Applied Catalysis B: Environmental 91 (2009) 516–523

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Ethanol oxidation reaction on $PtCeO_2/C$ electrocatalysts prepared by the polymeric precursor method

R.F.B. De Souza [a], A.E.A. Flausino [a], D.C. Rascio [a], R.T.S. Oliveira [a,b], E. Teixeira Neto [a], M.L. Calegaro [c], M.C. Santos [a,*]

[a] *LEMN – Laboratório de Eletroquímica e Materiais Nanoestruturados – CCNH - Centro de Ciências Naturais e Humanas, UFABC - Universidade Federal do ABC, CEP 09.210-170, Rua Santa Adélia 166, Bairro Bangu, Santo André, SP, Brazil*

[b] *Faculdade de Ciências Exatas e Sociais Aplicadas, Campus II Universidade Federal dos Vales do Jequitinhonha e Mucuri - Rodovia MGT 367 – Km 583, n° 5000, Bairro Alto da Jacuba, 39100-000 Diamantina MG, Brazil*

[c] *Grupo de Materiais Eletroquímicos e Métodos Eletroanalíticos – Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13566-590 São Carlos, SP, Brazil*

ARTICLE INFO

Article history:
Received 10 February 2009
Received in revised form 8 May 2009
Accepted 19 June 2009
Available online 26 June 2009

Keywords:
Ethanol oxidation reaction
Electrocatalysis
Pt nanoparticles
Ceria
Polymeric precursor method

ABSTRACT

This paper presents a study of the electrocatalysis of ethanol oxidation reactions in an acidic medium on $Pt-CeO_2/C$ (20 wt.% of $Pt-CeO_2$ on carbon XC-72R), prepared in different mass ratios by the polymeric precursor method. The mass ratios between Pt and CeO_2 (3:1, 2:1, 1:1, 1:2, 1:3) were confirmed by Energy Dispersive X-ray Analysis (EDAX). X-ray diffraction (XRD) structural characterization data shows that the $Pt-CeO_2/C$ catalysts are composed of nanosized polycrystalline non-alloyed deposits, from which reflections corresponding to the fcc (Pt) and fluorite (CeO_2) structures were clearly observed. The mean crystallite sizes calculated from XRD data revealed that, independent of the mass ratio, a value close to 3 nm was obtained for the CeO_2 particles. For Pt, the mean crystallite sizes were dependent on the ratio of this metal in the catalysts. Low platinum ratios resulted in small crystallites, and high Pt proportions resulted in larger crystallites. The size distributions of the catalysts particles, determined by XRD, were confirmed by Transmission Electron Microscope (TEM) imaging. Cyclic voltammetry and chronoamperometic experiments were used to evaluate the electrocatalytic performance of the different materials. In all cases, except $Pt-CeO_2/C$ 1:1, the $Pt-CeO_2/C$ catalysts exhibited improved performance when compared with Pt/C. The best result was obtained for the $Pt-CeO_2/C$ 1:3 catalyst, which gave better results than the Pt-Ru/C (Etek) catalyst.

1. Introduction

Direct alcohol fuel cells (DAFC) have received much attention due to their potential applications in transportation and portable electronic devices [1–7]. DAFC use methanol or ethanol as fuel directly, without an external reformer, which makes them simple and compact [1]. Regarding DMFC (direct methanol fuel cells), there are two major obstacles that limit the practical application of these devices: (i) the relatively low dynamics of methanol electro-oxidation, and (ii) the high methanol crossover through the polymeric Nafion® membrane [8–10]. Similar problems are observed with DEFC (direct ethanol fuel cells), and in comparison with DMFC, are in an early stage of development. Despite these problems, DEFC have attracted much attention in recent years, mostly related to several advantages of using ethanol instead of methanol as fuel. Ethanol has a higher energy density than methanol ($8.01\ kWh\ kg^{-1}$ *vs.* $6.09\ kWh\ kg^{-1}$) [1,8]. Ethanol is also safer, can be easily produced in large quantities from biomass, and is considered a "green fuel". The development of new catalysts is particularly important for direct ethanol fuel cells (DEFCs), mainly due to their slow dynamics and poisoning of the catalyst surface by the several intermediates produced during the oxidation processes in both methanol and ethanol oxidation reactions [8,10,11]. From a practical viewpoint, the main obstacles for the development of DEFC are associated with several details closely related to the reaction mechanism. Research on new catalytic materials for DEFC requires a detailed knowledge of the reaction mechanism. Although the mechanism of ethanol oxidation is still unclear, or even contradictory in some points, it is well accepted that in acidic solutions the reaction proceeds through a series of parallel

---

[*] Corresponding author. Tel.: +55 11 4996 0163; fax: +55 11 4437 8530.
E-mail address: mauro.santos@ufabc.edu.br (M.C. Santos).

0926-3373/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2009.06.022

reactions as summarized in the following scheme [12]:

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow C1_{ad}, C2_{ad} \rightarrow CO_2 \text{ (total oxidation)} \quad (1)$$

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow CH_3CHO \rightarrow CH_3COOH \text{ (partial oxidation)} \quad (2)$$

The complete electro-oxidation of ethanol to CO_2 involves the cleavage of the C–C bond. This requires rather high activation energy, and goes through two adsorbed intermediates, $C1_{ad}$ and $C2_{ad}$, which represent intermediates with one and two carbons, respectively.

Platinum-based materials are the most successful catalysts in DEFC anodes, especially PtRu, PtRuSn, and PtSn [13–17]. The combination of Pt with an oxophilic element is essential, since this allows for the activation of water at low potentials. This step provides oxygenated species that are necessary to oxidize some of the intermediates produced during the reaction, and avoids poisoning of the catalyst surface (the bi-functional mechanism). Several metal oxides, such as RuO_2 [18–20], WO_3 [21], ZrO_2 [22], MgO [23], and CeO_2 [24], have also been used to enhance the electrocatalytical activity toward ethanol or methanol electro-oxidation through a synergistic effect. Among these, rare earth oxides exhibit a number of characteristics that make them interesting in catalytic applications, such as ceria. Ceria has a fluorite oxide structure, where the metallic center surrounded by oxygen atoms is a cationic species capable of changing its oxidation state between +3 and +4. Ceria-based catalysts have been investigated for water–gas-shift reactions at low temperatures [25], and the good performance observed has motivated the use of such catalysts in fuel cell applications [8]. Several examples of the strong performance of ceria-based catalysts for methanol and ethanol oxidations in fuels cell systems have recently been reported in the literature [26–29]. The improved performance was attributed to a synergistic effect, and to the ability of ceria to supply sufficient OH_{ads} at low potentials, which is necessary to eliminate the poisoning species (especially CO_{ads}) formed during the methanol or ethanol oxidation reactions. It is important to point out that, to the best of our knowledge, only one paper [29] reports the ethanol oxidation in an acidic medium on Pt-CeO_2 electrodes. Although the catalytic performance of ceria-based catalysts for ethanol or methanol oxidation were similar to that obtained on PtRu catalysts, cerium oxide is an ideal substitute for ruthenium in such catalysts since it is much cheaper.

Different methods have been developed to prepare Pt-based electrocatalysts with cerium oxide, such as solid-state reactions under microwave irradiation [8], electrochemical processes [26], wet precipitation and reduction [27], sodium borohydride reduction [28], and co-precipitation [29]. In the work reported here, Pt-Ce based electrocatalysts were prepared by the polymeric precursor method (PPM) [30,31]. In the PPM, metallic salts are dissolved in a mixture of ethylene glycol (EG) and citric acid (CA), producing a polyester network containing metallic ions dispersed homogeneously. The polymeric solutions are applied to the support, and the final product, generally a metal oxide, is obtained by calcination at appropriate temperatures. This method has several advantages when compared to similar methods. The experimental procedure is extremely simple and the metallic precursors used are not sensitive to water, as is the case with the traditional sol–gel method, where metal alkoxides are used as precursors. Other advantages include the easy control of several variables that can lead to different defect densities or even to phase segregation in the final product, the direct decomposition of $(NH_3)_4PtCl_2$, the salt solubility at room temperature, and the low decomposition temperature. It is important to stress that the PPM method was already successfully used to prepare nanostructured materials with enhanced performance for methanol and ethanol oxidations [16,19,30,32].

The electrocatalysts produced were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive analysis of X-rays (EDAX), and cyclic voltammetric (CV) measurements. The electrocatalytic activity was evaluated by CV and chronoamperometry (CA). The aim of this work is to use PPM for the preparation of Pt-CeO_2/C electrocatalysts (to our best knowledge this is the first time this method is used for this purpose) with different mass ratios between Pt and CeO_2, and to determine the best catalyst composition for the ethanol oxidation reaction in acidic solutions. For all compositions studied, 20 wt.% of active material (Pt-CeO_2) on carbon was used.

2. Experimental

2.1. Preparation of Pt-CeO_2/C electrocatalysts

The electrocatalysts were prepared using different mass ratios of Pt:CeO_2 (1:0, 3:1, 2:1, 1:1, 1:2, 1:3, and 0:1, with the maximum Pt loading of 0.15 mg cm^{-2}) using the polymeric precursor method as described by Freitas et al. [19] and the mass proportion 1:50:300 (metallic precursor:CA:EG). After preparation, the polymeric resins were refrigerated. For catalyst preparation, a measured volume of each resin was placed in an appropriate amount of carbon vulcan XC-72R (from Cabot), followed by the addition of excess EG that is just enough to cover the carbon powder. These mixtures were homogenized in an ultrasonic bath for 60 min, then thermally treated at 400 °C for 2 h in an N_2 atmosphere.

2.2. Physical characterization

XRD patterns of the catalyst samples were recorded in a Rigaku diffractometer (Miniflex model) using Cu-Kα radiation (1.541 Å, 30 kV and 15 mA). Catalyst compositional information was acquired in a Noran System Six X-ray microanalysis system operating at 30 kV in a JEOL JSM-5900LV scanning electron microscope (SEM). Morphological information on the catalysts was obtained via TEM using a FEI Tecnai G2 20 microscope operating at 200 kV. The samples were prepared by ultrasonication of the catalyst powders in isopropanol. A drop of the resulting dispersion was placed on thin carbon films deposited on standard TEM copper grids and dried in air. The images were acquired after surveying many different areas of the samples, in order to assess its average characteristics.

2.3. Electrochemical measurements

Electrochemical measurements were performed at room temperature ($T = 25$ °C) using an Autolab PGSTAT 302N potentiostat. Glassy carbon electrodes were used (support for the working electrodes with 0.166 cm^2 of geometric area), as were a Pt counter electrode and a reversible hydrogen electrode as the reference. The GC support was polished to a mirror finish with 1 μm of alumina suspension, and washed in a water/ethanol mixture before each experiment. The water used in all experimental procedures was obtained from a Milli-Q system from Millipore®.

The working electrodes were constructed by dispersing 10 mg of electrocatalyst powder in 1 mL water and mixing for 5 min in an ultrasonic bath. After this procedure, 20 μL of Nafion® solution (5%) was added to the suspension, and it was mixed again in an ultrasonic bath for 15 min. 16 μL aliquots of the dispersion fluid were pipetted onto the glassy carbon support surface. Finally, the