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Synthesis and characterization of Au-modified macroporous Ni electrocatalysts for alkaline water electrolysis

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ABSTRACT

Au nanoparticles (Au-NPs) were successfully synthesized and incorporated into the surface of a macroporous Ni electrode fabricated via galvanostatic electrodeposition at high current densities in order to produce hydrogen by means of alkaline water electrolysis. The developed electrodes were morphologically characterized by means of confocal laser scanning and field emission scanning electron microscopes. The electrocatalytic behaviour towards the hydrogen evolution reaction was studied by Tafel polarization curves and electrochemical impedance spectroscopy. It was clear that enlarging the real surface area of an electrode its catalytic activity was greatly enhanced. This improvement was further increased when Au-NPs were added to the macroporous Ni surface. In this case, the improvement was not only caused by enlarging the surface area but also by an improvement in the intrinsic catalytic activity of the alloy, as it was shown by the exchange current densities values, calculated from the real surface area.

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Introduction

Nowadays, everybody is concerned about the shortage of fossil energy resources, and the importance of hydrogen as a “green” energy carrier, because it can be obtained directly from renewable energy sources by water splitting. In order to build up a hydrogen energy cycle for an environmentally friendly and sustainable economy it is mandatory to provide hydrogen at low cost. For this purpose, alkaline water

electrolysis is one of the most promising methods to produce clean and renewable hydrogen. Nevertheless, intensive research effort must be addressed in the reduction of both operating/energetic and initial investments to large-scale hydrogen production by means of this technique [1–5].

The energetic costs of alkaline electrolyzers can be reduced by diminishing the overpotentials of both hydrogen and oxygen evolution reaction (HER, and OER, respectively), which take place during the water electrolysis process. Focussing on the HER, noble metals such as platinum and ruthenium are

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the most active materials. However, their high cost goes against the fulfilment of low initial investment for the electrocatalytic material. For this reason, in the last years, a lot of work has been centred in the synthesis of active noble metal-free electrocatalysts [6].

The electrode performance toward HER can be improved by increasing its intrinsic catalytic activity and/or enlarging the material surface area. One of the most tested cathodes for alkaline water electrolyzers are Ni-based alloys, such as NiCo [7–11], NiFe [12–15], NiMo [12,16–24], NiW [12,19,25,26], NiCu [27], NiAl [28,29], NiZn [30,31]; due to the relatively high catalytic activity of Ni, and aiming at the synergism in the catalytic behaviour of the different components in the metallic alloy. Moreover, the development of nanoparticle catalysts has had a great interest because it not only allows using a small amount of material, but also provides a larger active surface area [32]. The metal nanoparticles need to be synthesized first and then assembled on the electrode [33]. The use of a macroporous electrode as a supporting material can reduce the dosage of noble metals [34]. This synthesis strategy has been successfully employed for HER. Amin et al. assembled dispersed silver nanoparticles (AgNPs) on titanium (Ti) substrates, yielding a better HER performance than bare platinum [32]. Abbaspour and Mirahmadi modified carbon paste electrodes with Fe and Ni mixed oxide nanoparticles. The obtained materials were renewable and showed a good stability. This, plus the low cost of Ni-ferrite NPs and facile large scale fabrication, postulated the Ni-ferrite NPs as a promising high-performance electrocatalyst for the HER in acidic media [35]. Abbaspour and Norouz-Sarvestani electrodeposited Au–Pd bimetallic nanoparticles on microwave irradiated carbon ceramic electrodes (MWCCE). A superior performance for HER was reported for the composite material in comparison with individual non-alloyed Au and Pd catalysts [36]. Hsieh et al. compared two different routes to deposit silver nanoparticles on oxidized carbon paper electrodes. From the results, microwave-assisted fabrication offered a fast and simple synthesis method with high activity for alkaline fuel cells with respect to the thermal reduction strategy [37]. Zheng and Mathe prepared single crystal tungsten oxide (WO₃) nanoparticles via a microwave-assisted method supported on carbon black. The overall experimental results revealed that the electrocatalytic activity for HER on WO₃/C is six order magnitude higher than those obtained with carbon black in 1 M KOH [38].

In the present work nanoparticles of gold have been successfully synthesized with a simple method and incorporated to a macroporous Ni electrodes with a thermal treatment. In this way, we combine the use of Ni as a support, which exhibits the best electrocatalytic activity among the non-noble materials and its highly porous structure, and Au nanoparticles which can further enhance the electrocatalytic activity. The presence of Au nanoparticles has been confirmed by means of field emission scanning electron spectroscopic microscopy (FE-SEM) and Energy-Dispersive X-Ray (EDX) analysis. The electrocatalytic behaviour towards HER was assessed by pseudo-steady-state polarization curves and electrochemical impedance spectroscopy (EIS) in alkaline media.

Experimental

Preparation of electrodes

Macroporous Ni electrodes have been obtained by means of electrodeposition at high current densities as it is described in our previous work [10], and briefly summarised as follows. First, the stainless steel AISI 304 substrate material is polished until mirror surface and cleaned with NaOH (degreased) and HCl (stripping). Then, in order to increase the adherence of the stainless steel substrate, the electrode is anodically treated in H₂SO₄ and electrodeposited with a thin nickel deposit from a Wood's nickel solution. Afterwards, the electrodeposition at high current density (1 A cm⁻²) is carried out from a bath containing 48 g L⁻¹ NiCl₂·6H₂O and 170 g L⁻¹ NH₄Cl, the pH of this solution was 4.5. A large-area graphite electrode of high purity was used as a counter-electrode, and an Ag/AgCl (3 M KCl electrolyte) electrode was used as reference. The experiments were carried out by means of an AUTOLAB PGSTAT302N potentiostat/galvanostat. Then, the Au nanoparticles were synthesized and added to one of the developed electrode surface (Macroporous Ni–Au NPs).

In order to obtain Au nanoparticles, a 2.5·10⁻⁴ M tetrachloroauric acid solution was prepared and heated to 100 °C. 25 mL of a 0.5 wt.% sodium citrate were added at the hot solution. The citrate ions are responsible for the reduction of Au (III) ions to Au (0) and also for being complexing agents of the formed nanoparticles. Thus, the nanoparticle colloidal suspension is stabilized.

The supporting macroporous Ni electrode was coated with gold slurry by dip coating. Prior to the coating, the gold suspension was modified to increase viscosity and lower surface tension by addition of Hydroxyethyl Cellulose (0.5 wt.%) and BYK 347 (1 wt.%). Then the electrode was dip coated four times allowing it to dry between the immersions. Finally, the electrode was treated thermally in a tubular furnace at 350 °C for 1 h under a nitrogen atmosphere.

The particle size distribution of gold suspension was analysed by Dynamic Light Scattering (Zetasizer Nano S90, UK). The surface morphology of the developed electrodes were studied by means of an OLYMPUS LEXT OLS3100-USS confocal laser scanning microscope, and a ZEISS ULTRA 55 FE-SEM coupled with an EDX analysis was used to observe the morphology and to confirm the presence of the Au nanoparticles on the electrode surface.

Electrochemical measurements

The electrocatalytic behaviour of the developed materials was studied by means of pseudo-steady-state polarization curves and EIS. These tests were performed in 30 wt.% KOH previously deaerated by bubbling N₂ during 15 min.

The pseudo-steady-state polarization curves consist of a potentiodynamic scan at 1 mV s⁻¹, from a cathodic potential of -1.6 V (vs. Ag/AgCl) until the equilibrium potential. These curves were performed at different temperatures from 30 °C to 80 °C. EIS measurements were accomplished after the corresponding polarization curves at 30, 50 and 80 °C, in the frequency range of 10 kHz to 5 mHz, with ten frequencies per

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