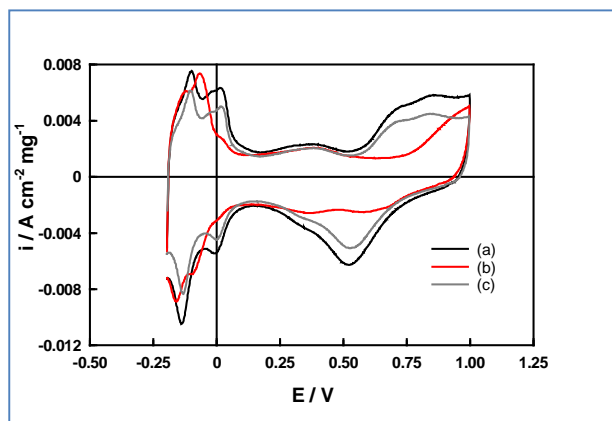


Fig. 1 Voltammetric profile for **Pt/C_ABSA** in a 0.5 M H_2SO_4 solution (a); 0.5 M H_2SO_4 + 5.10^{-3} M NaCl solution (b); 0.5 M H_2SO_4 after exposure to chloride (c).

Fig. 2 shows the voltammograms for **Pt/C_ABSA** catalyst in a 0.5 M H_2SO_4 + 1 M CH_3OH solution. The curve exhibits the characteristic features for the electrooxidation of methanol with a well defined peak in the forward scan preceded by a shoulder with an onset at 0.25 V. The typical reverse anodic peak is also evident. The appearance of anodic peaks for the electrooxidation of methanol in both anodic and cathodic sweeps has been attributed to the high catalytic activity of the catalyst for the electrooxidation of methanol. It also indicates that process is irreversible. Results will be discussed in terms of the onset potentials, peak currents and peak potentials. Comparison with values obtained for a commercial catalyst in the same experimental conditions will be made.

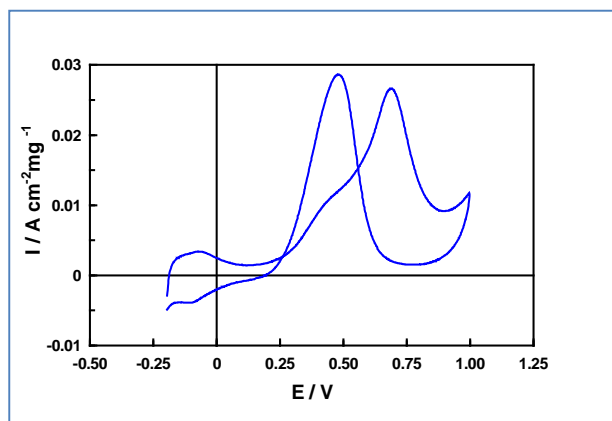


Fig. 2 Voltammetric profile for **Pt/C_ABSA** in a 0.5 M H_2SO_4 + 1 M CH_3OH solution at a scan rate of 50 mVs^{-1} .

4 Conclusions

The electrochemical characterization of a carbon supported Pt catalyst functionalized with aromatic sulphonic groups presented well defined voltammetric features in 0.5 M sulphuric acid solution.

The effect of chloride is found to be partially reversible as indicated when the electrode was removed from the chloride medium and placed in a fresh H_2SO_4 solution. Platinum dissolution with substantial ESCA losses were found, nevertheless

they were smaller than those obtained using commercial catalysts. Structure sensitive adsorption of anions is confirmed with the blocking effect of chloride ions on specific crystal planes namely (100) facets being suggested.

Pt/C_ABSA catalyst in a 0.5 M H_2SO_4 + 1 M CH_3OH solution is under study having presented high catalytic activity for methanol electrooxidation.

Research is in progress in order to make a fuller characterization of the catalyst and to ascertain the effect of the sulphonic groups.

5 Acknowledgements

This research is funded by the Portuguese Fundação para a Ciência e Tecnologia (FCT), Proj. PTDC/CTM-ENE/1585/2012.

6 References

- [1] Borup, R., Meyers, J., Pivovar, B., Kim, Y. S., Mukundan, R., Garland, N., Myers, D., Wilson, M., Garzon, F., Wood, D., Zelenay, P., More, K., Stroh, K., Zawodzinski, T., Boncella, J., McGrath, J. E., Inaba, M., Miyatake, K., Hori, M., Ota, K., Ogumi, Z., Miyata, S., Nishikata, A., Siroma, Z., Uchimoto, Y., Yasuda, K., Kimijima, K., Iwashita, N., Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation, *Chem. Rev.*, 107, pp. 3904-3951, 2007.
- [2] Kuo, P. L., Chen, W. F., Lin, C. Y., Multichelate-Functionalized Carbon Nanospheres Used for Immobilizing Pt Catalysts for Fuel Cells, *J. Power Sources*, 194, pp. 234-242, 2009.
- [3] Kim, Y.-T., Mitani, T., Surface Thiolation of Carbon Nanotubes as Supports: A Promising Route for the High Dispersion of Pt Nanoparticles for Electrocatalysts, *J. Catal.*, 238, pp. 394-401, 2006.
- [4] Kuo, P. L., Chen, W. F., Lin, C. Y., Multichelate-Functionalized Carbon Nanospheres Used for Immobilizing Pt Catalysts for Fuel Cells, *J. Power Sources*, 194, pp. 234-242, 2009.
- [5] Choi, H. J., Kang, J. Y., Jeon I. Y., Eo, S. M., Tan L. S., Baek, J. B., Immobilization of Platinum Nanoparticles on de 3,4- diaminobenzoyl- Functionalized Multi-Walled Carbon Nanotubes and its Electrocatalytic Activity, *J. Nanopart. Res.*, 14:704, pp. 1-11, 2012
- [6] Gonçalves, A.G., Figueiredo, J. L., Órfão, J. J. M., Pereira, M. F. R., Influence of the Surface Chemistry of Multi-Walled Carbon Nanotubes on their Activity as Ozonation Catalysts, *Carbon*, 48, pp. 4369- 4381, 2010.
- [7] Lu, J. D., Yang, M.-C., Dodecylamine-Modified Carbon Supports for Cathode in Proton Exchange Membrane Fuel Cells, *J. Power Sources*, 196, pp. 7450-7457, 2011.
- [8] Calderón, J. C., Mahata, N., Pereira, M. F. R., Figueiredo, J. L., Fernandes, V. R., Rangel, C. M., L. Calvillo, Lázaro, M. J., Pastor, E., Pt-Ru Catalysts Supported on Carbon Xerogels for PEM Fuel Cells, *Int. J. Hydrogen Energy*, 37, pp. 7200-7211, 2012.
- [9] Wu, J., Yuan, X., Martin, J., Wang, J., Haijiang, Zhang J., Shen, J., Wu, Shaohong, M., Walter. A Review of PEM Fuel Cell Durability: Degradation Mechanisms and Mitigation Strategies. *J. Power Sources*, 184, pp.104-119, 2008.