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The enhancement of methanol oxidation electrocatalysis at low and high overpotentials

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ABSTRACT

The preparation of new surfaces for anodic processes in methanol/air fuel cells has gained major attention due to the efficiency loss in the course of long-time operations. This paper proposes the use of electrochemical activated Pt/C, PtMo/C, PtRu/C, PtRuMo/C electrodes to study changes in the electrocatalytic behaviour of methanol oxidation under the potential ranges of interest for fuel cells. Electrochemical impedance spectroscopy together with polarization curves are applied to typify the interfacial behaviour of methanol electrooxidation on these activated electrodes. Impedance information discloses that these catalysts allow two distinct responses, i.e. methanol dehydrogenation as rate determining step in the low potential region (0.400-0.550 V), whereas a surface oxidation of adsorbed intermediates determining the process at high potentials (larger than 0.550 V). Moreover, we found new effects caused by molybdenum or ruthenium inclusions that are explained using the true Tafel slopes, that is, those corrected for mass transport. Thus, Tafel slopes of 0.060 V decade^{-1} are found for all carbon supported electrodes except for PtRu/C where the first electrochemical step as rate determining explained the experimental 0.120 V decade^{-1} value. The catalytic performance of carbon supported PtRuMo/C towards methanol electrooxidation showed the highest tolerance upon methanol intermediates formation.

1. Introduction

A large variety of hydrogen/oxygen fuel cells has been employed in many applications mainly because of their high efficiency and zero emission pollutants under operation. Beneath this scope, hydrogen is expected to be a clean and recyclable energy carrier after the finishing of fossil fuel uses. However, the development of fuel cell vehicles is facing a big barrier of onboard hydrogen storage due to its gaseous property of low density. The cruising range of vehicle is limited by the amount of hydrogen on-board and it has only 1/10 of energy compared with gasoline from the same volume [1].

To avoid the above fuel storage problems, the use of methanol in direct methanol fuel cells (*DMFC*) is proposed due to its high energy density, long operation time, no charging requirements and simple system design [2]. Therefore, the *DMFC* has been developed and encouraged to be used in portable and domestic devices. However, in the presence of carbon monoxide as contamination, such as in commercial methanol and hydrogen from reforming or cracking, the efficiency as a fuel seriously diminishes. More properly, in the case of the hydrogen produced *via* steam reforming or partial oxidation of methanol there is strong adsorption of carbon monoxide, which blocks hydrogen adsorption sites causing a drastic decrease of the energy density, even for trace levels of carbon monoxide [3].

It is widely accepted that carbon monoxide-type species produced in the course of methanol electrooxidation is the main poisoning intermediate that slows down the reaction kinetics, either from a series or a parallel mechanism. In order to solve this problem, platinum based binary and ternary catalysts have been prepared to improve the electrooxidation activity through either by an electronic effect or by a bifunctional mechanism [4–11]. On one hand, the formation of carbon supported platinum-based binary catalysts was reviewed in a previous work [12]. On the other hand, platinum ternary alloys preparation and performances are summarized in [13], so it is significant to declare the key parameters in the preparation of these catalysts.

(1) The actual Pt:M1:M2 atomic ratio, has to be ca. 1/3 to the rest of the metals.
(2) The amounts of M1 and M2 alloyed with platinum and the amount of metal oxides present in the catalysts has to be selected according to the nature of M1 and M2.
(3) The metal particle size and the electrocatalytic activity depend on the metal surface area, which are strongly related to methanol adsorption configuration.

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The problem of ternary alloys formation is the incessant changes in the morphology during cell operation that yields new surface compositions, yielding non-reproducible currents in the course of a constant potential alcohols oxidation. Carbon supported PtRuMo ternary electrocatalysts have attracted more attention than binary systems in recent years [14–16], since promising results have been obtained for polymer electrolyte fuel cells with reformate gas and alcohols. Generally, the procedure simply consists of the addition of a third element is added to the best binary catalyst (Pt–Ru) for anodes exhibiting tolerance for carbon monoxide adsorption and those for complete methanol oxidations.

Many electrochemical, chemical or physical methodologies have been applied to improve the catalysts performances upon their use as anodes in fuel cells. In a previous work [17], we have found that electrochemical pre-treatments lead to surface and structure modifications producing electrocatalytic improvements in current intensity and power efficiencies when using methanol as fuel. The electrochemical surface pre-treatment involves a net cathodic polarization, *ac* or *dc*, within the potential region of a net hydrogen evolution process [17]. The result of this cathodic process, that is, *cathodization*, is the “opening” of the noble metal crystalline lattice and the “widening” of the metal/acidic double layer as a result of two main forces; the bubble local pressure overpotential and the high local net electric field. The result of this process is a crystalline rearrangement able to expose noble metal centres to more water molecules as coordination centres yielding metallic sites with larger coordination numbers. These new core sites of nanocrystalline order exhibit a superior electrocatalytic activity towards fuels oxidation, such as methanol and ethanol, even for long-lasting experiments.

The purpose of this work is to study the changes in the performance of electroactivated Pt/C, PtRu/C, PtMo/C and PtRuMo/C anodes towards methanol electrooxidation in two different potential ranges of interest in *DMFC* devices.

2. Experimental

All platinum, ruthenium and molybdenum catalysts were supported on Vulcan XC-72 carbon with a designed metal loading of 20 wt % using the borohydride method as before [17]. The carbon slurry was prepared by dispersing 0.04 g of carbon in 40 mL of Millipore-MilliQ® plus water (18.2 MΩ cm resistivity) after 40 min sonication. In all cases, chloroplatinic acid hexahydrate, molybdenum(V) chloride and ruthenium(III) chloride were used as platinum, molybdenum and ruthenium precursors, respectively. To obtain the desired proportion at the catalyst the metal precursors were added to the carbon-containing solution to the 1:1 atomic ratio for PtRu/C and PtMo/C and to the 1:1:1 for PtRuMo/C. The powder was obtained by the chemical reduction of the previous solution (mother solution) with an excess of sodium borohydride in an ultrasonic bath during 90 min. The precipitate was isolated by centrifugation, washed with water and dried at 80 °C overnight. The ternary catalyst was synthesized changing the order in that carbon was impregnated with the metallic salt precursors. The electrode was prepared mixing, in an ultrasonic bath, 2.0 mg of the synthesized catalyst with 15 μL of Nafion® 5% and 485 μL of Millipore water. In all cases the activation was completed with an electrochemical pre-treatment, and more properly a *cathodization* program in the net hydrogen evolution region with a correct choice of the applied potential and time (-0.100 V for 30 min). The selected values avoid the electric field being shielded with large bubbles and guard the original current distribution of the cell during the program application. After then, the electrode surface was stabilized by ten cycles at 0.100 V.s^{-1} within the entire solvent stability potential range (0.05 and 1.450 V). This activation pre-treatment ensured the complete reduction of the chemical deposited metals (from salts precursors), as well as the required crystal lattice rearrangement [17].

Electrochemical runs were performed using a three-electrode compartment cell with the studied carbon supported catalysts deposited on a gold disc as working electrodes. A large area smooth platinum counter electrode and a reversible hydrogen reference electrode with a Luggin-Haber capillary tip completed the electrochemical system. Potential values in the text are given on the hydrogen reference electrode (RHE) scale. In addition, 1 M sulphuric acid was used as supporting electrolyte, which was prepared using Millipore MilliQ® water.

The electrochemical characterization of the catalysts was performed by cyclic voltammetry in the supporting electrolyte run between 0.050 and 1.450 V at 0.100 V s^{-1}. Surface active area was determined after the integration of the complete first positive-going carbon monoxide stripping profile with the previous double layer region subtractions. All electrochemical experiments were conducted using a PGZ 301 Voltalab® potentiostat-galvanostat-impedance with the Voltamaster 4 software. Catalysts were physical characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscope (SEM). X-ray powder diffraction data were collected using a Rigaku ULTIMA IV, 285 mm radius, Powder Diffractometer operating in Bragg-Brentano geometry. A CuKα radiation (λ=1.5418 Å) monochromatized with a diffracted beam bent germanium crystal was used to collect data over the 39 to 90 degree 2θ range in steps of 0.02 and 0.01 degree using a scintillation detector. Peak positions were extracted from the diffractograms using the program POWDERX [19]. Multiple datasets were collected for each sample in order to obtain representative values. We calculated the mean particle size of each catalyst using the Debye-Scherrer formula from XRD patterns.

In order to check the dispersion states and particle sizes we employed TEM with relative medium acceleration energy of 80 to 100 KV and 300000 and 600000 magnifications. On the other hand, the relative atomic ratio percentage and the atomic surface distribution for each catalyst were estimated from energy dispersive spectroscopy (EDS) micrographs using the SEM JEOL JSM 5900.

The electrocatalytic performance of the carbon supported electrodes towards methanol oxidation was characterised by different methodologies using an oxygen-free 0.1 M methanol + 1 M sulphuric as working electrolyte, namely, cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometric transients. Linear sweep voltammetry was performed on each surface starting from 0.05 V and scanning towards positive values up to 0.90 V run at 0.0005 V.s^{-1}. Besides, Tafel lines were obtained after performing quasi steady state polarization curves using the rotating disc methodology at 2500 rpm. All current densities were normalized by the real active area. Chronoamperometric curves were performed up to 20 minutes at the same potentials used to obtained the impedance spectra (from 0.450 to 0.600 V). The charge density values under the current transients during all the time of experiments were calculated in oxygen-free 0.1 M methanol + 1 M sulphuric media after the correction of the charge densities involved in chronoamperometric plots in 1 M sulphuric acid. Impedance spectra were obtained at the selected potential of the current transients at frequencies between 100 kHz and 50mHz with 20 points per decade of resolution. The amplitude of the sinusoidal potential signal was 10 mV in all cases.

3. Results and Discussion

3.1. Anode Catalyst Characterization

Fig. 1 depicts the cyclic voltammetric profile of the platinum based catalysts used as anodes run in the supporting electrolyte