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Modification of porous nickel electrodes with silver nanoparticles for hydrogen production

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ABSTRACT

Silver nanoparticles were electrodeposited into the surface of a macroporous Ni electrode. The developed electrodes were characterized morphologically by confocal laser scanning microscopy and field emission scanning electron microscopy. The activity of the developed electrodes towards the hydrogen evolution reaction was assessed by pseudo-steady-state polarization curves and electrochemical impedance spectroscopy in alkaline solutions at different temperatures. The incorporation of the silver nanoparticles on the surface of the electrode improved the catalytic activity towards the hydrogen evolution reaction due to an improvement in the electrochemically active surface area rather than in the intrinsic catalytic activity.

1. Introduction

Actually, about 81% of the primary world energy production comes from fossil fuels. However, fossil fuels are not reliable because their use leads to serious environmental problems derived from the greenhouse effect and due to the exhaustion of reserves [1]. Hydrogen can be considered an alternative to fossil fuels that meets all the criteria for an alternative clean energy source because it is versatile, environmentally compatible and it could be produced from renewable energy sources. However, hydrogen is not found in pure form on Earth, so it should be considered an energy carrier or storage medium rather than an energy source, and the climate change impact of using it depends on the raw material used for its production [1,2].

Alkaline water electrolysis is one of the most promising methods for hydrogen production, as it is environmentally friendly when combined with renewable energy sources such as wind or solar [3,4]. However, the use of this technique to produce hydrogen on a large scale is restricted by its high costs, both economic and energetic, the latter derived from the high overvoltages necessary to carry out the water oxidation and reduction reactions taking place at the electrodes. Noble metals such as Pt, Ir or Pd have the highest catalytic activity for both, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), and Ni is the most active non-noble elemental

electrocatalyst for HER in alkaline solutions [5,6].

The catalytic activity of an electrode can be increased by enlarging its real surface area and/or increasing its intrinsic activity. The increase of the active surface of the electrodes can be achieved by the utilization of Raney-type alloys [6–8], by electrodeposition at high current densities [9–11] or by means of electrodeposition on templates [12,13]. In order to improve the intrinsic catalytic activity, Ni-based alloys such as NiAl [14], NiZn [15,16], NiMo [17,18], NiCo [9,10,19–22], NiFe [23,24], NiCu [25,26], NiW [27,28] or modified electrodes [29–31] have been studied.

Recently, there has been a great interest in the development of nanostructured metallic materials to be used as electrocatalysts, since these materials have properties remarkably different from their bulk counterparts. In addition, small amounts of material are used and they provide a high surface area. In this way, different nanostructured materials have been used as electrocatalysts for water oxidation and reduction [32–38]. The catalytic activity of the nanoparticles depends on the preparation method [32]. In the case of silver nanoparticles, several methods, such as chemical reduction using a variety of organic and inorganic reducing agents, electrochemical methods, physicochemical reduction and radiolysis, have been used for their synthesis [33,39–41].

In this work, silver nanoparticles (AgNPs) were electrodeposited on Ni macroporous substrates to produce AgNP-modified Ni electrodes as

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effective electrocatalysts for the HER. The use of a macroporous electrode as a supporting material can reduce the dosage of noble metals. The resulting morphologies were characterized by confocal laser scanning microscopy and field emission scanning electron microscopy. The electrocatalytic activity of the synthesized catalysts towards the HER was studied in alkaline solution under various experimental conditions by pseudo-steady-state polarization curves and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Modification of the macroporous Ni electrodes with AgNPs

Macroporous Ni electrodes were obtained by means of electrodeposition at high current densities on a stainless steel AISI 304 substrate as described in our previous works [10,38]. Then, silver nanoparticles were electrodeposited under different conditions from a 50 mL solution of 0.5 mM AgNO₃ in distilled water. The electrodeposition process begins by applying a ramp of current density for a time, t_{ramp} , until a maximum current density of 1 A·m⁻² is reached, and then this maximum current density is maintained for a time, t_{const} . The operating conditions for the modification of the macroporous nickel electrodes are shown in Table 1. In this table, it is also shown the maximum loadings of Ag nanoparticles assuming that the electrodeposition current efficiency was 100%. The surface morphologies of the developed electrodes were studied by means of an OLYMPUS LEXT OLS3100-USS confocal laser scanning microscope, and a ZEISS ULTRA 55 field emission scanning electron microscope (FE-SEM) coupled with an Energy-Dispersive X-Ray (EDX) analysis was used to observe the morphology and to confirm the presence of the Ag nanoparticles on the electrode surface.

2.2. Electrochemical measurements

Pseudo-steady-state polarization curves and EIS techniques were used to characterize the developed electrodes towards the HER. All the experiments were performed in oxygen free 30 wt% KOH solutions which were achieved by bubbling N₂ for 15 min.

The pseudo-steady-state polarization curves were potentiodynamically recorded at a scan rate of 1 mV·s⁻¹ from -1.60 V vs. Ag/AgCl (-1.40 V vs. SHE) until the equilibrium potential. These curves were obtained at different temperatures from 30 to 80 °C. Before the experiments, the working electrode was held at -1.60 V vs. Ag/AgCl in the same solution, for the time needed to set up reproducible polarization curves.

EIS measurements were recorded after the corresponding polarization curves at different cathodic overpotentials from 0 to 100 mV in the frequency range of 10 kHz to 5 mHz, with ten frequencies per decade and a sinusoidal signal of 10 mV peak-to-peak. The complex nonlinear least square (CNLS) fitting of the impedance data was carried out with the ZView 3.0 software package.

The electrochemical measurements were carried out in an electrochemical cell developed by the Dpto. Ingeniería Química y Nuclear of the Universitat Politècnica de Valencia (Spain) described in previous works [10,11,20].

Table 1
Profile of the current density applied for silver nanoparticles electrodeposition.

	E1	E2	E3
t_{ramp} (s)	10	70	10
t_{const} (s)	60	30	170
Q (C)	0.00325	0.00325	0.00875
m_{Ag} (mg·cm ⁻²)	0.00727	0.00727	0.0196

3. Results and discussion

3.1. Morphology characterization

Fig. 1 shows the FE-SEM (A) and confocal laser micrographs (B) of the macroporous Ni electrode without AgNPs. As can be seen the electrode surface structure consists of a continuous matrix provided by circular macropores evenly distributed on the whole surface. This structure is a consequence of the high current densities applied originated by the random nucleation of the dissolved hydrogen, which produces microbubbles attached to the electrode surface, as it has been previously reported [13,22,38,42]. No significant differences were observed in this porous macrostructure due to the deposition of AgNPs.

Fig. 2 shows the surface morphology of the Ag nanoparticles deposited on the surface of the macroporous Ni electrodes. In the electrodes E1 and E2 (Fig. 2A and B respectively), obtained by electrodeposition, it is observed that for the same applied electric charge of 3.25·10⁻³C, dispersed spherical AgNPs of about 50 nm, and some aggregation of such nanoparticles was observed. The amount of deposited nanoparticles was greater at electrode E2, where the duration of the applied current density ramp was higher. In the case of electrode E3, obtained with the highest applied electric charge, the nanoparticles showed dendritic growth (Fig. 2C).

3.2. Polarization measurements

The electrocatalytic activity of the Ni-AgNP developed electrodes towards the HER was studied by means of pseudo-steady-state polarization curves and EIS and was compared with a macroporous Ni electrode without AgNPs.

Fig. 3 shows the cathodic polarization curves recorded in a 30 wt% KOH solution at 50 °C on the developed electrodes. The curves were corrected with respect to the reversible HER potential at the given conditions and for the jR -drop. All curves present a linear behavior at high overpotentials, indicating that the HER on the developed electrodes is kinetically controlled and can be described by the Tafel equation:

$$\eta = a + b \log j \quad (1)$$

where η (V) is the overpotential, j (A·cm⁻²) is the measured current density, b (V decade⁻¹) is the Tafel slope and a (V) is the intercept, which is related to the exchange current density, j_0 (A·cm⁻²) through the equation:

$$a = \frac{2.3 RT}{\alpha F} \log j_0 \quad (2)$$

where R is the gas constant, F is the Faraday constant, and α is the charge transfer coefficient, which can be calculated from the Tafel slope:

$$b = -\frac{2.3 RT}{\alpha F} \quad (3)$$

From the fitting of the linear part of the Tafel curves shown in Fig. 3 it is possible to determine the kinetic parameters a , b , j_0 and α . The values of the kinetic parameters are reported in Table 2. In this table, it is also reported the overpotential at a fixed current density of 100 mA·cm⁻², η_{100} . This parameter is an indication of the energy that has to be invested to produce a fixed amount of hydrogen. For a given electrode, the lower the overpotential at a fixed current density, the higher the catalytic activity of the electrode.

As can be concluded from the Tafel curves shown in Fig. 3 and from the values of the kinetic parameters shown in Table 2, the electrodes modified with AgNPs show the best performance, and therefore the higher catalytic activity to the HER, since they present higher values of j_0 and lower values of η_{100} than the macroporous electrode without AgNPs. With respect to the electrodes modified with silver

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