Synthesis and characterization of macroporous Ni, Co and Ni–Co electrocatalytic deposits for hydrogen evolution reaction in alkaline media

C. González-Buch, I. Herraiz-Cardona, E. Ortega, J. García-Antón, V. Pérez-Herranz*

Ingeniería Electroquímica y Corrosión (IEC), Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de València, Camino de Vera, s/n. 46022 Valencia, Spain

ARTICLE INFO

ABSTRACT

In this work, macroporous Ni, Co and Ni–Co electrodes have been developed by co-deposition at high current density on stainless steel (AISI 304) substrates. The obtained materials were characterized both morphologically and chemically by confocal laser scanning microscopy, and SEM coupled with EDX analysis. The activity for hydrogen evolution reaction (HER) on the obtained layers was assessed by using pseudo-steady-state polarization curves and electrochemical impedance spectroscopy (EIS) in alkaline solution (30 wt.% KOH). The electrochemical results show that HER on these electrodes takes place by the Volmer–Heyrovsky mechanism. The synthesized coatings present higher catalytic activity for HER than commercial smooth Ni electrode. As the Co content increases in the electrodeposition bath the obtained structures show lower surface roughness factors. Ni–Co deposit with a Co content of 43 at.% manifests the highest intrinsic activity for HER as a consequence of the synergetic combination of Ni and Co.

1. Introduction

Current global energy system is mainly based on fossil fuels: oil, natural gas and coal [1]. In fact, 81% of the primary world energy production comes from these fuels, originating serious problems, which will grow with time [1]. The most important drawbacks of this system are: (1) environmental problems derived from the greenhouse effect gasses emission; and (2) fossil fuels reserves are finite.

Hydrogen is one of the most promising candidates as an energy carrier, and it can be positioned as the main alternative to fossil fuels to reduce CO_2 emissions. It is a versatile, efficient, and clean fuel [1–3]. Most of the methods used for H_2 production are based on fossil fuels, due to their easy usage in present designed machines and low costs [4–6]. Nevertheless, it is not consistent with the policies on the way to a green energy system. On the other hand, H_2 generation from alkaline water electrolysis has a lot of possibilities of coupling renewable energy sources, minimizing pollution emissions [7]. However, this technique is not widely used in global H_2 generation due to its low energy efficiency (high operating costs) [6,8]. This problem may be solved by the development of inexpensive electrode materials with low HER overpotentials, i.e. with good electrocatalytic activity. The increase in the electrode catalytic activity can be carried out by enlarging its real surface area and/or its intrinsic activity [9]. In this way, Ni,

---

and Ni-based compounds and alloys are the most important and studied electrode materials, which respond to their high catalytic activity and stability at low cost [10–12].

Different techniques have been used to enlarge the electrode real surface area, being one of them the electrodeposition at large current densities [13–16]. Alternatively, Ni intrinsic activity has been improved by means of the combination of Ni with metals such as: NiCo [17–19], NiFe [20–22], NiMo [20,23,24], NiW [20,25,26], NiLa [27,28].

The objective of the present research is the development of macroporous Ni and Ni–Co coatings deposited on stainless steel (AISI 304) at high current density from Ni chloride baths modified with different cobalt amounts. The influence of Co incorporation in the Ni porous matrix was tested by means of SEM, confocal scanning microscopy and EDX. The activity towards hydrogen evolution reaction (HER) was assessed by pseudo-steady-state polarization curves and electrochemical impedance spectroscopy (EIS) in alkaline media.

2. Experimental

2.1. Preparation of electrodes

The electrocatalytic layers were deposited onto AISI 304 stainless steel disc electrodes (0.5 cm^2 geometric area). These substrate materials were set up with the pre-treatment process described in our previous works [15–17,19], as an initial step.

A porous nickel electrode (Ni electrode) was galvanostatically synthesized at a current density of 1 A cm^{-2}, in a bath composed of NiCl$_2$·6(H$_2$O) and NH$_4$Cl (Ni electrode). Nickel–cobalt electrodes were obtained under the same operating conditions by adding different amounts of CoCl$_2$·6(H$_2$O), diluted in the minimum distilled water volume (ca. 1 mL), to the electrodeposition bath. The cobalt salt was not initially added to the electrodeposition bath in order to avoid the Co occlusion down to a Ni layer, as a consequence of the anomalous co-deposition of NiCo alloys [29]. Both the synthesis operating conditions and the electrode nomenclature used in the following are collected in Table 1. Note that the parameter t_{Co} in Table 1 is the time during the electrodeposition process at which Co is added to bath. Cobalt electrode was fabricated in two steps, firstly a nickel layer was electrodeposited onto AISI 304 stainless steel with the same electrodeposition bath that the Ni electrode during 45 min and then a Co layer is obtained in a bath composed of CoCl$_2$·6H$_2$O and NH$_4$Cl. Chemical grade reagents used for electrolyte preparation with distilled water were not subjected to a supplementary purification. Ni, Co and/or Ni–Co electrodeposition at high current densities takes place simultaneously to the gas bubbling, i.e. gas bubbles act as a dynamic template [13,15,16], following the schema shown in Fig. 1.

Electrodepositions were accomplished in a thermostated one-compartment cell with the substrate surface to be coated in horizontal "face-up" position (see Fig. 2), allowing the free departure of the generated gas bubbles [16]. A three-electrode configuration was employed for the electrodeposition process. A large-area graphite electrode of high purity was used as a counter-electrode, and an Ag–AgCl (3 M KCl electrolyte)

Table 1 – Synthesis operating conditions, bath composition and nomenclature of employed the developed macroporous Ni, Co and NiCo electrodes.

Ni electrode		
Nomenclature	Base bath composition	g L^{-1}
Ni	NiCl$_2$·6(H$_2$O)	48
	NH$_4$Cl	170

NiCo electrodes			
Nomenclature	Base bath composition	g L^{-1}	t_{Co} (min)
NiCo1	NiCl$_2$·6(H$_2$O)	48	55
	NH$_4$Cl	170	
	CoCl$_2$·6(H$_2$O)	10	
NiCo2	NiCl$_2$·6(H$_2$O)	48	45
	NH$_4$Cl	170	
	CoCl$_2$·6(H$_2$O)	10	
NiCo3	NiCl$_2$·6(H$_2$O)	48	15
	NH$_4$Cl	170	
	CoCl$_2$·6(H$_2$O)	10	
NiCo4	NiCl$_2$·6(H$_2$O)	48	15
	NH$_4$Cl	170	
	CoCl$_2$·6(H$_2$O)	15	
NiCo5	NiCl$_2$·6(H$_2$O)	48	15
	NH$_4$Cl	170	
	CoCl$_2$·6(H$_2$O)	40	

Co electrode				
Nomenclature	Step	Base bath composition	g L^{-1}	t (min)
Co	1	NiCl$_2$·6(H$_2$O)	48	45
		NH$_4$Cl	170	
	2	CoCl$_2$·6(H$_2$O)	48	15
		NH$_4$Cl	170	

Operating conditions	
Temperature (°C)	25
Current density (A cm^{-2})	1
Time (min)	60
pH	4.5

electrode was used as reference. The experiments were carried out by means of an AUTOLAB PGSTAT302N potentiostat/galvanostat.

The surface morphologies and compositions of the obtained electrocatalytic coatings were studied by means of an OLIMPUS LEXT OLS3100-USS confocal laser scanning microscope, and a JEOL JSM-3600 scanning electron microscope coupled with an Energy-Dispersive X-Ray (EDX) analysis.

2.2. Electrochemical measurements

HER on the synthesized electrocatalysts was accomplished by pseudo-steady-state polarization curves and electrochemical impedance spectroscopy (EIS) in oxygen free 30 wt.% KOH solutions, obtained by bubbling N$_2$ (15 min) before the tests.

Potentiodynamic polarization curves were recorded at a scan rate of 1 mV s^{-1} from −1.60 V vs Ag/AgCl (−1.40 V vs SHE) up to the equilibrium potential, at 30, 40, 50, 60, 70 and 80 °C. The working electrode was held at −1.60 V vs Ag/AgCl (−1.40 V vs SHE) in the same solution before the experiments, for the time needed to set up reproducible representations.