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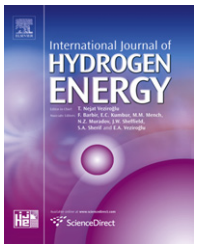

Electrocatalytic activity of nickel oxide nanoparticles-modified electrodes: Optimization of the loading level and operating pH towards the oxygen evolution reaction

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ABSTRACT

The current study addresses the superior electrocatalytic activity of nickel oxide nanoparticles (nano-NiO_x) modified GC, Au and Pt electrodes towards the OER. The electrodeposition of nickel oxide nanoparticles (with an average particle size of 80 nm) are believed to enhance the OER reaction. NiOOH phase, as shown from XRD data, participates in the OER mechanism in such a way to facilitate the charge transfer during various steps in the reaction mechanism through a reversible transformation of NiOOH to NiO_2. Optimizing the loading level and the operating pH of the proposed catalyst has been carried out.

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1. Introduction

With the increase demand for clean fuel and consciousness of environmental issues, the use of hydrogen (H_2) gas as a clean, efficient and portable fuel has become one of the attractive alternatives for energy consumption. Therefore, there is a great need to develop a more active, efficient, stable, and cheap electrocatalysts for water splitting that would offer low overpotentials for the hydrogen and oxygen evolution reactions. The oxygen evolution reaction (OER) on oxide surfaces is in the focus of electrochemical research for more than three decades mainly because it is the main source of overpotential in the industrial water electrolysis [1–9].

There is an extensive work in the literature addressing the development and characterization of suitable anodic materials for the applications in water electrolysis and batteries technology. As alternative to precious metals, metal oxide-based electrodes, particularly Ni and Co oxides, have long been used as electrocatalysts for the OER in alkaline electrolyzers due to their great stability and high activity [1–6,9].

Dimensionally stable anodes (DSA) have been successfully developed early in 1960s and stimulated a technological revolution in oxygen evolution and chlor-alkali industry [10–18].

In this context, tailoring the electronic and structure properties of a surface by modification with nanoparticles opens the door for smart electrocatalysts of unique properties for several electrochemical applications [19]. In some cases, alloying or just a slight modification of an electrode results in a synergistic catalytic effect enhancing the rate of OER by

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orders of magnitude compared with that obtained on the bare (i.e., unmodified) electrodes [20–23]. For instance, iridium oxide electrodes modified with platinum nanoparticles have shown an extraordinary synergistic catalytic enhancement for oxygen evolution reaction [20].

Among these tailored electrodes used for the electrocatalysis of the OER are the nano-crystalline forms of transition metal oxides with rutile structure (e.g., RuO_2, IrO_2) [10,24,25] which are primarily targeted for OER in acid media. Also, the oxohydroxides nano-structured (e.g., MnOOH [21] and NiOOH [1,26,27]) exhibit interesting electrocatalytic activities towards the OER.

In the present study, the modification of GC, Au and Pt electrodes with nano-structured Ni oxide (nano-NiO_x) results in a significant enhancement in the electrocatalytic activity towards the OER. This enhancement is found to be substrate independent. The effect of pH of the electrolyte and the effect of extent of loading of the electrocatalyst on the electrocatalytic activity have been investigated. The formation of NiOOH (the active oxide phase towards the OER) is believed to enhance the OER via facilitating the charge transfer through various steps of the reaction.

2. Experimental

Glassy carbon (GC, $d = 3.0$ mm), polycrystalline Au ($d = 1.6$ mm) and polycrystalline Pt ($d = 1.6$ mm) were used as the working electrodes. An Ag/AgCl/KCl (sat.) and a spiral Pt wire were served as the reference and counter electrodes, respectively. Conventional pretreatment methods were applied to clean the GC, Au and Pt electrodes. Typically, the electrodes were mechanically polished with aqueous slurries of fine alumina powder with the help of a polishing microcloth. Moreover, Au and Pt electrodes were electrochemically pretreated in 0.5 M H_2SO_4 solution by cycling the potential until obtaining a typical cyclic voltammogram (CV) for characteristic clean poly-Au and poly-Pt electrodes (cf. Fig. 1C, curve a).

The fabrication of nano-NiO_x on the pretreated electrodes was made in two steps; the first step is the deposition of metallic nickel from an aqueous solution of acetate buffer pH 4.0 containing 1 mM $Ni(NO_3)_2 \cdot 6H_2O$ by applying a constant potential electrolysis at −1.0 V vs. Ag/AgCl/KCl(sat) for 4 min. The second step is the passivation of the electrodeposited metallic nickel, the partially modified electrode was placed into a fresh PBS (pH 7.0) and was then passivated electrochemically by cycling the potential between −500 and 1000 mV vs. Ag/AgCl/KCl(sat) for 10 cycles at 200 mV s^{-1} [28–30] (cf. Fig. 3).

All of the chemicals used in this investigation were of analytical grade. All measurements were performed at room temperature (25 ± 1 °C). All current densities were calculated on the basis of the geometric surface area of the relevant working electrode. Electrochemical measurements were performed using an EG&G potentiostat (model 273A) operated with Echem 270 software.

Scanning electron microscopy (SEM) was performed using Philips, XL30 to reveal the electrode morphology. Moreover, X-ray diffraction (XRD), using PANalytical, X'Pert PRO machine with Cu target ($\lambda = 1.54$ Å), was used to probe the electrode composition and crystal structure.

3. Results and discussion

3.1. Characterization of nano-NiO_x modified electrodes

The SEM image (shown in Fig. 1A) reveals that the electrodeposited Ni has a dendritic nanostructures with an average particle size of 80 nm that partially covers the surface of GC electrode. After the electrochemical passivation step, XRD measurements were carried out at nano-NiO_x modified GC electrode and the corresponding results are shown in Fig. 1B. Inspection of this figure indicates the presence of nickel oxide-hydroxide (NiOOH) phase at the electrode surface as evident from the peaks located at 2θ equal 25.2, 37.9 and 43.1, which are assigned to NiOOH phase (PDF card 00-006-0075) the other peaks at 2θ equal 62.2 and 78.6 are assigned to NiO phase (PDF card 01-071-4750).

Fig. 1C shows CV responses of the unmodified (solid curve) and the nano-NiO_x modified (dashed curve) Pt electrodes measured in 0.5 M H_2SO_4. Inspection of this figure depicts that the deposition of nano-NiO_x leads to: (i) a noticeable decrease of the intensity of the cathodic peak current (at ca. 500 mV), corresponding to the reduction of the Pt oxide layer formed during the anodic-going potential scan, and (ii) a remarkable decrease of the current in the hydrogen adsorption/desorption region in the potential range of ca. −200 to +50 mV. These two observations reflect a decrease in the real surface area of Pt [31,32], from which the surface coverage of the nano-NiO_x on Pt electrode can be estimated.

3.2. OER at nano-NiO_x modified electrodes

The electrocatalytic activity of nano-NiO_x modified GC, Au, and Pt electrodes towards the OER was investigated by recording the linear scanning voltammograms (LSVs) in an aqueous solution of 0.5 M KOH. Table 1 lists the potential of the individual electrodes measured at a current density of 10 mA cm^{-2} (E_{10}). This table shows a significant decrease in the values of E_{10} at the nano-NiO_x modified electrodes compared to the unmodified electrodes. This indicates a significant enhancing role of the nano-NiO_x towards the OER. This corresponds to an equivalent decrease in the energy consumption accompanying the overall electrolysis process. The observed enhancement calls for optimization of the loading level of nano-NiO_x and operating pH of the proposed catalyst.

3.3. Effect of nano-NiO_x loading

The extent of nano-NiO_x loading on the electrocatalytic activity towards the OER has been investigated. Fig. 2A shows CV responses of (a) unmodified and (b,c) nano-NiO_x modified Au electrodes with various extents of loading measured in 0.5 M H_2SO_4. This figure shows a typical characteristic behavior of a clean polycrystalline Au electrode (curve a), i.e., the formation of a surface oxide layer starts at a potential of ca. 1100 mV and extends to 1500 mV. The broad nature of this oxidation peaks originates from the fact that polycrystalline Au electrode is composed of several low facet orientations with various formation potentials of the oxide

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