

Energy Efficiency Improvement of Alkaline Water Electrolysis by using 3D Ni Cathodes Fabricated via a Double-Template Electrochemical Process

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Alkaline water electrolysis is one of the easiest methods for hydrogen production, offering the advantage of simplicity. Moreover, it represents an environmentally friendly technology for production of high purity hydrogen. Nevertheless, the elevated production costs due to low conversion efficiency and electrical power expenses can be named as the main drawbacks of electrochemical hydrogen production.

This work is focused on the development and characterization of 3D porous Ni cathodes for alkaline electrolyzers. The electrodes were synthesized by nickel electrodeposition on copper foams obtained from hydrogen bubbles dynamic templates (double-template electrochemical process). The developed electrodes were characterized by SEM, confocal laser scanning microscopy, and EDX. The electrocatalytic performance of the developed electrodes for hydrogen evolution reaction (HER) was evaluated in 30 wt.% KOH solution by using hydrogen discharge curves and galvanostatic tests. Results show that the use of the developed electrodes as cathodes in electrolysis systems makes possible an energy saving of ca. 25% in conditions at which industrial alkaline water electrolysis is carried out, in comparison with the smooth commercial Ni electrodes.

1. Introduction

Hydrogen is considered an ideal energy carrier that can be an alternative to fossil fuels due to the fact that hydrogen is a clean and fully recyclable substance with a practically unlimited supply (Kunzru, 2008). The electrochemical production of hydrogen by alkaline water electrolysis is one of the most promising methods with great potential of using renewable energy sources (Miltner et al., 2009). Furthermore, it represents an environmentally friendly technology for production of high purity hydrogen (Veziroglu et al., 1992). However, the high energy consumption of alkaline water electrolyzers retracts its large-scale application at present.

Although platinum shows the highest activity for the hydrogen evolution reaction (HER), new electrode materials have been investigated, aiming at the reduction of the cost associated with the electrocatalyst development. Among these materials, nickel and its alloys show a high initial electrocatalytic activity toward the HER. The electrode activity can be enlarged by increasing the real surface area and/or the intrinsic activity of the electrode material (Lasia, 2003).

The increase of the real surface area can be achieved by several methods: depositing Ni together with an active metal like Al or Zn (i.e. by electrodeposition, thermal spray, etc.) followed by the dissolution of the secondary component (Raney type electrodes); electrodeposition of Ni at large current densities, electrodeposition of Ni on metallic opals (made of silica or polystyrene) with proper porosities and layer/thickness, followed by a selective removal of the opal. As a result, a porous, three-dimensional (3D) structure is obtained, characterized by a high surface roughness factor, R_f .

In our previous work (Herraiz-Cardona et al., 2012), different electrode materials were prepared by means of a double electrochemical template technique, consisting of the nickel coating of metallic foams obtained

from copper electrodeposition during the vigorous hydrogen bubbling at high current densities. The hydrogen evolution reaction (HER) on these electrodes was assessed by steady-state polarization curves and electrochemical impedance spectroscopy (EIS). From this study it was determined the electrode synthesis operating conditions that yielded the highest catalytic activities for HER. In the present work, only the best electrode material has been fabricated and thoroughly characterized by means of hydrogen discharge curves and galvanostatic tests in conditions simulating the industrial alkaline water electrolysis, with the aim of determining the energy savings that the use of this material as cathodes would suppose. In this study the results obtained by using smooth commercial nickel electrodes were included, in order to compare the results.

2. Experimental

2.1 Cathode fabrication

The electrocatalytic layers were deposited onto AISI 304 stainless steel disc electrodes (0.5 cm² geometric area). These substrate materials were set up with the pre-treatment process described in our previous work (Herraiz-Cardona et al., 2012), as an initial step.

The formation of electroactive coatings on such prepared AISI 304 stainless steel substrate was done by electrodeposition, according to the following steps: first of all, it was constructed a 3D porous copper structure by means of electrodeposition at high current densities in an acidic bath at room temperature. The hydrogen bubbles generated in highly acidic media and at high cathodic current densities function as a dynamic template during Cu deposition. Afterwards, the Cu macroporous layer acted as a template for the nickel coating, which is electrodeposited from a modified Watts bath at 50°C. The bath composition and deposition conditions of the fabricated electrode are summarized in Table 1.

The structures, morphologies and compositions of the developed materials were examined by means of a JEOL JSM-3600 scanning electron microscope (SEM) coupled with an Energy Dispersive X-Ray (EDX) Spectrometer, and an OLYMPUS LEXT OLS3100-USS confocal laser scanning microscope.

Electrodepositions were carried out in a one-compartment cell made of Pyrex glass with a Teflon cover having adequate holes to lodge the electrodes. The solution inside the cell had an initial volume of 50 mL. The substrate surface was placed in horizontal position, allowing the free release of the produced hydrogen bubbles. The counter electrode was a large-area platinum electrode. The reference electrode was a commercially available silver-silver chloride (Ag-AgCl) electrode with 3 M KCl solution. The experiments were accomplished by using an AUTOLAB PGSTAT302N potentiostat/galvanostat.

Table 1. Bath compositions and operating conditions used to obtain the 3D CuNi catalyst

Cu template formation		Ni electrodeposition	
Bath composition / M			
CuSO ₄	0.05	NiSO ₄	1.26
H ₂ SO ₄	0.50	NiCl ₂	0.19
		H ₃ BO ₃	0.60
Operating conditions			
$j_d / A\ cm^{-2}$	0.20	$j_d / A\ cm^{-2}$	0.05
Time / s	450	Time / s	3600

2.2 Electrochemical measurements

The developed electrodes were characterized by means of hydrogen discharge curves, and galvanostatic tests. All these tests were performed in oxygen free 30 wt.% KOH solutions, which were achieved by bubbling N₂ for 15 min before the experiments.

In order to obtain the hydrogen discharge curves, a progressively increasing voltage was applied, starting from 0 V between the anode (smooth Ni) and cathode (3D CuNi electrode) and going up to 3 V. The curves were recorded at temperatures ranging from 30 and 80 °C. With the aid of these curves, the minimum discharge potentials were experimentally determined for each electrode pair.

The galvanostatic experiments were carried out at three different applied current densities of 20, 50 and 100 mA cm⁻² during 1 hour and at six different temperatures: 30, 40, 50, 60, 70 and 80 °C.

The electrochemical measurements were carried out in an electrochemical cell developed by the Dpto. Ingeniería Química y Nuclear of the Polytechnic University of Valencia (Patent P200803389). It is a three-electrode cell that allows monitoring the volume of gas generated at the anode and the cathode. Also, this system has a heating circuit to control the temperature.

3. Results and Discussion

Figure 1 shows both the SEM (Figure 1.a) and the confocal laser scanning (Figure 1.b) images of the porous 3D CuNi electrodeposit synthesized according to the electrochemical deposition conditions reported in Table 1. The deposited film is characterized by a 3D foam structure. The origin of this unique structure is as discussed elsewhere by Shin et al. (2003) and briefly summarized in the experimental section. As depicted in the SEM image, the electrodeposited catalyst has a cauliflower microstructure. From the chemical composition analysis accomplished by means of energy dispersive X-ray (EDX) spectrometry, the developed electrocatalyst present a superficial continuous pure nickel layer.

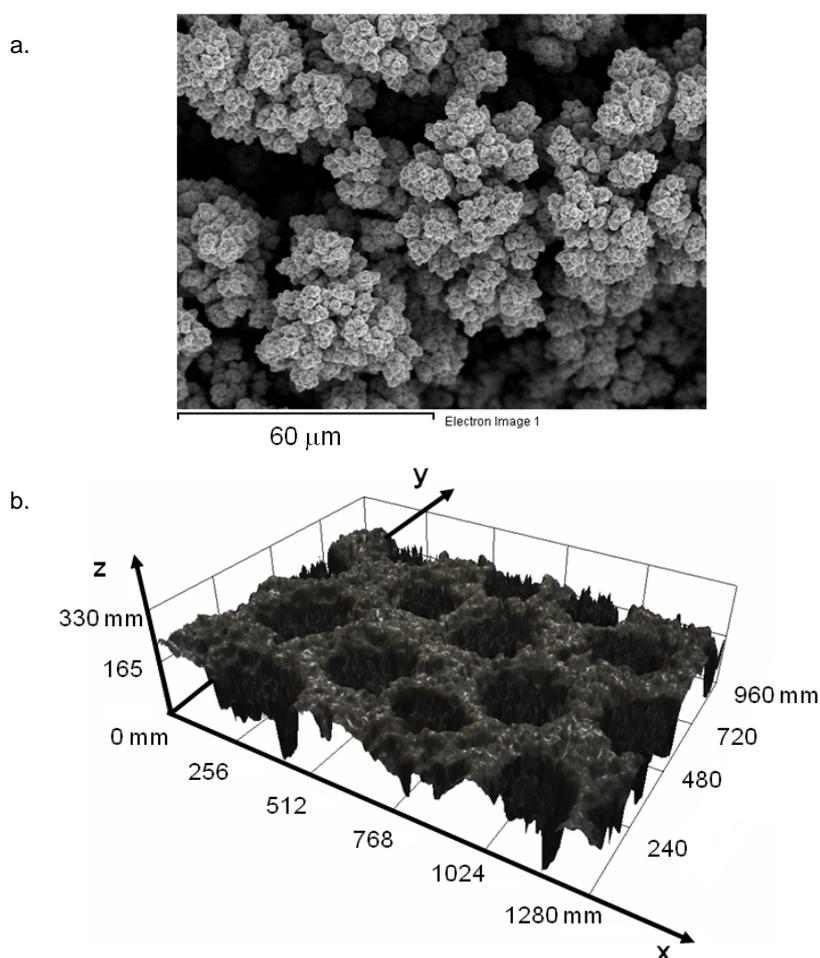


Figure 1: Scanning electron (a) and 3D confocal laser scanning (b) microscopy images of the 3D CuNi synthesized electrocatalyst.

Figure 2 shows the hydrogen discharge curves obtained using as cathodes both the 3D CuNi and the smooth Ni electrodes in 30 wt.% KOH solution at 80 °C. After the discharge of gasses, there is a rapid increase in the current with increasing applied voltage, because of the evolution of hydrogen at the cathode and oxygen at the anode. As seen in Figure 2, the discharge of gasses starts at lower potential for the 3D CuNi electrode, and the current passing through the solution is larger with this cathode, compared with the smooth Ni cathode, at all potentials.

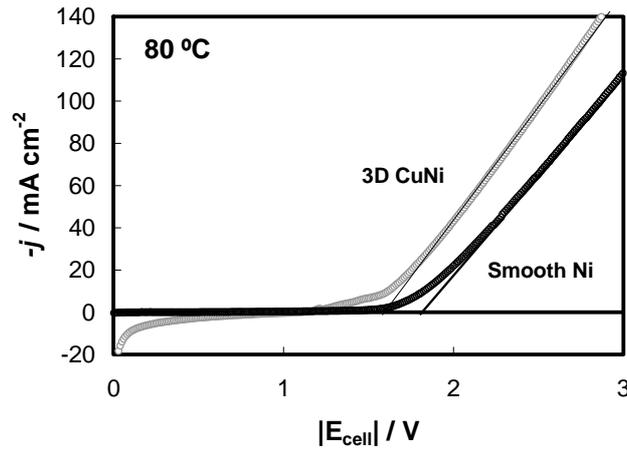


Figure 2: Hydrogen discharge curves recorded on 3D CuNi, and smooth Ni electrocatalysts in 30 % wt. KOH solution at 30 °C.

The minimum hydrogen discharge potentials (E_{exp}), given in Table 2, were experimentally determined by extrapolating the linear part of the hydrogen discharge curves (between 2 and 3 V) to the zero current. The E_{exp} values decrease with temperature due to the increased conductivity of the electrolyte and higher electrode activities. The reversible discharge potential for water splitting (E_{rev}) also reduces with an increase in operating temperature as given by the relation (Leroy et al., 1980):

$$E_{rev}(T/K) = 1.5184 - 1.5421 \cdot 10^{-3} \cdot T + 9.523 \cdot 10^{-5} \cdot T \cdot \ln T + 9.84 \cdot 10^{-8} \cdot T^2 \quad (1)$$

The difference between the measured and theoretical calculated values of these systems ($E_{exp} - E_{rev}$) can be taken to be the experimental overpotential required to overcome the losses in the cell (η_{exp}). As derived from Table 2, the overpotential of the 3D CuNi coating is lower than that registered for the smooth Ni electrode which can be attributed to a lower cathodic overpotential associated with the reaction kinetics of the synthesized electrode with respect to the smooth commercial Ni electrode.

Table 2. Experimental discharge potentials (E_{exp}) and overpotentials (η_{exp}) obtained from the H_2 discharge curves recorded in 30 % wt. KOH solution

Catalyst	Temperature (°C)						
	30	40	50	60	70	80	
Smooth Ni	E_{exp} (V)	1.830	1.820	1.810	1.801	1.794	1.780
	η_{exp} (V)	0.605	0.603	0.602	0.601	0.602	0.596
3D CuNi	E_{exp} (V)	1.637	1.628	1.618	1.594	1.574	1.567
	η_{exp} (V)	0.412	0.411	0.410	0.394	0.382	0.383

When temperature is considered it is accurate to use the higher heating value voltage (E_{HHV}) for efficiency calculation (Leroy et al. 1980). E_{HHV} corresponds to the heat content of the dry product gases with respect to the liquid water at 25 °C. Therefore,

$$\varepsilon = \frac{E_{HHV}}{E_{cell}} \quad (2)$$

where ε is the energy efficiency, E_{cell} is the cell voltage, and the absolute temperature dependence of E_{HHV} can be given by the relation (Leroy et al. 1980):

$$E_{HHV}(T / K) = 1.4146 + 2.205 \cdot 10^{-4} \cdot T + 1.0 \cdot 10^{-8} \cdot T^2 \quad (3)$$

The maximum efficiency of the hydrogen evolution process can be calculated from the minimum hydrogen discharge potentials, by using E_{exp} as E_{cell} in Eq. (1). As it is shown in Fig. 3, the higher operating temperature conditions the higher energy efficiencies for a hydrogen production are obtained, due to an increase in the mobility of the molecules and ions. Moreover, the efficiencies obtained for the 3D CuNi catalyst are higher than that reported for the smooth Ni electrode, as a consequence of the improvement in the apparent catalytic activity of the developed electrode associated to its higher roughness factor (Herraiz-Cardona et al., 2012).

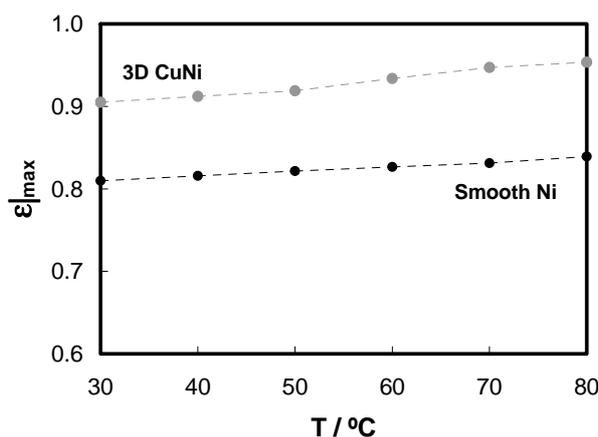


Figure 3: Effect of temperature on the maximum efficiency of 3D CuNi, and smooth Ni electrocatalysts in 30 % wt. KOH solution.

Galvanostatic tests have been carried out in order to verify the performance behaviour of these alloys in long duration experiences for the HER, at different current densities and temperatures. The energy requirements for the electrolytic hydrogen evolution process are calculated with the aid of these experiments using the relation:

$$Q = \frac{I \cdot E_{cell} \cdot t}{mole H_2} \quad (4)$$

where Q is the energy consumption per one mole of hydrogen evolved (kJ mole^{-1}), I is the absolute applied current in A, and t is the time in seconds. To obtain the correct number of hydrogen moles, the hydrogen pressure was determined as follows:

$$P_{H_2} = P_{atm} + \rho(T)gh - P_v(T) \quad (5)$$

where P_{atm} is the atmospheric pressure, $\rho(T)$ is the mass density of a 30 wt. % KOH solution, g is the gravitational acceleration, h is the height difference between the liquid levels of the cathodic and central compartments, and $P_v(T)$ is the water saturation pressure in 30 wt.% KOH solutions. In this way, the moles of evaporated water at the temperature conditions can be subtracted from the measured volume in the cathodic compartment of the voltammeter. The obtained results are presented in Figure 4.a as a three-dimensional diagram of energy consumption. In this Figure it is shown an expected type of dependence: the higher the applied current density, the higher the energy consumption. On the other hand, the energy requirement decreases with increasing temperature, which indicates an increase in the reaction rate, thus the lower voltage requested for a certain current density. As it is clearly shown in Figure 4.a, energy consumption of the electrolysis cell considerably decreases using the 3D CuNi catalyst coating as cathode, with respect to the commercial smooth Ni electrode.

The energy efficiency, ε , was also determined for each point of the surface plot of Figure 4.a, obtaining Figure 4.b. As it is shown, the efficiency of the electrolysis is inversely proportional to the cell potential. Therefore, as the cell potential increases with the electrolysis current, it can be seen that the efficiency slightly decreases at increasing H_2 production. The obtained efficiencies of the unity electrolysis cell can not be compared to that reported in literature, due to the specific cell geometry. Nevertheless, it has been

observed an improvement in the energy efficiency of about 10-30 % when comparing with the commercial smooth nickel electrode.

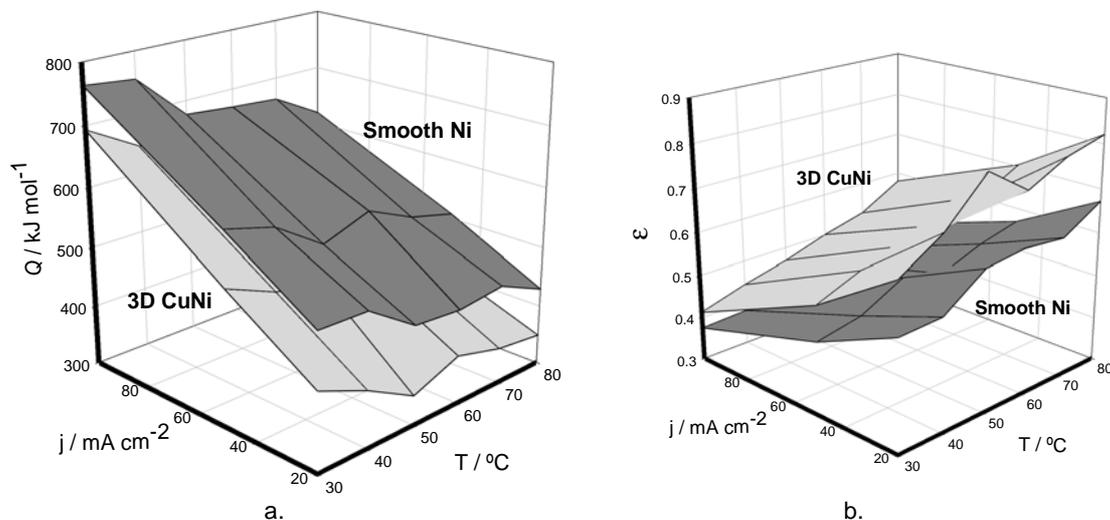


Figure 4: (a) 3-D diagram of the energy consumption per 1 mol of H₂, Q , and (b) 3-D diagram of efficiency, ϵ , obtained in 30 % wt. KOH solution. Comparison between the smooth pure Ni and 3D CuNi cathodes.

4. Conclusions

3D CuNi stainless steel-based electrodes, produced by a double-template electrochemical procedure, were characterized both morphological and electrochemically for hydrogen evolution reaction in conditions at which industrial alkaline water electrolysis is carried out, showing significant electrocatalytic effects. From both hydrogen discharge curves and galvanostatic tests it has been pointed out that energy savings per mass unit of electrolytically evolved hydrogen from alkaline aqueous solutions on 3D CuNi cathodes can be beyond 25 % at certain operating conditions, compared with the standard nickel electrodes. Moreover, 3D CuNi electrode shows a most efficient behaviour than that obtained for the smooth pure Ni electrode.

Acknowledgements

I. Herraiz-Cardona is grateful to Fundaci3n Iberdrola for the financial support. This work was supported by Generalitat Valenciana (Project PROMETEO/2010/023) and Universitat Polit3cnica de Val3ncia (PAID-06-10-2227).

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