Investigation of the Electro-oxidation of Ethanol on Different Alloys

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Introduction

Ethanol is an attractive liquid fuel for polymer electrolyte fuel cell applications: it is convenient to store, it has less toxicity, it is the major renewable biofuel from fermentation of biomass, its partial oxidation products are less toxic than those of other alcohols, it posses a high theoretical mass energy density of 8.1 kWh/kg, it has an electrochemical activity comparable to that of methanol, and its permeability through the polymer electrolyte membrane is low[1-9]. Among the electrodes used to electro-oxidize ethanol, Platinum-based electrocatalysts are well-known for the electro-oxidation of organics molecules such as ethanol, but they are subject to poisoning due to the adsorbed CO molecules over the Pt which reduces drastically the catalyst activity [1-11]. Therefore, addition of other metals (M) and metal oxides (MO) such as Ru, Rh, Sn, Re, Pd, Mo, Ti, Co, Ni, CoO_2, RuO_2, SnO_2, is necessary to improve the catalytic activity of Pt [2-12].

Several studies has shown that the addition of Ru favors the adsorption of oxygen-containing species, while at the Pt sites there are strongly adsorbed carbon containing species, thus the oxidation of those carbon species can be achieved at lower potentials [2,5,12]. Some other studies found that by adding metals such as Sn, Re, Pd the ethanol electro-oxidation is improved. [7-9]

There are is still several uncertainties about the specific details of the reaction mechanisms and intermediate species formed, such as: What are the species that interact with the Pt/M sites? How can the C-C bond be broken in order to have a higher oxidation of ethanol and to improve CO_2 formation? What M atoms can be used to effectively favor the complete oxidation of ethanol to CO_2?

The objective of this work is to investigate the electrolysis of ethanol in different Pt-M electrodes as to address these questions, leading to a better understanding of the electro-oxidation reaction of ethanol on Pt-M electrodes. Electrochemical techniques, combined with computational chemistry will be used to achieve the objectives. This work is important for the development of new alloys to improve the electro-oxidation of ethanol for fuel cell applications.

Methodology

The desirable conditions for total oxidation of the ethanol to CO_2 were pursued. Different solutions in acidic and alkaline media with different electrode materials were investigated, by using cyclic voltammetry (CV) and potentiostatic techniques. The working electrodes consisted of a Pt electrode and bimetallic alloys of $Pt_{0.95}$-$Ru_{0.05}$, $Pt_{0.80}$-$Ir_{0.20}$, and $Pt_{0.80}$-$Rh_{0.20}$, with a surface area of about 3 - 4 cm^2. Theoretical investigations were performed to have a better understanding of the reaction mechanisms involved. Gaussian 03 software [13] was used to perform the quantum mechanics calculations, focusing on the interactions of Pt/M with CO, CO_2, OH^-, H^+, and ethanol.

Results

Figures 1 and 2 shows the steady cyclic voltammetry performance of a 1M ethanol solution in alkaline (KOH) and acidic media (H_2SO_4) at room temperature, with a 10mV/s scan rate. The results indicate that the media as well as the electrode strongly affects the electro-oxidation of ethanol. The first peak (which is related to the ethanol oxidation) starts at about -0.6 V vs Ag/AgCl, and at about 0.15 V vs Ag/AgCl, for the alkaline and acidic media, respectively. In addition, Pt-Ru and Pt-Ir electrodes present higher current density values in both alkaline and acid media. This suggests that different mechanisms of reaction may be taking place.

Additional results and an analysis of the thermodynamics of the reaction will be presented.

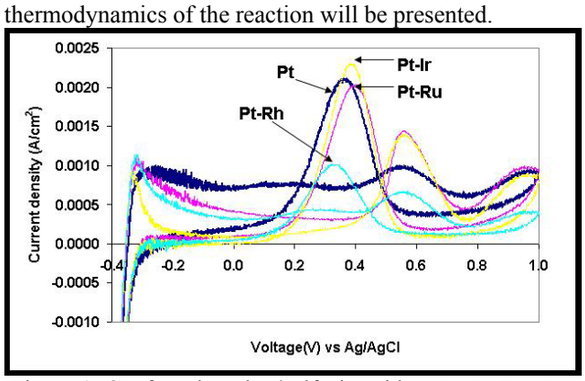

Figure 1. CV for ethanol w/sulfuric acid on Pt, Pt-Ru, Pt-Rh and Pt-Ir electrodes

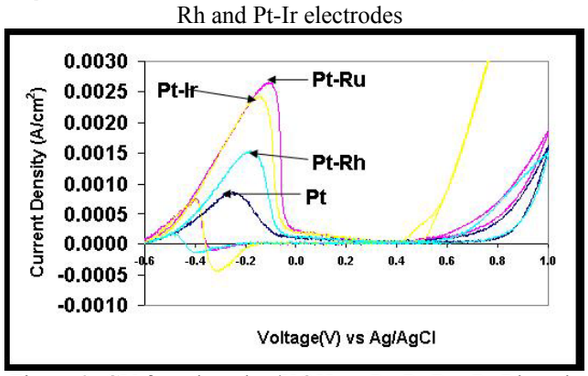

Figure 2. CV for ethanol w/KOH on Pt, Pt-Ru, Pt-Rh and Pt-Ir electrodes

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