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Metal oxide promoters for methanol electro-oxidation

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ABSTRACT

Noble metal oxides (IrO_x , RuO_x) and valve metal oxides (SnO_x and VO_x) have been investigated as promoters of Pt electrocatalyst for methanol oxidation in acidic environment. Pt modification was made using low oxide content (5 wt%) in order to evaluate the possibility of using such oxide promoter in a multifunctional catalyst. At this low level of oxide content, IrO_x provided a larger promoting effect than RuO_x . This occurred in the absence of specific alloying with Pt and also in the presence of lower catalyst dispersion. The electrocatalytic enhancement produced by the valve metal oxides was significantly lower than IrO_x and RuO_x . These results are interpreted in terms of the different water displacement mechanism for the various oxides. Such evidences seem to indicate that a multifunctional catalyst may represent a valid route to enhance methanol electro-oxidation.

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Introduction

A large number of efforts are currently performed to develop highly active methanol electro-oxidation catalysts for application in direct methanol fuel cells (DMFCs) [1,2]. This technology is of relevant interest for the fuel cells early market and may compete in the near future with Lithium-batteries for portable applications [2,3]. Most of the studies in this field are addressed at improving the state-of-the-art Pt–Ru electrocatalysts and in parallel multifunctional compounds of various formulations are actively investigated for this reaction [4–10]. Previous studies have underlined the importance of both nature and strength of adsorbed oxygen species in the reaction mechanism. Water discharging occurs at high potentials on Pt surface [11–14]. Since the role of Pt as catalyst

for methanolic species adsorption and dehydrogenation appears almost unique in the acid environment, there are several transition metals such Sn [15], W [16], Ni [17], beside Ru, which may promote water displacement at low potentials. Pd may represent an alternative to Pt for dehydrogenation but the reactions rates are significantly lower [18].

Most of the studies carried out on methanol oxidation especially those dealing with Pt–Ru have been focused on the optimization of the composition e.g. the Pt/M atomic ratio and on a better understanding of the role of alloy and oxides on promoting the oxidation mechanism [19–22]. In this regard, the effect of lattice parameter, oxidation states, particle size and dispersion have been investigated [21,22].

Several reports not only have emphasised the need of an alloy formation to allow for an atomic mixing of the active catalytic sites but also the need to have specific

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crystallographic planes on the surface [4,5,22–24]. Most of the studies that have been carried out in the last three decades clarify the fact that the unsupported or carbon supported Pt–Ru alloys with equimolar composition provide the best performance, therefore these alloys represent the best anode catalysts for DMFCs [20,25]. The methanol electro-oxidation is a slow transfer reaction and represents the rate determining step of the DMFC process. Cross-over through the membrane can be significantly decreased if methanol is efficiently oxidised at the anode [26]. Accordingly, considerable efforts are made in developing new compositions and preparation methods in order to provide effective routes for methanol oxidation.

There is an important analogy among the methanol oxidation and oxygen evolution; both processes require water discharging on the electrode followed by the adsorption of active oxygen species [2]. These give rise to a surface reaction with adsorbed methanolic residues in DMFCs or desorb as oxygen molecule in the electrolysis mode [2]. These processes occur in a quite different potential window.

The catalysts were prepared using a simple polyol method involving precursor reaction in ethylene glycol. Metal oxide modifications of Pt at low contents, i.e. 5 wt%, to individuate a guideline for the development of a multifunctional catalyst. Structure, chemistry and morphology of these catalysts were analysed by X-ray diffraction (XRD) and Transmission electron microscopy (TEM).

The aim of this work is to investigate the effect of adding noble metal oxides (e.g. IrO_x , and RuO_x) and valve metal oxides (e.g. SnO_x and VO_x) to Pt as promoters for electro-oxidation of methanol in acidic medium.

Experimental

Preparation of PtMO_x electrocatalysts

The dispersion of V_2O_5 and IrO_2 nanoparticles on carbon (Vulcan XC-72R, Cabot Corp., USA) was carried out via a solid-state reaction under intermittent microwave heating (IMH) method. In a first step, the V_2O_5 or IrO_2 (99.9% purity) powder was well dispersed over Vulcan XC-72R carbon using a mixture of 50 ml 2-propanol + 50 ml doubly distilled H_2O . The V_2O_5 and IrO_2 loadings fixed at 5 wt%, the mixture was stirred for 30 min, and then dried in oven at 80 °C for 6 h. After drying the mixture was introduced into a household microwave (50 GHz, 1400 W) and heated six times, each time for 20 s followed by a 60 s pause. In a successive step, the Pt nanoparticles were supported over $\text{V}_2\text{O}_5/\text{C}$ or IrO_2/C via a microwave-polyol (M-P) process by using sodium borohydride and/or ethylene glycol as the reducing agent. The Pt loading was fixed at 25 wt%. An appropriate amount of the prepared powder and a Pt salt (H_2PtCl_6) were ultrasonically mixed in double distilled water. 15 ml of ethylene glycol and 0.4 M KOH (in ethylene glycol) was added dropwise to adjust the pH of the solution to about 10 in order to induce the formation of small and uniform Pt nanoparticles. The resulting mixture was subjected to microwave heating for 50 s (continuous), and then the resulting sample was filtered, washed at least for 6 times with double distilled water and dried in an oven at 80 °C

for 6 h. The reason why the IrO_x and VO_x were not precipitated directly on carbon, as for PtRuO_x and PtSnO_x (see below), but dispersed directly in their oxide form, was due to the low yield achieved in this case using the precipitation procedure.

The preparation of Pt– SnO_2/C and Pt– RuO_2/C nanoparticles supported on carbon (Vulcan XC-72R, Cabot Corp., USA) was carried out in two steps; first, an appropriate amount of M-precursors (SnCl_2 and RuCl_3) and carbon were mixed together with double distilled water. The metal oxide loading was fixed at 5 wt%. The solution pH was adjusted at 10 by using 1 M NaOH solution and the mixture was stirred constantly for 3 h to allow for a complete precipitation of the hydroxide. Thereafter, the mixture was filtered, washed at least for 6 times with double distilled water and dried in an oven at 80 °C for 6 h. The dried mixture was then calcined at 400 °C for 3 h in air to form oxides. The second step involved the dispersion of Pt nanoparticles over Pt– SnO_2/C and Pt– RuO_2/C via a microwave-polyol (M-P) process as described above.

Physico-chemical characterization

The Pt/C and metal oxides catalyst were characterized by recording powder X-ray diffraction (XRD) patterns on a Philips X-pert 3710 X-ray diffractometer, using Cu K_α radiation, operating at 40 kV and 30 mA. The peak profile of the (2 2 0) reflection in the face centred cubic structure was obtained by using the Marquardt algorithm and used to calculate the crystallite size by using the Debye–Scherrer equation. The morphological characterization was carried out by transmission electron microscopy (TEM) analysis using a FEI CM12 microscope. Particle size distribution has been obtained by measuring the diameter of 200 particles assumed spherical in shape, in different regions of each sample. X-ray fluorescence was carried out with a Bruker S4 Explorer instrument.

Electrochemical characterization

The electrocatalytic activity towards methanol electro-oxidation of the prepared electrocatalysts was investigated in 0.5 M H_2SO_4 solution using slow scan rate (5 mV s^{-1}) electrochemical polarization and cyclic voltammetry techniques. Voltmaster 6 potentiostat was employed for the electrochemical measurements; it was connected to a personal computer as data interface. The electrochemical tests were carried out in three electrode configuration; it consisted of a reference electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4/1.0 \text{ M H}_2\text{SO}_4$ (MMS)), a Pt wire (as the counter electrode), and a working electrode made of the electrocatalyst powder deposited on the surface of a commercial carbon rod with active surface area of 0.5 cm^2 . The surface of the electrode for each experiment was mechanically polished with emery papers of different grades. The polished surface was then rinsed with acetone followed by washing with double-distilled water. Prior to electrocatalyst deposition, an activation step was carried out by cycling the carbon electrode in 0.5 M H_2SO_4 solution in the potential range from -800 to $+1600 \text{ mV}$ (MMS) for 50 cycles at a scan rate of 50 mV s^{-1} . 1.1 mg of the catalyst was then deposited onto the carbon surface using 5 wt% Nafion solution (dissolved in isopropyl alcohol). A uniform distribution of the

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