

Electrochemical behaviour of ionic liquid functionalized carbon supported Pt-Ru Catalysts

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Abstract

Ionic liquid (IL) functionalized carbon supported nanocatalysts, including platinum-ruthenium catalysts, have been under investigation to achieve better catalytic performance on polymer electrolyte membrane fuel cells. Ionic liquids have particular physical properties, which usually improve the stability and dispersion of metal nanosized particles, providing an increase of the electrochemical active surface area. In this work, the synthesis and the electrochemical behaviour of two new ionic liquid functionalized carbon supported Pt-Ru nanocatalysts is investigated regarding the methanol oxidation reaction. Preliminary obtained results show that IL functionalization of carbon can produce supported catalysts with improved performances depending on the ionic liquid and on the reduction process used to produce the catalyst metal nanosized particles.

Keywords: Pt-Ru electrocatalysts, ionic liquids, polymer electrolyte membrane fuel cells

1 Introduction

Platinum-Ruthenium supported nanocatalysts are among the catalysts with better performance for direct methanol fuel cells (DMFC). However achieved results so far do not comply with proposed 2015 targets (EU and DOE) regarding metal loading, mass/specific activity or surface area loss. Even though new binary catalysts have been considered as possible alternative materials, it is also true that new routes for catalysts synthesis can still improve the performance of the Pt-Ru supported catalysts. The use of carbon materials functionalized with ionic liquid (IL) as supports for DMFC catalysts is recently being considered as a valid approach to improve stability and dispersion of catalyst metal nanoparticles and consequently its activity and reusability [1,2].

In this work preliminary results of the synthesis and the electrochemical behavior of new Pt-Ru catalysts, prepared from commercial Vulcan XC-72R and its IL functionalized derivatives, are presented.

2 Experimental

In this work, two new 20 wt % Pt-10 wt % Ru supported catalysts were prepared by metal deposition in two different IL-functionalized carbon supports, **C_IL1** and **C_IL2**. **C_IL1** was prepared by covalent attachment of 1-(3-aminopropyl)-3-methylimidazolium bromide to oxidized Vulcan XC-72, **Vulcan-COOH** [3]. For **C_IL2**, a different synthetic strategy was followed in which the ionic liquid functionality was sequentially constructed in the carbon support [4,5]. First **Vulcan-COOH** was transformed in its acyl chloride derivative, **Vulcan-**

COCl, which then reacted with 1-methyl imidazole. In the final step the IL functionality is obtained upon reaction with bromobutane. The Pt-Ru catalysts **Pt-Ru/C_IL1** was synthesized by the formate ions reduction method using as support **C_IL1**. **Pt-Ru/C_IL2** was synthesized by sequential Ru and Pt reduction with ethylene glycol using **C_IL2** as support. A Perkin-Elmer Spectrum BX v5.3.1 and NMR BRUKER AVANCE 400 MHz Ultra Shield spectrometers were used in the ILs characterization.

The catalysts were prepared as an ink by dissolving 10 mg of the catalysts in a nafion + isopropanol solution, followed by sonication for 30 min and drying at 50 °C. Physical characterization was performed by scanning electronic microscopy (SEM) using a JEOL 8500F FEG instrument with associated Energy Dispersive X-Ray Spectroscopy (EDX). A commercial catalyst **Pt-Ru/C_Com**, ECHEM, also supported in Vulcan XC-72, was used as reference. The voltammetric experiments were carried out with a PAR potentiostat (model 273), using a Greene cell with a three electrode configuration. The auxiliary electrode was a Pt rod and the reference electrode was a commercial Ag/AgCl electrode, to which all potentials are referred. The methanol oxidation reactivity was measured in 0.5 M H₂SO₄ + 1 M CH₃OH solution at a sweep rate (v) of 50 mV s⁻¹. The working electrode was prepared by depositing 20 μL of the catalyst ink on glassy carbon specimens. All the measurements were carried out at 25 °C.

3 Results

The composition of the catalysts is similar to that of a commercial catalyst (ECHEM) also supported in Vulcan XC-72 with 20 wt % Pt - 10 wt % Ru, **Pt-Ru/C_Com** (Fig. 1). SEM observation at

high magnification did not identify any metal clusters formation.

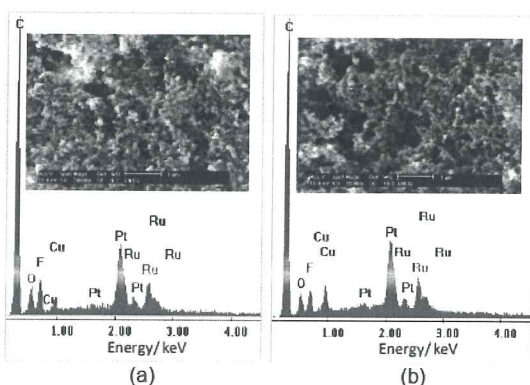


Fig. 1. SEM micrographs showing morphology of the dry catalyst ink deposited on copper substrates and corresponding EDX spectra for Pt-Ru/C_IL2 (a) and Pt-Ru/C_Com (b).

The electrochemical behaviour of the Pt-Ru nanocatalysts, including the commercial one, is analysed by cyclic voltammetry regarding the methanol oxidation reaction (MOR). The results show that the catalyst Pt-Ru/C_IL1 has a high peak current density for the methanol oxidation reaction (forward sweep at 50 mV s^{-1}), however the onset potential for the methanol oxidation peak is shifted to more positive potentials (Fig. 2). In contrast, the Pt-Ru/C_IL2 catalyst shows a relatively lower current density for the methanol oxidation reaction, suggesting a less effective surface area.

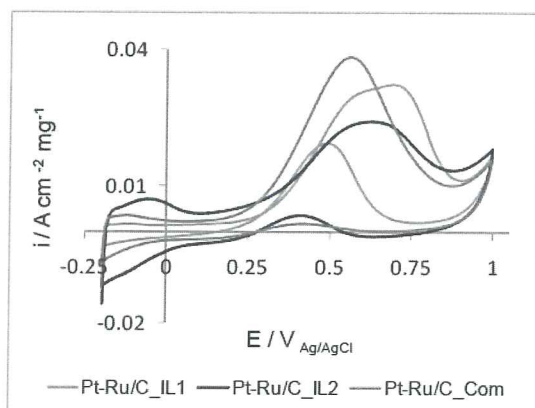


Fig. 2. Cyclic voltammograms for the catalysts Pt-Ru/C_IL1, Pt-Ru/C_IL2 and Pt-Ru/C_Com in $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ solution at 50 mV s^{-1} (first sweep).

Repeated potential cycling was also performed in the same solution at a sweep rate of 50 mV s^{-1} and up to 300 cycles (Fig. 3). The electrochemical behaviour is now different, since the catalyst Pt-Ru/C_IL1 shows a significant loss of the MOR activity, evaluated by the ratio of the peak current density of the 1st and 300th cycle. The catalyst Pt-Ru/C_IL2 has practically maintained the activity. Both catalysts show a strong increase of

the current density peak associated with the backward sweep, as it is usually observed.

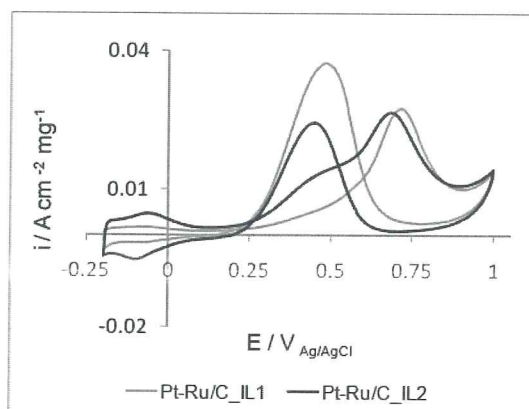


Fig. 3. Cyclic voltammograms (300th cycle) for the catalysts Pt-Ru/C_IL1 and Pt-Ru/C_IL2 in $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ solution at 50 mV s^{-1} .

4 Conclusions

Preliminary results obtained in this work show that IL functionalization of carbon can produce supported catalysts with improved performances depending on the ionic liquid and on the reduction process used to produce the catalyst metal nanosized particles. A better understanding of the effects of functionalization in the morphology and structure of the nanoparticles is necessary in order to improve the stability and dispersion of nanoparticles. Possible modifications in the reaction kinetics are to be ascertained.

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5 References

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