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Short communication

Bifunctional amorphous alloys more tolerant to carbon monoxide☆

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Abstract

The aim of this work is the study of the electrochemical behaviour of methanol and CO electro-oxidation reaction with amorphous metallic alloys of compositions $(NiNb)_{99}(PtX)_1$ (X = Ru, Sn, compositions in at.%), which are obtained by mechanical alloying, that results to in powders used as modified carbon paste electrodes (MCPEs).

The presence of tin drastically decreases the reactivity towards methanol electro-oxidation of the alloy, followed by the $Ni_{59}Nb_{40}Pt_1$ and $Ni_{59}Nb_{40}Pt_{0.6}Ru_{0.4}$ alloys. Differential electrochemical mass spectrometry (DEMS) studies demonstrate that the $Ni_{59}Nb_{40}Pt_{0.6}Ru_{0.4}$ and $Ni_{59}Nb_{40}Pt_{0.6}Sn_{0.4}$ electrodes show the best tolerance to CO produced by methanol deprotonation, giving rise to more negative onset potential values for the CO_2 production, although the voltammograms for the stripping of a CO monolayer clearly show that the electrode that possesses a better tolerance to CO adsorbed on the surface of the electrode is $Ni_{59}Nb_{40}Pt_{0.6}Sn_{0.4}$, decreasing the onset potential values 281 and 158 mV with regard to the $Ni_{59}Nb_{40}Pt_1$ and $Ni_{59}Nb_{40}Pt_{0.6}Ru_{0.4}$, respectively. The catalytic activity of the electrode formed might be attributed to an adsorbed state of CO unique in this alloy.

Keywords: Amorphous alloys; Modified carbon paste electrodes; Electrocatalysis; Fuel cells

1. Introduction

Vehicles powered by fuel cells are currently considered by the automotive industry as a realistic alternative to the internal combustion engine. The search for alternative propulsion systems is experiencing an excellent and extensive development concerning health issues, global warning and oil reserves during the last decade.

Nowadays, some types of fuel cells are approaching commercialization. The most expected types are direct methanol fuel cells (DMFC) and polymer electrolyte membrane fuel cells (PEMFC). Unlike other types of fuel cells, DMFC need no fuel processor to reform hydrocarbon fuels. This fact makes DMFC advantageous to be applied to small and portable devices. But the intrinsic low power density of such fuel cells is a problem that must be overcome.

Catalysis by amorphous materials is no more an incipient area of research. Although some amorphous materials have been found to be useful in industrial catalysis, the rapid progress that is being made in the preparation and stabilization of new materials has opened new possibilities for developing new catalysts, which works as anodes for DMFC.

These amorphous materials are expected to have a high concentration of low coordinate active sites at their surfaces [1,2]. They are single phase, and the concentration gradients should be minimal so they offer the advantage, compared with other materials, minimizing the catalytically important phenomena such as surface segregation. Above all of these characteristics, the lack of a specific orientation of the metals used as electrocatalytically active sites is of great importance because of the behaviour of such electrodes towards a defined process (i.e. methanol, CO or ethanol, . . ., electro-oxidation), contrary to what has been inferred in many works regarding the surface orientation dependence of methanol electro-oxidation processes, on Pt, Au single crystal electrodes and Pt polycrystalline based alloys [3–5].

Relatively much electrochemical work has been carried out on metal–metal glasses, but not many have been focused on the polyphasic crystalline (Ni–Nb)-based alloys [6,7]. The composition $Ni_{60}Nb_{40}$ is very similar one of the eutectic compositions in the Ni–Nb phase diagram, so glasses of this composition are readily formed. Ni_{60}–Nb_{40} polyphasic alloys have been recently used as a matrix in new amorphous alloys [8]. These have been alloyed with $Pt_{(1-x)}$ Y_x (Y = Ru, Sn, x = 1, 0.6 at.%) metals, and further used as catalyst components for anode materials for

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