

### Activity of Platinum-based nanoparticles for the oxidation of C1 and C2 alcohols

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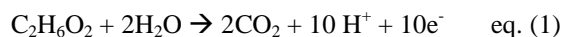
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Primary alcohols such as ethanol, 1-propanol, ethylene glycol (EG), and glycerol have been arising much interest as fuels in Direct Alcohol Fuel Cell for several reasons, for example, their low toxicity, high boiling point, high specific energy and less prominent crossover due to their larger molecular size [1-5]. Ethanol is the most promising alcohol for fuel cells because it can be easily produced in large scale from biomass. It is renewable and its complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O produces a high yield of 12 electrons per molecule [2,3]. Another important aspect with respect to the ethanol molecule is the fact that it has a simple carbon chain with two carbon atoms. Thus, the study of ethanol is important for the development of catalysts capable of C-C bond breaking [6].

Nowadays, ethylene glycol is widely used in the automotive industry, and its supply chain is well established. Moreover, ethylene glycol has several advantages that make it a good choice as fuel for fuel cell applications [7]. For example, it can be produced from biomass, it is less toxic and flammable compared to methanol, and its boiling point (bp. 197 °C) is higher than those of ethanol and methanol (bp. 78.3 and 64.5 °C, respectively) [8]. However, we must emphasize here that a direct ethylene glycol fuel cell does not present a complete oxidation of alcohol at the present stage, thus, it is necessary and important to develop catalysts for a complete oxidation of this fuel.

The probable EG electrooxidation can take place in a typical Pt-based electrocatalyst which is represented, as follows [9]:



It is easily observed that this reaction can undergo additional complicated reaction steps in comparison to the methanol electrooxidation (e.g. CH<sub>3</sub>OH + H<sub>2</sub>O → CO<sub>2</sub> + 6H<sup>+</sup> + 6e<sup>-</sup>) because there are more C-C and C-H bonds for breaking. There will be more intermediate CO-like species for removal. Therefore, the electrocatalysts materials need more ability for C-C and C-H bond breaking and more activity for efficient removal of poisoning adsorbed intermediates [1]. In order to enhance the catalytic activity of Pt-based materials towards alcohol electrooxidation, a secondary (e.g. Ru [10], Sn [5,9]) and ternary (e.g. Ir [5,10] and W [11,12]) metal is usually introduced as co-catalyst in the Pt-based catalysts. PtSn catalyst is generally considered as the best anode for ethanol oxidation [3]. Sn and/or the third metal provides O-species for CO removal from the Pt active sites during the dissociative oxidation of ethanol [3]. Salazar-Banda et al. [13] have investigated ethanol oxidation by cyclic voltammetry on a boron-doped diamond (BDD) electrode modified with Pt-RuO<sub>2</sub>-RhO<sub>2</sub>. They found that the CO poisoning effect was largely inhibited on the composite electrode containing rhodium oxide, indicating the ability

of the rhodium oxide to promote either the CO to CO<sub>2</sub> oxidation or a weaker adsorption of CO on Pt neighboring atoms in the composite thus facilitating its subsequent removal [13]. The aim of this paper is focused on the development of binary and ternary Pt-based electrocatalysts prepared by thermal decomposition of a polymeric precursor (DPP) and their application in alcohols C1 and C2 electrooxidation.

A systematic investigation of alcohol adsorption and oxidation on binary and ternary electrocatalysts in acid medium was performed. Nominal compositions were characterized by energy dispersive X-ray and X-ray diffraction (XRD) techniques. The XRD results showed that the Pt<sub>80</sub>Rh<sub>20</sub>/C and Pt<sub>70</sub>Sn<sub>10</sub>Rh<sub>20</sub>/C electrocatalysts consisted of the Pt displaced phase, suggesting the formation of a solid solution between the metals Pt/Rh and Pt/Sn.

Electrochemical investigations on these different electrode materials were carried out as a function of the electrocatalyst composition, in acid medium (0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>), and in the absence and presence of different alcohols (methanol, ethanol and ethylene glycol). The electrochemical results obtained at room temperature have shown that the Pt<sub>70</sub>Sn<sub>20</sub>Rh<sub>10</sub>/C catalyst display better catalytic activity for alcohol oxidation compared with the binary catalyst.

*In situ* Reflectance Infrared Spectroscopy measurements have shown that the oxidation of alcohols mentioned produced CO<sub>2</sub> at low potentials indicating that the materials synthesized could be used as efficient anodes in the fuel cell applications.

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