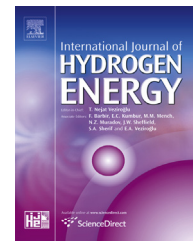




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Surface state and proton adsorption phenomena on CoRu-based materials during hydrogen evolution reaction in acid conditions

J.V. Medina-Flores^a, A. Manzo-Robledo^b, J.M. Mora-Hernández^a,
E.M. Arce Estrada^{a,*}

^a Departamento de Ingeniería en Metalurgia y Materiales, ESIQIE, Instituto Politécnico Nacional, UPALM Ed. 7, Ciudad de México, 07738, Mexico

^b Laboratorio de Electroquímica y Corrosión-DIQI, ESIQIE, Instituto Politécnico Nacional, UPALM Ed. 7, Ciudad de México, 07738, Mexico

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ABSTRACT

The electrocatalytic activity for hydrogen evolution reaction (HER) of cobalt-ruthenium based nanomaterials (Co₈₀Ru₂₀ and Co₈₀Ru₁₅Pt₅) synthesized by high energy mechanical milling was studied in acid medium. The synthesized materials were immersed in a carbon paste electrode matrix (20 wt.%). X-ray diffraction, scanning electron microscopy and transmission electron microscopy were used to characterize the synthesized powders. The composition of the nanomaterials was established by means of energy dispersive spectroscopy (EDS). SEM and TEM analysis showed the formation of agglomerates of 1–5 μm, constituted by particles of ca. 20 nm. The electrocatalytic activity of the prepared materials was evaluated in 0.5 M H₂SO₄ at 25 °C using linear sweep voltammetry and electrochemical impedance spectroscopy (EIS) techniques. EIS diagrams were obtained in a frequency range from 100 kHz to 10 mHz at selected potentials. Nyquist diagrams showed the presence of two semicircles. The kinetic parameters for HER obtained from analysis of polarization and impedance data showed that both materials exhibit good performance toward HER. According to the electrochemical parameters, the material with the best performance was Co₈₀Ru₁₅Pt₅.

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Introduction

The carbon dioxide emissions from human activities and the expected depletion of oil reserves are the subject of a global debate about energetic sustainability and climatic stability, accelerating global initiatives for developing new renewable energy systems [1]. Thus, the energy sources of the future

must be not only clean, safe, efficient and versatile, but also easy to handle that can be efficiently delivered to the final user [2]. Nowadays, electricity is one of the energy carriers most important worldwide because it is a convenient form of energy produced from various sources and distributed over large distances. Nevertheless, the production of electricity from fossil fuel sources generates also air pollution. The global

* Corresponding author. Fax: +52 5557295426.

E-mail address: earce@ipn.mx (E.M. Arce Estrada).

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dependence on fossil fuels can be lessened by using environmentally-friendly and sustainable renewable sources of energy, resulting as an effective decrease of the net flow of CO₂ to the atmosphere [3–5]. On the other hand, it is well-known that solar panels and wind turbines generate electricity with less air and water contamination; however, the energy obtained cannot be easily stored, so it should be transformed into chemical energy through water splitting.

In this context, hydrogen, another clean, efficient and versatile energy carrier, has attracted worldwide interest on addressing research efforts for developing efficient and low-cost strategy for its large-scale production [6,7]. These carriers might satisfy all the energetic demand and form an energy system that is permanent and independent [8,9]. However, hydrogen is not a resource that can be found in its molecular form, only taking part of other compounds, being water the most abundant. Hydrogen can be produced from a wide variety of materials, including fossil fuels, biomass and water electrolysis [10]. Water electrolysis is a method to produce hydrogen with efficiency of ca. 70%. However, as it is necessary the use of electricity, this method is expensive and controlled by thermodynamics [11]. On the other hand, hydrogen can be produced using electricity from renewable energy sources such as solar and wind, decreasing costs [12].

One of the main factors, being crucial in the cost of hydrogen produced by a proton exchange membrane (PEM) electrolyzer, is the choice of the electrode materials due to noble metals are used in order to obtain good performance for hydrogen and oxygen evolution. Generally, the exchange current density is a parameter to measure the ability of a given metal to catalyze the HER. In fact, three properties are considered in selecting an active material for hydrogen evolution i) a high intrinsic electroactivity effect, characterized by a high exchange current density; ii) a large electroactive surface area, directly related with intrinsic overpotential for operation at a determined current density; and iii) the catalyst stability [13].

Until now, platinum and its alloys have been found to be electrode materials on the top of which hydrogen evolves with the minimum overpotential [14]. Unfortunately, the application of Pt in the future is going to be limited because of its high price, limited resources, self-poisoning and poor durability [5,15,16]. One of the main challenges in PEM technologies is to reduce noble metal contents or to replace them and to maintain the same level of efficiency [17]. A way to reduce Pt content is by alloying it with other elements and by using a suitable support [18–20]. Besides, well-engineered materials have to be employed in order to facilitate the release of hydrogen bubbles from the surface of the electrode, increasing the performance of the electroactive materials. From an economic viewpoint, the technology and the knowledge for hydrogen production, especially from PEM water electrolysis, are still limited by the development of efficient electrocatalysts from relatively cheap and earth-abundant materials [21]. Alternatively non-precious metals, such as Ni, Mo, Co and their alloys with other elements and compounds as P, Al, Ti, W, TiO₂, have been studied for HER electrocatalyst and have shown a good performance in alkaline medium [22–26], but the activity of some of these systems evaluated in a PEM electrolyzer is poor because of their

instability in acid medium [27]. Other investigations have been focused in the anode side for oxygen evolution reaction using a trimetallic system composed of Pt, Ru and Co [28], and for the evaluation of the hydrogen evolution reaction [29] using steady-state electrochemical techniques.

Therefore, in this work the catalytic properties toward HER obtained by Linear Polarization and Electrochemical Impedance Spectroscopy (EIS) techniques were studied, by using cobalt-ruthenium based nanostructured materials (Co₈₀Ru₂₀) modified with platinum (Co₈₀Ru₁₅Pt₅) and synthesized by mechanical alloying. The intrinsic nature (morphology and structure) of the as-prepared materials were analyzed by scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy and X-ray diffraction. Besides, the crystallite size was evaluated using Scherrer and Williamson–Hall methodologies.

Experimental

Electrode preparation

Preparation of the catalytic powders was performed by mechanical alloying technique. Two different systems were synthesized: Co₈₀Ru₂₀ and Co₈₀Ru₁₅Pt₅. Co (Sigma–Aldrich 325 mesh powder), Ru (Sigma–Aldrich 200 mesh powder) and Pt (Sigma–Aldrich 1 μm) were introduced in a high energy ball mill Spex 8000 during 40 h, using a stainless steel vial and balls, with a ball to powder ratio of 4:1. The chemical composition (wt.%) was obtained by energy dispersive spectroscopy (EDS). The modified carbon paste electrode used as working electrode was prepared as follows: 0.1 g of metallic phase and 0.4 g of graphite were mixed with 0.25 mL of silicone oil. The carbon paste obtained was packed into a polypropylene holder to control the exposed surface. Electrical contact to the paste was established via a thin platinum rod passed through the polypropylene holder.

Electrochemical setup

A conventional electrochemical-glass cell was used with a separated compartment for the reference electrode. The reference electrode was a mercury-potassium sulfate electrode Hg/K₂SO₄ (E = 0.64 V/NHE). All potentials are referred to NHE. A Pt mesh was used as counter electrode. The electrochemical experiments were carried out in aqueous acid 0.5 M H₂SO₄ solution purged with ultra-high purity nitrogen to remove dissolved oxygen. The flux of nitrogen was maintained above the electrolyte surface during the measurements. All experiments were carried out at room temperature, controlled by an isothermal bath. A Potentiostat/Galvanostat Autolab-30 was used. Linear sweep voltammetry measurements of hydrogen evolution were carried out by first stabilization at open circuit potential (OCP), then a linear scan was conducted starting from OCP to negative direction, at a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy measurements were performed in a frequency range from 100 kHz to 10 mHz at selected potentials of 0, -0.010, -0.025 and -0.035 V. The EIS data were adjusted using Nova 1.8 software, employing a non-linear fit method.

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