

CO-CATALYTIC EFFECT OF NICKEL IN Pt-Ru/C AND Pt-Sn/C ELECTROCATALYSTS FOR ETHANOL ELECTROOXIDATION

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Abstract--In the present study, we examined the effect of adding nickel to Pt-Ru and Pt-Sn catalysts for ethanol electrooxidation. The alcohol-reduction process with ethylene glycol was used to prepare ten electrocatalysts. These were microchemically and physically characterized by EDX and XRD analysis. The electrocatalysts were evaluated at mini-electrodes with cyclic voltammetry at 25 and 50 °C in sulfuric acid and ethanol solutions, and as anodes in fuel cell tests. Nickel addition to Pt-Ru mixtures significantly increased the catalytic activity toward ethanol electrooxidation. For Pt-Ru-Ni catalysts, the current density was around five times greater than all other investigated mixtures. Nickel also duplicated the catalytic activity of the Pt-Sn catalyst. Furthermore ethanol electrooxidation increased with temperature for most catalytic mixtures, and the electrocatalytic activity of mixtures containing nickel, demonstrate a considerable increase with temperature. Pt-Ru-Ni catalytic activity was higher than that of all other investigated mixtures. The fuel cell test demonstrated that the addition of nickel to Pt-Ru and Pt-Sn catalysts enhances the performance of the DEFC.

Keywords-- Ethanol; Electrooxidation; PtRuNi; PtSnNi; Fuel cell.

I. INTRODUCTION

The development of direct ethanol fuel cells (DEFCs) is important for obtaining an alternative and efficient energy converter. Within this objective, there is an interesting topic that is considered fundamental to the development of these devices: the preparation of electrocatalysts and their evaluation in the ethanol electrooxidation process (Lamy *et al.*, 2004; Léger *et al.*, 2005; Song and Tsikaras, 2006).

Numerous groups have investigated the preparation of different electrocatalytic mixtures. Currently, the most commonly investigated electrocatalysts are Pt-Ru, Pt-Sn, and Pt-Ru-Sn mixtures (Antolini, 2007a; Antolini, 2007b; Antolini *et al.*, 2007; Jiang *et al.*, 2007; Jiang *et al.* 2005; Simoes *et al.*, 2007; Spinacé *et al.*, 2004) and two electrocatalytic mixtures that contain nickel, Pt-Ru-Ni (Wang *et al.*, 2006) and Pt-Sn-Ni (Spinacé *et al.*, 2005; Ribadeneira and Hoyos, 2008).

In these works, the results obtained for Pt-Ru-Ni and Pt-Sn-Ni mixtures show that nickel could be an excellent co-catalyst for ethanol electrooxidation. However, it

remains difficult to make a fair comparison and establish if there is a real increase in catalytic activity because these mixtures have not been compared under the same experimental and evaluation conditions.

As a consequence, we conducted a direct comparison of ten electrocatalytic mixtures using the same reduction process, electrocatalytic preparation, atomic relations, metal load, cyclic voltammetry (CV), and single fuel cells, evaluation conditions. In this study, we determined if the addition of nickel to Pt-Ru and Pt-Sn catalysts really increases their catalytic activity toward ethanol oxidation.

II. EXPERIMENTAL PROCEDURES

A. Electrocatalyst preparation

Six different catalytic mixtures were prepared without nickel: Pt:Ru (85:15 and 75:25), Pt:Sn (85:15 and 75:25) and Pt:Ru:Sn (75:15:10 and 75:10:15). In order to establish the effect of nickel addition, four additional catalytic mixtures were prepared: Pt:Ru:Ni (75:15:10 and 75:10:15) and Pt:Sn:Ni (75:15:10 and 75:10:15). All electrocatalysts were prepared with a metal load of 20 wt% using the alcohol reduction process (Oliveira *et al.*, 2007; Jiang *et al.*, 2006), with H₂PtCl₆·6H₂O (Merck), RuCl₃·3H₂O (Merck), SnCl₄·5H₂O (Erbo) and NiCl₂ (Erbo) as metal sources.

During the reduction process, ethylene glycol was used as a solvent and reduction agent. Vulcan Carbon[®] XC-72 was used as a support for all electrocatalysts. All mixed solutions were prepared with a 75/25 v/v ethylene glycol/water ratio throughout the alcohol reduction process. For each electrocatalytic mixture the precursor solutions were ultrasonically scattered for 30 min, and the pH was then adjusted to 11.5. The metal reduction process was conducted at 140°C for 3h. All mixtures were filtered for 2 hours and dried at 70°C for an additional 2 hours. In the reduction process there is not any type of unexpected precipitate.

Each electrocatalytic powder was added to a Nafion[®] suspension to produce an ink with a 5:2 catalyst: Nafion weight ratio (Lister and McLean, 2004), which was ultrasonicated overnight (12 hours). The electrocatalytic ink was supported at the top of a vitreous carbon rod (the working electrode) for evaluation by cyclic voltammetry (CV). The covered electrocatalyst area in the working electrode was geometrically determined using an optical microscope, and the area-values ranged between 0.22 and 0.36 cm².