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Pt catalysts modified with Bi: Enhancement of the catalytic activity for alcohol oxidation in alkaline media

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ABSTRACT

Recent developments on anion-exchange membranes for fuel cell application renewed the interest in the study of alcohol oxidation at high pHs for applications in anion-exchange membrane direct alcohol fuel cells (AEM-DAFC). Although platinum is still the most studied catalyst for oxidation of alcohols in alkaline media, the introduction of one or more metals in order to increase the oxophilicity of the catalyst is a common approach in the development of improved materials for these reactions. In this manuscript, we report the enhancement of the catalytic activity of Pt/C toward ethanol, methanol, and propanol oxidation in alkaline media by simple adsorption of Bi surface. The activity was checked by cyclic voltammetry, and the reaction products and intermediates were analyzed by "in situ" infrared spectroscopy. The presence of Bi was shown to increase the activity of Pt toward the oxidation of the referred alcohols by acting as a third body (impeding surface poisoning) and also by an electronic effect (on water adsorption at the surface).

1. Introduction

Electrooxidation of alcohols is one of the most important subjects in electrocatalysis [1,2]. This importance is due to the use of these compounds as fuels in direct alcohol fuel cells (DAFC) that emerged in the last decades as promising alternatives for power sources in portable applications. The use of alcohols as fuels presents several advantages when compared with the "traditional" hydrogen powered fuel cells because, in addition to their high energy densities (comparable to gasoline, from 6.1 kW h/kg for methanol to 8.0 kW h/kg for ethanol) they can be easily handled, stored and transported [3]. However, further development of direct alcohol fuel cell technologies is limited by the sluggish kinetics of the alcohol oxidation reaction, the formation of catalyst poisoning intermediates (such as CO), and undesired final products (acetic acid, popanoic acid). From this point of view, investigation and development of low-cost or highly effective electrocatalysts for the oxidation of alcohols at the anode that increases current densities and shows low overvoltage is still a requirement.

Most of the studies concerning alcohol oxidation were performed in acidic media [4–7]; though, it is known that the oxidation of organic fuels is faster and has smaller overpotential in alkaline media [6,8]. Moreover, the use of alkaline conditions is more favorable for the cathode side (oxygen reduction) where a variety of non-noble metal catalysts can be used. Despite all these advantages, the development of alkaline fuel cells has been hindered by the undesirable progressive carbonation of the alkaline electrolyte due to the carbon dioxide from the air or from the oxidation of the fuel. However, recent developments of alkaline solids have allowed the use of anion-exchange membranes [9–11] direct alcohol fuel cells (AEM-DAFC) instead of caustic liquid fuels, renewing the interest in the study of alcohol oxidation at high pHs.

Similar to acidic environments, in alkaline electrolytes, the majority of the studied catalysts are based on noble metals with special attention for platinum and palladium, mono- or multimetalic [12–14]. Pt catalysts are considered the most active materials for alcohol electrooxidation in alkaline media due to the capability of Pt to catalyze C—H bond rupture at comparatively low overpotentials. Though, oxidation of the intermediate product CO on a pure Pt surface occurs only at high overpotentials and is therefore rate determining. Alloying these noble metals with more oxophilic elements can lower the electrocatalyst electronic binding energy by facilitating the adsorption of OH at lower potentials and promoting the oxidation of the organic species. The improved performance of binary and ternary electrocatalysts including Pt—Ru [15–17], Pt—Sn [15,16,18,19], PtSnRu [15], PtSnNi [19], PtRuNi [20], PtRuMo [21], and PtCuCo [22] has been extensively studied in both acidic and alkaline media.

Recently, elements as Bi have been found to promote formic acid [23], methanol [24] (at Pt single crystals), and ethanol oxida-

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tion [4,25] (Pt/C nanoparticles) in acidic media. Bi can be spontaneously adsorbed onto Pt surfaces resulting in a stable bimetallic surface in which the surface coverage of the adatom can be easily modified [26]. It has been reported that the presence of the adatom can affect the oxidation path in the mechanism of the reaction inhibiting the poison formation and enhancing the direct oxidation [24,27]. The enhancement of the reaction in catalysts containing Bi has also been reported in alkaline media for methanol [28], ethanol [25,29], and ethylene glycol [30] as bi- or tri-metals. However, most of these studies concern multimetallic nanoparticles, and full understanding on the effect of Bi is still missing.

In this work, we report the enhancement of the catalytic activity of Pt/C catalysts with irreversibly adsorbed Bi toward ethanol, methanol, and propanol oxidation in alkaline media. In this way, the effect of Bi in the catalyst surface can be accessed. The presence of Bi at the catalyst surface increases the catalytic activity of Pt toward the alcohol oxidation (ethanol, methanol, and propanol) in alkaline media. Bi showed to have a mixed behavior in the catalyst acting as a third body (impeding Pt surface poisoning) and providing OH for the reaction at lower potentials (bifunctional mechanism). The effect of the Bi coverage was studied, and experiments were performed in conditions close to "in situ" fuel cell measurements aiming to obtain information about performance and durability of the catalyst. The reaction intermediates and products were investigated using in situ infrared spectroscopy. The enhanced catalysis showed to be dependent on the alcohol and, for Bi coverages around 70% of the Pt surface, the direct oxidation path to CO_2 is preferred in smaller alcohols (methanol and ethanol) and the incomplete oxidation toward other products is favored when increasing the carbon chain in the alcohol (propanol). In any case, Pt/C catalysts modified with Bi irreversibly adsorbed at the surface showed to be a very good candidate for application in AEM-DAFC.

2. Experimental

The working electrode was prepared by the deposition of 4 µl of an ink onto a glassy carbon electrode (0.1963 cm^2 of geometric area) previously cleaned by polishing with an alumina suspension and rinsing in an ultrasonic bath. The ink was prepared using 5 mg of carbon-supported Pt catalyst (60 wt.%, Alfa Aesar), 20 µl of Nafion® solution (5 wt.% Aldrich), and 200 µl of ethanol (p.a., Altia) that were carefully mixed with a magnetic stirrer and sonicated. The electrodes prepared with this procedure have a Pt loading of ~0.02 mg.

The electrochemical experiments were performed in a classical three electrode cell at controlled temperature (20 °C) and under nitrogen purge (AGA, 99.999%) (Fig. 1). A platinum coil was used as a counter electrode and a reversible hydrogen electrode as a reference. The experiments were performed with a potentiostat/galvanostat PGSTAT100 Autolab system and a rotating device from Pine Instruments.

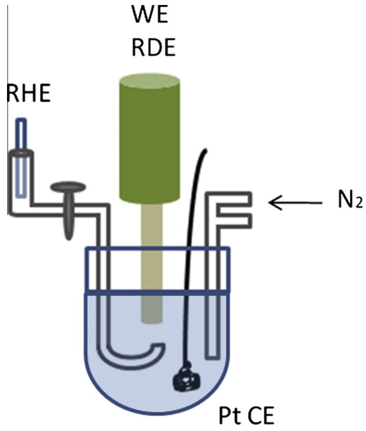

Fig. 1. Scheme of the electrochemical cell used.

Cyclic voltammetry in 0.5 M H_2SO_4 (Merck) was done for the electrochemical characterization of the catalysts and for the electrochemical active area determination. Following the procedure previously described [13], prior to the use of the nanoparticles for alcohol oxidation, they were cleaned by CO (AGA, 99.999%) adsorption and stripping [14]. The active surface area of the Pt nanoparticles was determined by the charge involved in the so-called hydrogen UPD region assuming 0.23 mC cm^{-2} for the total charge after the subtraction of the conventional current attributed to double-layer charging contribution [14].

The adatom layer was adsorbed on the electrode surfaces by contact with a 0.5 M H_2SO_4 solution containing 10^{-5} M of Bi_2O_3 at open circuit. The electrode was then rinsed with ultra-pure water and transferred to the cell containing the supporting electrolyte (0.5 M H_2SO_4) where the voltammogram was recorded. The Bi surface coverage was measured according to the previously reported methods [26]. Then, the electrode was transferred to the electrochemical cell containing 1 M of the alcohol (ethanol – p.a. Altia, methanol – Merck and propanol – Merck) in 0.1 M NaOH (Merck) where the catalysis was accessed.

Fourier transform infrared spectroscopy (FTIR) experiments were performed with a Nicolet Magna 850 spectrometer, equipped with an MCT detector. The spectroelectrochemical cell was provided with a prismatic CaF_2 window beveled at 60°. Spectra shown are composed of 100 interferograms collected with a resolution of 8 cm^{-1} and p-polarized light. They are presented as absorbance, according to $A = \log(R/R_0)$, where R and R_0 are the reflectance corresponding to the single-beam spectra obtained at the sample and reference potentials, respectively [31]. All the spectroelectrochemical experiments were conducted at room temperature, with a reversible hydrogen electrode (RHE) and a platinum wire used as the reference and counter electrodes, respectively. For these experiments, a gold collector electrode was used and the inks were prepared without the ionomer (Nafion) in order to avoid the undesirable bands coming from the polymer [32].

The contact of the electrodes with the ethanol solution was performed at controlled potential (0.1 V) where, apparently, no adsorption or reaction process takes place. This potential was maintained until the electrode was pressed against the CaF_2 window. After collecting the reference spectrum at this potential, the potential was stepped progressively to higher potentials up to 0.8 V.

3. Results and discussion

3.1. Ethanol oxidation

Fig. 2 shows the effect of irreversibly adsorbed Bi on Pt/C catalyst for ethanol oxidation in alkaline electrolyte (0.1 M NaOH) at 0 (A) and 1800 rpm (B). As an inset of the figure, the blank cyclic voltammograms (CVs) obtained for the surfaces in 0.1 M H_2SO_4 after cleaning (with the respective CO stripping) are presented as reference. As it can be observed, the presence of Bi on the surface leads to the decrease in the charge of H adsorption at potentials lower than 0.40 V due to the presence of less free Pt sites, in agreement with the previous literature [26]. On the other hand, the redox peaks characteristic from Bi are observed at higher potentials (0.60–0.70 V).

The experiments were performed in unstirred solutions as well as under electrode rotation in order to mimic the real conditions in a fuel cell anode, where the solution is always flowing through the