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C₁₆MI.OTf ionic liquid on Pt/C and PtMo/C anodes improves the PEMFC performance

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ABSTRACT

The effect of 1-hexadecyl-3-methylimidazolium trifluoromethanesulfonate (C₁₆MI.OTf) ionic liquid (IL) on the catalytic activity of Pt/C or PtMo/C anodes is studied in a proton exchange membrane fuel cell (PEMFC). PtMo nanoparticles (NPs) are synthesized with two different Pt:Mo proportions (13 or 31 at.% Mo) by a borohydride method on the carbon support. The composition, crystalline structure, morphology of the PtMo/C are evaluated by energy-dispersive X-ray spectroscopy, X-ray diffraction and transmission electron microscopy, respectively. The stability tests of the electrocatalysts are carried out in acid medium using cyclic voltammetry measurements. Pt/C or PtMo/C electrocatalysts containing C₁₆MI.OTf are assessed in the anode in a H₂/air PEMFC by polarization curve and ac electrochemical impedance spectroscopy. The synthesized PtMo nanoparticles show spherical shape and average particle size of 3.5 nm. The PEMFC performance of PtMo (13 at.% Mo) at anode is very similar than of Pt/C anode. The presence of 15 wt% C₁₆MI.OTf in the Pt/C or PtMo/C (13 at.% Mo) anodes let to an increase of the maximum power values, 71 and 107 W g_{Pt}⁻¹ cm⁻², respectively. The catalytic surfaces of nanoparticles are modified due to C₁₆MI.OTf presence which improved the PEMFC performance. This result agrees with the EIS analysis, where the resistances of charge transfer and mass transfer decrease in the C₁₆MI.OTf presence. However, this effect is more pronounced for PtMo/C (13 at.% Mo) catalyst, demonstrate that PtMo/C anodes with a small amount of Mo and C₁₆MI.OTf ionic liquid improve significantly the PEMFC performance.

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Introduction

Proton exchange membrane fuel cells (PEMFC) are devices that may use hydrogen as combustible to produce clean

energy [1,2]. Pt nanoparticles supported on carbon (Pt/C) are efficient to hydrogen oxidation reaction (HOR) when pure hydrogen is used as combustible. However, most of the hydrogen currently has been obtained by the steam reforming

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process of natural gas, ethanol or methanol [3–5]. These processes generate an impure hydrogen, with carbon monoxide (CO) traces [6,7]. However, the CO blocks the activity sites of the Pt catalyst decreasing the PEMFC performance, hindering the HOR [8]. PtSn/C, PtRu/C and PtMo/C electrocatalysts are efficient to HOR, promoting the electro-oxidation of CO [9–13].

PEMFC performance depends on the good contact of the three-phase junction (electrocatalysts/H₂/water) and electrocatalysts/membrane interaction. Studies describe the use of ionic liquids (ILs) as modifying agents of nanoparticle surface, suggesting an enhance in the adsorptive and ion exchange properties of electrode [14–17]. Small ILs amounts change the catalyst activity due to three aspects: (i) block specific sites (IL-induced site blocking); (ii) modification of the hydrogen/electrocatalyst interaction (IL reactant filter) or (iii) short ranged electronic effects (IL-induced electronic ligand effect) [18].

Brummel et al. [18] studied the influence of the co-adsorbed 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (C₁C₂MI.OTf) ionic liquid (IL) on the indirect reaction pathway of methanol oxidation, i.e., the dehydrogenation to CO and subsequent oxidation to carbon dioxide (CO₂). They found a strong inhibiting effect of C₁C₂MI.OTf on the formation of CO by site blocking of the adsorbed [OTf][−] anion on the Pt surface. In addition, they used the adsorbed CO as a probe molecule to study co-adsorbate effects of the [OTf][−] anion. They suggested the direct influence of IL on the co-adsorbed CO by the local electric field and by short ranged electronic effects.

In this paper, the C₁₆MI.OTf was selected due to the presence of an anion similar to the sulfonic group in the Nafion membrane structure. In addition, this anion when associated with a long-alkyl chain cation present in C₁₆MI.OTf provides a higher hydrophobicity. This feature can prevent the leached of IL present on electrode during the PEMFC operation.

Herein, we investigate the influence of the C₁₆MI.OTf on the catalytic activity of anodes Pt/C or PtMo/C in a PEMFC. PtMo nanoparticles (NPs) were synthesized by borohydride method on the carbon support while the Pt/C was obtained commercially. The synthesized electrocatalysts were characterized as their composition, crystalline structure and morphology. The influence of the C₁₆MI.OTf on the anode in the PEMFC performance was evaluated through the polarization curves and ac impedance measurements.

Experimental

The 1-hexadecyl-3-methylimidazolium trifluoromethanesulfonate (C₁₆MI.OTf) ionic liquid (IL) (Fig. 1) was prepared according to previously published procedures [19].

The PtMo/C electrocatalysts were prepared by borohydride method with 20 wt.% metal loading on Vulcan XC-72R carbon

(Cabot, 240 m² g^{−1}) and different Pt:Mo proportions [20]. The hexachloroplatinic acid (IV) hexahydrate (H₂PtCl₆·6H₂O, Merck) and the ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Sigma-Aldrich) were simultaneously mixed in water/isopropanol 1:1 (v/v) and Vulcan XC-72R carbon previously treated with HNO₃ [21]. The metals were reduced using sodium borohydride (NaBH₄, 95%, Vetec) at 25 °C for 30 min. The mixture was filtered, and the solid was washed with water and dried at 80 °C for 2 h.

The relative proportions of the carbon, platinum and molybdenum were obtained by energy-dispersive X-ray spectroscopy (EDX) coupled with scanning electronic microscope (JEOL-JSM 5800) using a 20 kV incident electron beam. The measurement precision was ±3%.

The crystalline structure and lattice parameter of the PtMo/C electrocatalysts were determined by X-ray diffraction (XRD). The X-Ray diffractograms were obtained using a D500 Rigaku diffractometer (Siemens) operating at a scan rate of 0.05° s^{−1} in the range of 2θ = 20–90° using CuKα radiation (1.54056 Å). An estimate of the average size of the crystallite was determined by the Scherrer equation using the Pt (220) peak of the diffraction patterns [20].

The nanoparticles dispersion on carbon support and the size distribution obtained by counting at least 600 nanoparticles were analysed by transmission electron microscopy (TEM) using a JEOL JEM 1200ExII microscope operating at 120 kV. The interplanar distances of crystalline structure of the nanoparticles were obtained employing high resolution transmission electron microscopy (HRTEM) with JEM2019 microscope operating at 200 kV. SigmaScan Pro 5 and Gatan Digital Micrograph softwares were used to analyse the data.

Stability tests of electrocatalysts were performed by cyclic voltammetry (CV) with Autolab PGSTAT 30 potentiostat coupled with GPES and FRA 2 modules in a half-cell. A double junction saturated calomel electrode (SCE) was used as the reference electrode, a Pt grid was used as the counter electrode and the synthesized electrocatalysts were used as the working electrodes. The potentials are presented relative to a reversible hydrogen electrode (RHE). The working electrodes were prepared using the thin porous coating technique. The ink was prepared with 10 mg of PtMo 15 electrocatalyst, 15 mg of Nafion[®] solution (5 wt.% perfluorinated resin solution, Sigma-Aldrich) and 30 mg of isopropanol. Another ink, with the same composition, was prepared and it was also added C₁₆MI.OTf (15 wt.%) named as PtMo 15 IL-15 [22]. These inks were fixed on a glassy carbon rotating disc electrode (GCRDE). The stability test was performed with the GCRDE at 1800 rpm in a de-aerated 0.5 mol L^{−1} H₂SO₄ solution at 25 °C while cycling the potential between −0.1 and 0.6 V versus RHE for 1000 cycles and scan rate of 0.02 V s^{−1} [20,23].

The PEMFC performance was evaluated by polarization curve and ac electrochemical impedance spectroscopy (EIS) using a FC5-1H cell (4.84 cm²). The polarization curve was carried out in a CDR50A-2 dynamic charge (Electrocell) and the EIS was performed in an Autolab PGSTAT 30 potentiostat coupled with GPES and FRA 2 modules. Separately, PtMo/C (synthesized in this study) and Pt/C (20 wt.% Pt EC-20-PTC commercial) electrocatalysts were used as the anode while the Pt/C electrocatalyst (20 wt.% Pt EC-20-PTC, Carbon XC-72R) was held as the cathode.

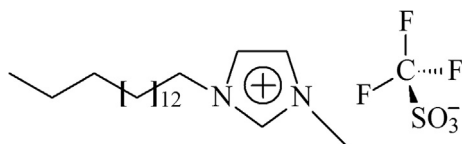


Fig. 1 – Structure of the C₁₆MI.OTf ionic liquid.

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