INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 12448–12456

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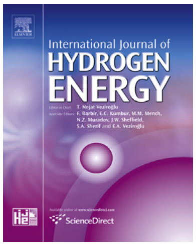

Study of Co–W crystalline alloys as hydrogen electrodes in alkaline water electrolysis

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ARTICLE INFO

Article history:
Received 28 March 2014
Received in revised form
26 May 2014
Accepted 15 June 2014
Available online 9 July 2014

Keywords:
Co-W alloys
Hydrogen evolution reaction (HER)
Electrocatalytic activity
Alkaline solution
Electrochemical impedance spectroscopy (EIS)

ABSTRACT

Binary Co–W crystalline alloys, $Co_{95}W_5$, $Co_{90}W_{10}$, $Co_{85}W_{15}$, $Co_{80}W_{20}$ and $Co_{70}W_{30}$ (atomic %) were investigated in view of their possible applications as electrocatalytic materials for hydrogen evolution reaction (HER). The electrocatalytic efficiency of the electrodes was studied on the basis of electrochemical data obtained from steady-state polarization and electrochemical impedance spectroscopy (EIS) techniques in oxygen-free 1 M NaOH solution at 298 K. The results were compared with those obtained on polycrystalline Co. Moreover, literature data concerning the electrocatalytic activity of polycrystalline Ni and Ni–Mo alloys, which are considered good electrocatalyst materials for the hydrogen evolution reaction in alkaline solutions, were also reported for comparison. The values of Tafel slope, b, exchange current density, j_0, and overpotential at the current density of 250 mA cm^{-2}, η_{250}, indicated outstandingly high electrocatalytic activity of Co–W electrodes. The best performance towards the HER demonstrates the $Co_{90}W_{10}$ alloy in accordance with the prediction based on the electronic structure calculations and the enhanced density of states at the Fermi level of the 3d Co band.

Introduction

Hydrogen evolution reaction (HER) is one of the most intensively studied reactions in electrochemistry. The study of this reaction is of primary importance in the area of the fuel cells [1,2], metal hydride batteries [3,4], hydrogen production through water electrolysis [5,6] and even in the inhibition of hydrogen gassing [7].

Many papers have dealt with ways of increasing effectiveness of cathodes for the HER in alkaline solutions. Research in the area of HER catalysts development has been mainly focused on several areas of interest: (i) intrinsic nature of the reaction, (ii) electrode composition, (iii) surface morphology, (iv) structural, chemical and electronic properties and (v) physical, chemical and electrochemical activation treatments. Two properties play an important role in selecting catalytically active materials for the HER: (a) the actual electrocatalytic effect of the material, which is directly dependent on the (over)potential used to operate the electrolyzer at significant current densities and (b) the catalyst stability. A desired decrease in overpotential can be achieved by choosing

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http://dx.doi.org/10.1016/j.ijhydene.2014.06.082

an electrode material of high intrinsic catalytic activity for the HER and/or by increasing the active surface area of the electrode. In respect to the former, the catalytic activity for hydrogen evolution can be enhanced by modification of the electronic structure of electrode metals by alloying or by use of suitable preparation methods which allow obtaining electrodes with highly developed rough or porous surfaces [8,9].

The kinetics of H_2 evolution from alkaline solutions has been investigated on cobalt, owing its relatively good catalytic activity and corrosion stability. There are two possibilities to enhance the activity of bare Co, (i) to increase the surface area by various methods or (ii) from a catalytic point of view, to alloy Co with other metals to obtain alloys with optimal adsorption characteristics [10–13].

From the theory of electrocatalysis [14] the electrocatalytic activity depends on the heat of adsorption of the intermediate on the electrode surface, in a way giving arise to the well known “volcano curve”. Miles [15] suggested that a combination of two metals from the two brunches of volcano curve could results in enhanced activity. Jacksic [16] showed that a combination of Ni or Co with Mo or W could result in a substantial enhancement of HER. In recent years, there has been a substantial effort to investigate the structural, electronic and chemical properties of bimetallic systems. Bimetallic surfaces are extensively used in many industrial processes in the area of catalysis, electrochemistry and microelectronics fabrication. Alloys are superior over single metal counterparts in terms of catalytic activity and/or selectivity.

A few studies investigated the kinetics and mechanism of HER at Co–W [17,18] alloys of various compositions, obtained by electrodeposition from suitable baths. All these electrodes are characterized by having a high roughness factor. However, to the best of our knowledge, no works are available on the electrocatalytic properties of Co–W alloys synthesized by melting as cathodes for alkaline water electrolysis.

The present work aims to investigate the electrocatalytic activity of some metallurgically prepared binary Co–W alloys as catalysts for the HER in 1 M NaOH solution at 298 K. The electrodes were mechanically polished to avoid the problem of “geometric” effect and to find out eventually presented true catalytic effect for the HER. The kinetics of the HER on these electrode materials was studied by using steady-state polarization and electrochemical impedance spectroscopy measurements.

Experimental details

The metals used were cobalt and tungsten (99.99 mass %, nominal purity), supplied by NewMet Koch, Waltham Abbey, UK. Binary Co–W alloys, $Co_{95}W_5$, $Co_{90}W_{10}$, $Co_{85}W_{15}$, $Co_{80}W_{20}$ and $Co_{70}W_{30}$ (atomic %), with a mass of about 2 g each, were metallurgically prepared by arc melting from starting metals in pieces, in inert Ar atmosphere. The samples were melt and reversed at least five times to assure homogeneity.

All the electrochemical measurements were performed in a two-compartment conventional double-walled Pyrex glass cell. The experiments were carried out in a 1 M NaOH electrolyte at 298 K. A large platinum foil (10 cm^2) was used as the counter electrode. The reference electrode was a saturated calomel electrode (SCE). With these experimental conditions, the equilibrium potential for hydrogen was −1070 mV. Oxygen was removed from the solution by bubbling nitrogen gas for 30 min before each test. The geometrical area of all electrodes used was 0.30 cm^2. The experimental results are referred to this geometric surface area. Before each electrochemical measurement the electrodes were mechanically polished with diamond paste down to 1 μm and finally rinsed with distilled water. The surface morphology of catalysts was examined using a Zeiss scanning electron microscope, model EVO 40, working at a 20 KV acceleration, equipped with the SmartSEM™ software.

Tafel curves were recorded potentiostatically in the potential range of −1070 to −1500 mV/SCE using a Solartron 1286 Electrochemical Interface. The kinetic parameters (i.e., Tafel slope, *b*, exchange current density, i_0, and overpotential at the current density of 250 mA cm^{-2}, η_{250}) were obtained after correction for the ohmic drop. Impedance spectroscopy measurements were performed over seven frequency decades, from 100 kHz to 10 mHz, using a frequency response analyzer Gamry EIS300. The *ac* amplitude was 10 mV peak to peak. Impedance spectra were recorded at selected overpotentials mainly located in the linear portion of Tafel plots.

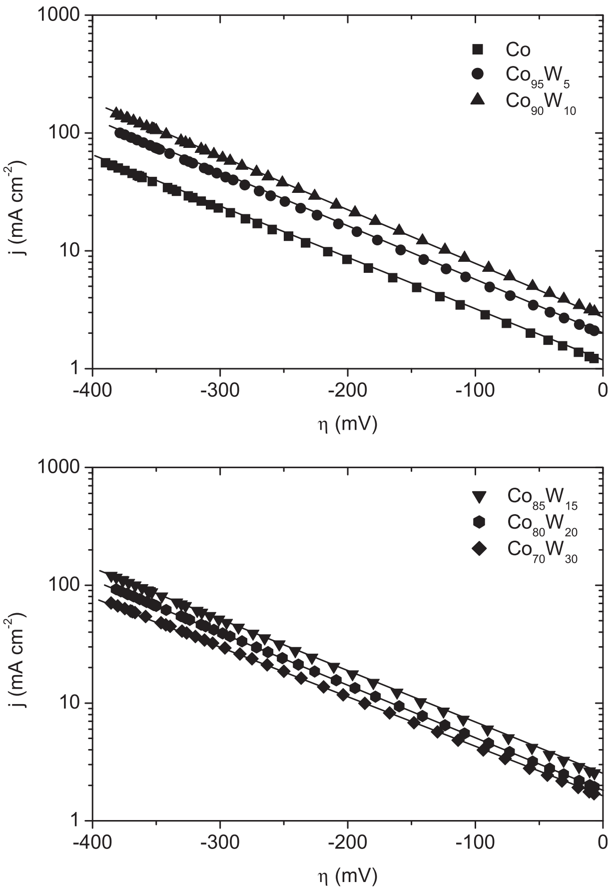

Fig. 1 – Quasi-potentiostatic polarization curves recorded on pure Co and Co–W electrodes in 1 M NaOH solution at 298 K.