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Electrocatalysis of the Ethylene glycol oxidation reaction and *in situ* Fourier-transform infared study on PtMo/C electrocatalysts in alkaline and acid media

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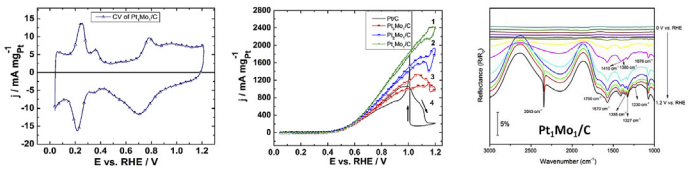
HIGHLIGHTS

- PtMo/C alloys synthesized by the formic acid method.
- PtMo/C anodes more active than Pt/C for the EGOR in alkaline and acid media.
- In alkaline media the PtMo/C alloys show selectivity for the C_2 pathway.
- In acid media PtMo/C catalysts promote the EGOR preferentially *via* the C_1 pathway.
- Overall, Pt_1Mo_1/C is more active for the EGOR in KOH and H_2SO_4.

GRAPHICAL ABSTRACT



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ABSTRACT

PtMo/C (Pt:Mo atomic ratios of 1:1, 2:1 and 3:1) and Pt/C electrocatalysts synthesized by the formic acid method are investigated for the ethylene glycol oxidation reaction (EGOR) in alkaline and acid media. From XRD measurements, the crystallite sizes are between 2.5 and 4.3 nm. Electrochemical characterization of the EGOR on the electrocatalysts shows that the PtMo/C series exhibit higher electrocatalytic activity. When comparing the two electrolytes, the mass current densities obtained in alkaline media are significantly higher than in the acid counterpart. Among the bimetallic anodes, Pt_1Mo_1/C delivered a high performance in both media. *In situ* FTIR spectroscopy analysis has been performed to study the pathway of the EGOR. In alkaline media, the PtMo/C electrocatalysts have a higher selectivity for the C_2 pathway resulting in the formation of species such as glycolate, glyoxal and glyoxylate. On the other hand, in acid electrolyte, the PtMo/C anodes show a preferential C_1 pathway at high potentials and the main intermediate is identified as glycolic acid. The results indicate that the higher catalytic activity of PtMo/C electrocatalysts towards the EGOR may be attributed to the bifunctional mechanism and also to an electronic effect because of the incorporation of Mo atoms into the catalysts structure.

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1. Introduction

The so called Direct Alcohol Fuel Cells (A-DAFCs for alkaline and DAFCs for acid) have attracted significant attention as power source for mobile and stationary applications, in part due to the simplicity of fuel handling and high energy density related to their operation [1–5]. Different liquid organic molecules such as methanol, ethanol, ethylene glycol, propanol, among others, have been proposed as fuel for DAFCs due to their excellent physicochemical properties [6,7]. The Methanol Oxidation Reaction (MOR) has been extensively studied aiming for applications in Direct Methanol Fuel Cell. Nevertheless, it is known that methanol is a toxic substance for human beings [8]. Thereby, the Ethanol Oxidation Reaction (EOR) has been evaluated considering the advantages of this molecule as fuel, since is non-toxic and has higher energy density than methanol (8.01 vs 6.09 kWh kg^{-1}). However, the kinetics of both reactions is limited by the difficulties associated to the C-C bonds breaking, necessary to carry out the complete oxidation to CO_2 at low potentials and temperatures [9,10].

In this context, ethylene glycol (EG) is an attractive liquid fuel because of its non-toxicity, high boiling point, high volumetric energy density and the fact that it can be produced from renewable biomass *via* high efficiency processes [11,12]. From these advantages, different studies have been carried out to elucidate and understand the mechanism of the EGOR on Pt anodes in alkaline and acid media [13,14]. Pt-based electrocatalysts have demonstrated to be highly selective for the adsorption and dissociation of EG Refs. [13,14].

Li et al. studied the EGOR pathway on Pt/C and Au/C electrocatalysts in 0.1 mol L^{-1} KOH, clarifying that glycolic, oxalic and formic acid were produced at the platinum catalysts [13]. The authors showed that the C-C bond cleavage of EG leads to the formic acid formations. Sun et al. evaluated the EGOR in 0.1 mol L^{-1} H_2SO_4 on Pt(100) by *in situ* time-resolved FTIRS, identifying linearly bonded CO and CO_2 at low potentials, while at higher potentials intermediate species containing carboxylic acid were detected [14]. Schnaidt and co-workers investigated the EGOR on a Pt-film electrode by *in situ* FTIR spectroscopy in 0.5 mol L^{-1} H_2SO_4 [15]. They found the presence of CO_{ads} in a rather large potential interval that is further oxidized to CO_2 at potentials higher than 0.5 V. Also, the presence of glycolic acid, glycolaldehyde and adsorbed glycolate as intermediates was detected.

Furthermore, several studies have demonstrated that the activity of plurimetallic nano-anodes were enhanced compared to Pt-alone electrodes for the EGOR. Several reports showed that Pt-Ru/C alloys are more active than Pt/C [16,17]. Recent works on nanostructured NiPt anodes, rGO-supported Pt-Pd alloys have revealed higher catalytic activity for the EGOR compared to Pt/C [18,19]. Thus, it clearly appears that an enhancement in catalytic activity for the EGOR in alkaline and acid electrolytes can be achieved by developing plurimetallic electrocatalysts.

In a recent report, we have shown that the combination of Mo and Pt as the PtMo/C electrocatalysts lead to a great catalytic activity for the EOR in alkaline media. In comparison with Pt the enhancement in performance of alloys has been attributed to their higher tolerance to CO_{ads} and a promotion of the reaction *via* a $4e^-$ route in the presence of Mo [20]. PtMo electrocatalysts supported on silica also show an increased performance for the MOR in alkaline media [21]. Besides that, PtMo/C alloys have been evaluated for several fuel cell anode reactions [22–25], but to the best of our knowledge, their performance for the EGOR either in alkaline or acid media is not yet reported. Moreover, from an economic perspective, Mo has the advantage of being widely available and inexpensive [26], thus a relatively cheap electrocatalysts for fuel cells can be developed based on this oxophilic metal.

In this work, the catalytic activity of PtMo/C electrocatalysts for the EGOR is evaluated and compared to that of Pt/C, in alkaline and acid media. *In situ* characterization using the single potential alteration infrared spectroscopy (SPAIRS) technique, allows the identification of the reaction intermediates and products. Therefore, a comparison of the reaction pathways of the EGOR on the electrocalysts is presented in KOH and H_2SO_4.

2. Experimental

2.1. Materials

The following reagents were used to synthesize the PtMo/C and Pt/C electrocatalysts: chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), ammonium molybdate tetrahydrate ($(NH_4)_6 Mo_7O_{24}$), formic acid (HCOOH), ethanol (C_2H_5OH) and potassium hydroxide (KOH), all obtained from Sigma-Aldrich. N_2 and CO gases (from Praxair) were of UHP grade. Carbon Vulcan XC-72 (Cabot®) was the electrocatalyst support.

2.2. Physical and chemical characterization

The chemical composition of the nanomaterials was obtained in a Phillips XL30 Scanning Electron Microscope, equipped with an Energy Dispersive X-ray Spectroscopy (EDS) analyzer operating at 20 kV. X-ray Diffraction (XRD) patterns were obtained from a Phillips-X'pert diffractometer using CuKα radiation source, by scanning from 10 to 100° in the 2θ scale. With the aid of the Scherrer equation and analyzing the Pt (220) reflection, the crystallite size of each sample was determined.

2.3. Synthesis of the electrocatalysts

The synthesis of the PtMo/C and Pt/C electrocatalysts (metal loading 20 wt %) using the formic acid method has been reported previously [20]. For example for Pt_3Mo_1/C electrocatalysts, 80 mg of carbon Vulcan XC-72 were dispersed for 30 min by ultrasound in 40 mL of 0.1 mol L^{-1} formic acid. The mixture was heated to 80 °C under magnetic stirring, then 48.7 mg of $H_2PtCl_6 \cdot 6H_2O$ and 5.5 mg $(NH_4)_6$ Mo_7O_{24} dispersed in deionized water were added drop by drop, maintaining the temperature for 2 h. The solution was allowed to cool down to room temperature and the final products was filtered, washed and dried.

2.4. Electrode preparation and electrochemical measurements

A Voltalab PGZ 301 potentiostat/galvanostat and a three electrode cell (Pine Inst.) were used for the evaluation of catalytic activity for the EGOR. The working electrode was formed by a thin film glassy carbon inserted in a Teflon support (Pine Inst.), one Ag/AgCl reference electrode, even though all potentials reported in this paper were referenced top the RHE scale, and platinum sheet as counter electrode. A catalytic ink composed of 5 mg of the catalysts in amixture of 0.5 mL isopropyl alcohol and 25 μL Nafion® was prepared. From this solutions, 10 μL were deposited on the glassy carbon (5 mm diameter) to complete the working electrode.

Cyclic voltammograms (CVs) were acquired in 0.5 mol L^{-1} KOH or 0.5 mol L^{-1} H_2SO_4 electrolytes previously deaerated by bubbling N_2, in the potential range between 0.05 and 1.2 V vs. RHE and at a