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ELECTROCATALITIC ACTIVITY OF PLATINUM DEPOSITED ON CARBON FUNCTIONALIZED WITH SULPHONIC GROUPS

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Abstract – **Results are presented for Pt deposited on 4-aminobenzenesulphonic acid-functionalized carbon, Pt/C_ABSA. Vulcan XC-72R was functionalized in order to influence catalyst dispersion and decrease the resistance of three phase boundary, by introducing sulphonic groups and lessening the amount of Nafion® added to the catalyst layers.**

Electrochemical characterization of the supported catalyst was done in a 0.5 M H_2SO_4 solution with added methanol or chloride demonstrating well defined features and stable voltammograms after cycling, with apparent higher currents when compared with commercial catalyst. The structure sensitive adsorption of anions on platinum is confirmed by either the blocking effect of chloride ions or methanol, evident in both anodic and cathodic features of the voltammograms. Optimal performance was found for a Nafion® concentration of 15-20 wt %.

Keywords – **Pt electrocatalysts, chemically modified carbon, sulphonic groups, methanol oxidation, Pt dissolution, chloride.**

I. INTRODUCTION

Carbon blacks surface chemistry modifications, with a view to increase the number of anchoring sites, loading and dispersion of metal catalyst, have received a great deal of attention [1-3].

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 their reaction with aminoaromatic sulphonic groups. 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, key to transport properties, and also to modify the acid/base properties of the support. Better catalyst utilization is envisaged. Preliminary results obtained with Pt deposited on 4-aminobenzene-sulphonic acid-functionalized carbon are reported.

II. 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-COCl** and 4-aminobenzenesulphonic acid-functionalized carbon, **C_ABSA**, were prepared following published procedures [2]. The synthesis of catalyst, **Pt/C_ABSA**, was performed by a formate ion reduction method previously described [3]. The preliminary physical characterization of the catalysts was performed by SEM and EDX analysis using a JEOL8500F 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, 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 10 μL of a catalyst ink on a glassy carbon rod base surface with 7 mm diameter. The ink was prepared by mixing the catalyst, isopropanol and 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 potential range from – 0.2 to 1 V, run at a scan rate of 50 mVs^{-1} in 0.5 M H_2SO_4 solution.
Before running the experiments the solution was purged with N_2 for 30 min, in order to remove any oxygen present. During the experiments the gas purging was maintained above the solution. Methanol oxidation reactivity was studied by exposure of the catalyst ink, at the open circuit potential, to a 0.5 M H_2SO_4 + 1 M CH_3OH solution after N_2 purging for 30 min. Oxidation and voltammetric features recovery were assessed in a 0.5 M H_2SO_4 solution, at a sweep rate of 50 mVs^{-1}. Chloride contaminations were undertaken introducing NaCl in a concentration of 0.005 M. The effect of Nafion® was studied covering concentrations from 2 to 25 wt%. All measurements were carried out at 25°C.

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