

Fabrication and Characterization of Nanostructured Ni and Pd Electrodes for Hydrogen Evolution Reaction (HER) in Water-Alkaline Electrolyzer

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In the field of water-alkaline electrolyzer, the development of nanoporous low cost nickel electrodes is one of the potential approaches to increase electrocatalytic activity. Template electrodeposition is a facile and cheap technique for obtaining Ni nanowires (NWs) with high surface area. These nanostructures were fabricated by a two-step procedure. In the first step, a Ni compact layer was deposited on one side of the template where a gold film was previously sputtered, while, in the second-step, an ordered array of Ni-NWs was obtained by electrodeposition inside the template channels. The NWs were firmly connected to the underlying Ni layer, acting as a current collector. In order to enhance the catalytic activity, Pd nanoparticles were deposited onto the NW surface by metal displacement. All electrodes were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The comparison between the two types of electrodes revealed that the composite electrode (Ni+Pd) shows better electro-catalytic features, which quickly decay under operation, so that after 5 min. of polarization at a constant current in 30% w/w aqueous solution of potassium hydroxide, the other electrode performs better.

1. Introduction

One of the most important challenges of the 21st century is to save the planet from global warming and its consequences. To reach this goal, it is necessary to change the current energetic system, based on fossil fuel, into a more environmentally sustainable one (Momirlan and Veziroglu, 2002; Rashid et al., 2015). Among all the possible alternatives, hydrogen is one of the most suitable candidates, even if it is an energy carrier rather than a primary energy source. In fact, the hydrogen production generated by electrochemical water splitting is often combined with a renewable energy source such as solar (Blanco et al., 2014; Rzyayeva et al., 2001) and/or wind (Sherif et al., 2005; Sovacool and Hirsh, 2008).

The idea of hydrogen as an energy carrier has already been in use for decades (Ulleberg, 2003). However, at the present time, hydrogen is not economically competitive enough. To overcome the problem, the research is focused on the improvement of electrolyzer in terms of performance and cost reduction (Marcelo and Dell'Era, 2008). Some researchers are oriented to find new materials able to improve the kinetic of oxygen evolution reaction (OER) and of hydrogen evolution reaction (HER). For instance, Rosalbino et al. (2013) have reported good catalytic property of NiCo-based alloy (with Cr, Mn and Cu) and in particular, they found that the best electrocatalysts for OER were Ni₆₀Co₃₀Cr₁₀ and Ni₆₀Co₃₀Mn₁₀ alloys. Rafailovic et al. (2013) fabricated nanodendritic NiCoFe foam electrode with higher surface area than NiCoFe smooth electrode. Cyclic voltammograms showed better catalytic activity of NiCoFe foam for both HER and OER. In a very recent study, Elias et al. (2015) have synthesized and characterized Ni-W alloy coatings with various compositions. They observed that Ni-W alloy with high concentration of W (about 12.49 wt. %) was favoring HER while a low concentration of W (about 0.95 wt.%) was favoring OER.

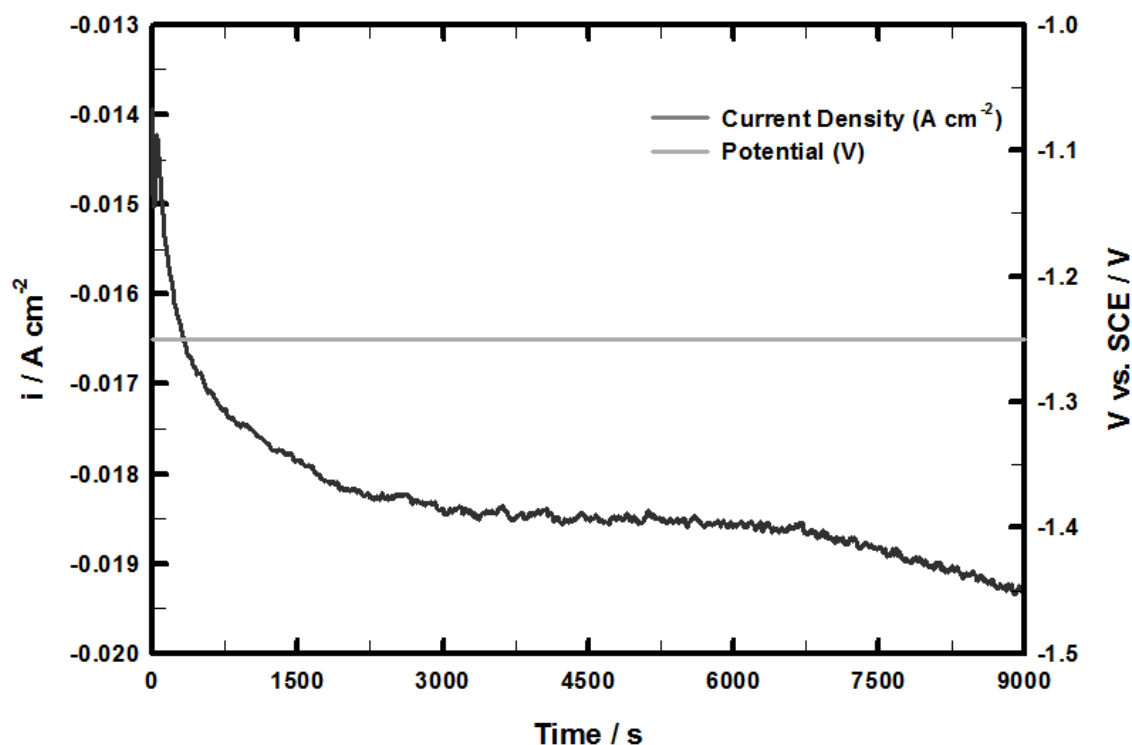


Figure 1: Ni layer electrodeposition potential and current density vs. time curves.

In this work, we have fabricated nanostructured Ni and Ni-Pd composite electrodes using a low cost technique (Sunseri et al., 2016). The advantage of such a morphology in improving electrocatalytic activity is due to the high surface that cannot be achieved with other methods. Electrode morphology and structure were investigated by SEM. The electrochemical characterization was carried out through quasi steady state polarization (QSSP) and it showed how the Ni-Pd catalyst has improved performance, compared to electrode without deposit. In light of this finding, electrodes were tested as cathodes in an electrolyzer having 1 cm gap configuration and containing 30 % w/w KOH solution.

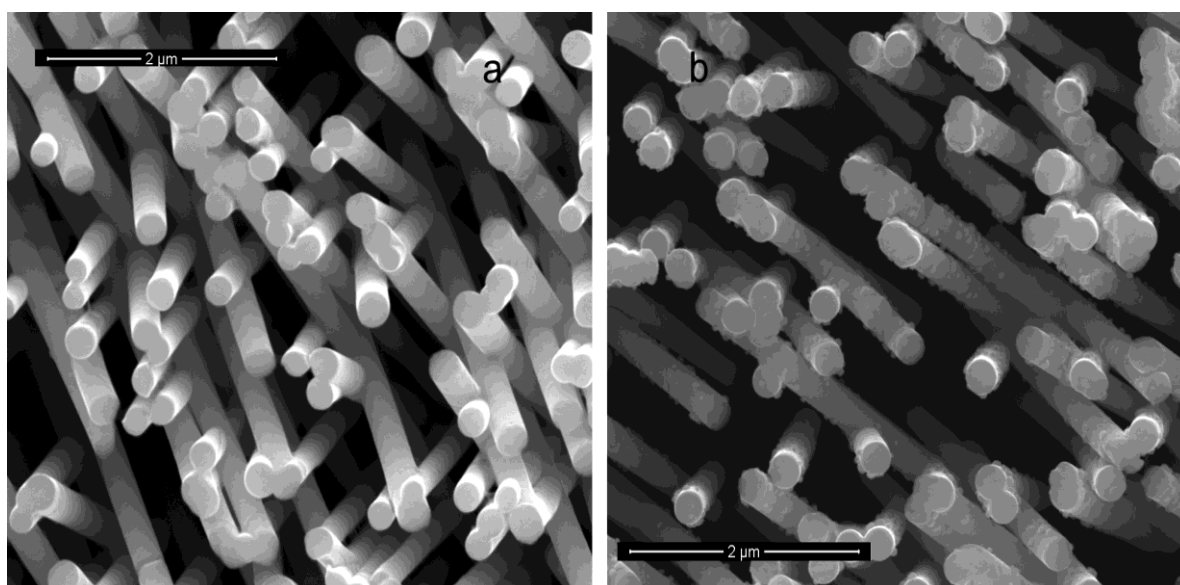


Figure 2: SEM images of nanostructured electrodes; a) Ni nanowires, b) Ni nanowires with Pd nanoparticles.

2. Experimental

For nanostructured Ni electrodes fabrication, commercial porous polycarbonate membrane (PCM - Whatman, Cyclopore, thickness 20 μm) has been used as a template. A thin gold film was initially sputtered onto one side of the template to make it electrically conductive. A Ni layer was potentiostatically deposited (Figure 1) on the gold film at -1.25 V (vs. SCE) and room temperature for 9000 s in a Watt's bath (300 g/l Nickel Sulphate Hexahydrate, 45 g/l Nickel Chloride, 45 g/l Boric Acid). The Ni layer acts as a current collector and support for the NWs.

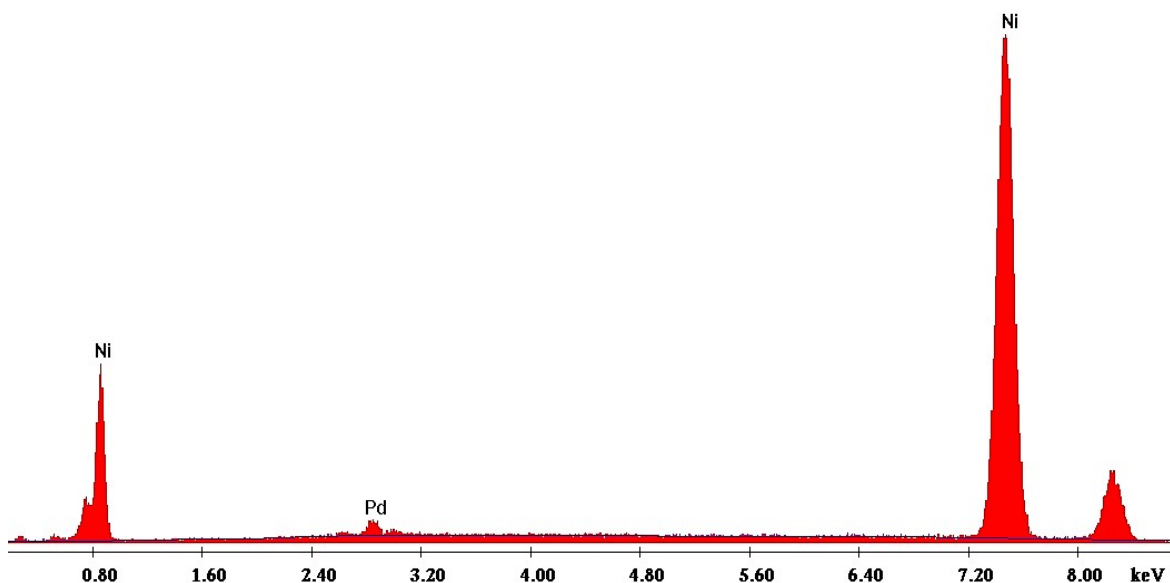


Figure 3: EDS pattern of a Ni nanowires electrode with Pd nanoparticles

Ni NWs has been electrodeposited into the pores of PCM by pulsed potential between open circuit potential (OCP) and -1.5 V (vs. SCE) for 90 cycles (Battaglia et al., 2014; Inguanta et al., 2008).

After the fabrication of the NWs, the template was dissolved in dichloromethane at room temperature. To ensure the total removal of the PMC, this operation was repeated four times in fresh dichloromethane.

Pd nanoparticles were deposited on Ni-NW surface according with reaction Eq(1), which was conducted in a 5 mM $\text{Pd}(\text{NH}_3)_4$ aqueous solution with 0.1 M H_3BO_3 at room temperature. Solution was acidified using HNO_3 to shift pH to 2 and sonicated during the 5 minutes long electrodeposition.



All electrochemical depositions and characterizations were performed using a Cell Test System (Solartron, Mod. 1470 E, 8 channels). Data were recorded by a desk computer through MultiStat Software (Mod. UBS147010ES).

Morphological analysis was performed by a FEI Quanta 200 scanning electron microscope, equipped with EDS.

3. Results and discussion

In order to check the complete PCM dissolution, NWs uniformity, and Pd nanoparticles deposition, SEM and EDS analyses were conducted.

Figure 2a shows cylindrical Ni-NWs having a regular shape with almost 250 nm diameter and around 5 μm long. They are highly interconnected owing to geometry of the template. Figure 2b shows Pd nanoparticles, deposited onto the Ni-NWs surface. As can be seen, the Pd nanoparticles have a spherical shape of about 70 nm diameter and they are randomly distributed on the lateral surface of the Ni-NWs.

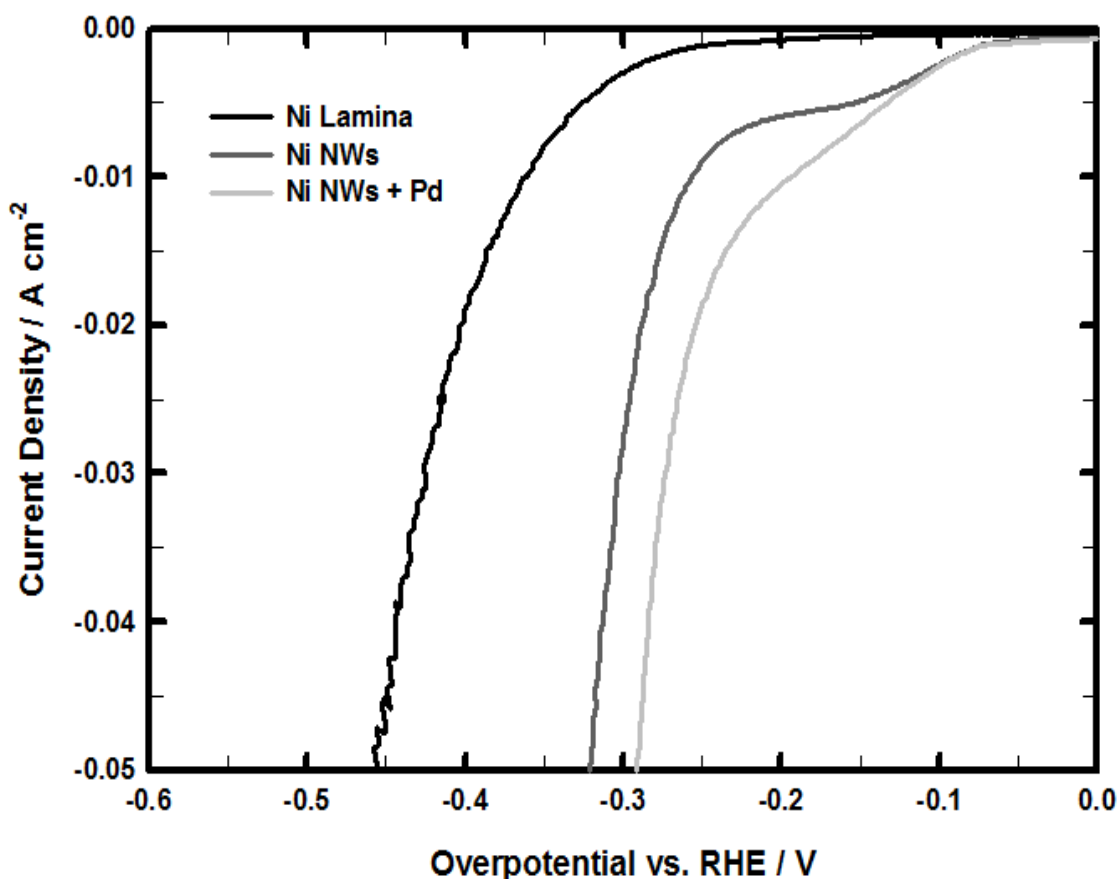


Figure 4: Quasi steady state polarization curves (scan rate 0.167 mV/s) measured for different electrodes in 30% w/w KOH solution at room temperature.

Figure 3 shows a typical EDS pattern of Ni-NWs electrode with Pd nanoparticles. As expected, the pattern exhibits high Ni and low Pd peaks. The absence of carbon peak ensures the complete membrane dissolution. The analytical results through EDS are highly reliable, because only a qualitative identification was concerned. In addition, two elements have atomic number, far from Na that is the threshold element for reliable quantitative determination by EDS, because a favorable signal to noise ratio is required. The result can be accepted also for carbon, because, despite its atomic number is less than 11, only a qualitative identification was conducted. Therefore, in this case, the EDS analysis can be considered as appropriate and useful.

The electrocatalytic activity of Ni Lamina, Ni-NWs, and Ni-NWs with Pd nanoparticles was characterized through recording QSSP curves shown in Figure 4. The potential was scanned from -0.5 to -2.5 V (vs. SCE) at a rate of 0.167 mV s⁻¹ in 30% w/w KOH aqueous solution at room temperature.

The standard electrochemical potential of the H₂/H⁺ couple at pH=14 was assumed as zero for abscissa axis of Figure 4. In addition, ohmic drop, specifically calculated for each type of electrode, was subtracted from the QSSP curves, in order to evidence the charge transfer overpotential, which is the exclusive indicator of electrocatalytic quality. Figure 4 shows that nanostructured electrodes possess a higher catalytic activity because HER starts on them about 0.2V before that on Ni Lamina. This conclusion is further supported by Figure 5, which shows that at 0.05 A cm⁻², HER on the nanostructured electrodes occurs at 0.29 V less than on Ni Lamina.

Figure 5 also shows that, the nanostructured electrodes within less than 300 s reach a steady-state condition that is held for all the investigated time. A slight difference can be observed in the first seconds between the QSSP curves relative to the two types of nanostructured electrodes. Initially, the polarization of the Ni NWs electrode functionalized with Pd nanoparticles is less than that one without Pd. This behavior can be attributed to the great affinity of Pd for hydrogen. In practice, Pd can be considered as a Pd sponge, so that it has been proposed as a hydrogen filter for purifying syn-gas. When used as a cathode for water splitting, Pd nanoparticles act as hot spots for HER with the formation of Pd-hydride. The successive saturation of the

nanoparticles with hydrogen produces a fast decay of the specific catalytic activity of Pd, so that HER continues exclusively on Ni-NWs. As a consequence, the QSSP curves of the two nanostructured electrodes are coincident after less than 5 minutes.

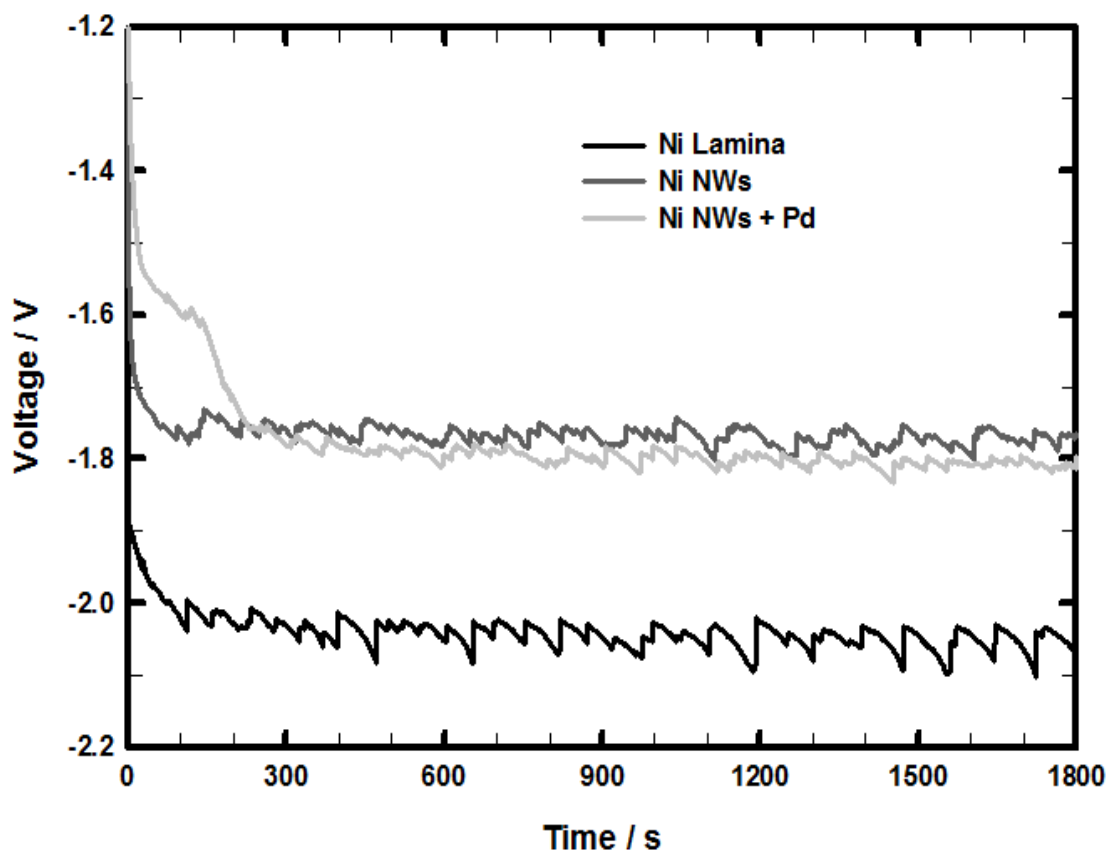


Figure 5: electrode voltage as a function of time at 0.05 A cm^{-2} for alkaline water electrolyzer assembled with different cathodes and Ni Lamina as anode in 30% w/w KOH solution at room temperature.

4. Conclusions

In this work, we presented a simple method for fabricating nanostructured Ni electrodes based on electrodeposition inside the channels of a polycarbonate membrane acting as a template. The aim was to provide an electrode with high electrocatalytic activity for water splitting. In this scenario, also Ni nanostructured electrodes functionalized with Pd nanoparticles for kinetically enhancing HER were prepared. After fabrication, the electrodes were characterized by SEM, EDS, and electrochemical tests. In particular, SEM images showed that the Pd nanoparticles were randomly distributed onto the surface of the Ni-NWs. The electrochemical tests conducted under hydrogen evolution in 30% w/w KOH solution, showed better performance of the nanostructured electrodes in comparison to Ni Lamina. Minor difference in the electrocatalytic activity between the two types of nanostructured electrodes was found, with an advantage for the Ni nanostructures functionalized with Pd. The advantage is only apparent because it is limited to the initial minutes (less than 5) of working. As Pd nanoparticles are saturated with hydrogen due to hydride formation, the electrocatalytic activity of the two types of nanostructured electrodes becomes almost identical. More work is in progress for testing long-time stability of an electrochemical cell assembled with nanostructured anode and cathode.

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