



Nanostructured Ni-Fe-S Based Electrode for Hydrogen Production by Water Electrolysis

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Green hydrogen is a real alternative to change the current energy system. Electrochemical water splitting is considered an attractive solution to convert and store the surplus of renewable energy sources. However, hydrogen production by water electrolysis is not economically sustainable due to the use of high noble metals as catalysts (generally platinum or palladium). In order to reduce costs, in this work we have synthesized a ternary alloy of nickel, iron and sulfur and used it as the cathode in an alkaline electrolyzer to produce hydrogen from water.

Furthermore, to increase the features of the proposed alloy, this material was synthesized into the pore of a polycarbonate membrane to obtain a nanostructured electrode that exposes a very high surface area to the solution and consequently a large number of electrocatalytic active sites. The electrode fabrication was carried out by potential-controlled pulsed electrochemical deposition where the potential switch from -0.45 V to -1.3 V vs. SCE for 60 cycles. The electrode was characterized by SEM and EDS showing the nanostructured nature and the composition of the electrode. Then it was tested as the cathode in an alkaline electrolyzer (30% KOH) at room temperature. Preliminary results show that the addition of sulfur to the alloy permits to increase in the electrode features compared to the binary alloy of nickel and iron.

1. Introduction

In 2014 the global energy consumption was 8760 TWh and more than 85% of it was obtained from fossil fuels. In 2019, the global energy consumption increased by 16%. This trend is growing every year and the overuse of fossil fuels leads to well-known environmental concerns (Tester, 2005). Thus, the development of sustainable and clean energy production systems is of great importance. Different renewable energy sources (RES) have been developed in the last decades, such as solar and wind energy reaching very high efficiency in terms of energy production (Ansaf et al., 2023; B. Liu et al., 2023). Nevertheless, energy production from RES suffers of irreproducibility, uncertainty and non-programmability that decrease their application in a large scale. Water electrolysis can represent a fundamental stage of the hydrogen economy (HE). It consists of the production of electrolytic hydrogen from the surplus electricity of renewable sources and is then used as fuel to produce energy when it is the most in demand. Focusing on hydrogen production through electrolysis, the HE chain can be summarized in four steps:

- Production of hydrogen through electrolysis powered by renewable sources.
- Hydrogen storage.
- Transport of hydrogen from the point of production to the place of consumption.
- Conversion of Hydrogen into electricity or other forms of energy.

Concerning the HE chain, both the production of hydrogen through electrolysis and the conversion of it into electricity or other forms of energy require the use of power electronic converters. Indeed, regarding the production, the electrolyzer needs to be electrically supplied in Direct Current (DC) either directly from renewable sources or from the existing electrical grid, so that in the latter case the renewable energy represents a surplus

power. Direct connection between the intermittent renewable sources and the electrolyzer requires the integration with storage systems, to guarantee a permanent production of hydrogen; a grid-connected electrolyzer is robust against the intermittency of renewable energy but represents a challenge in terms of harmonic distortion that the rectifier generates (Chen et al., 2022). On the hydrogen use side, the DC power generated by a fuel cell supplied through hydrogen needs to be managed correctly in order to efficiently provide electrical power to the load, while preserving the lifetime of the fuel cell (Barhoumi et al., 2021).

For efficient water splitting, very expensive catalysts must be used to reduce the overpotential of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Among them, noble metal-based catalysts such as IrO_x, RuO_x, Pd and Pt have been widely used (Santos et al., 2013; Xie et al., 2022).

The synthesis of new, efficient and cheap catalysts for HER and OER has largely attracted the scientific community (W. Liu et al., 2023; Lv et al., 2023). This goal can be achieved by using nanostructured electrodes: indeed, electrochemical reactions occur at the electrode/electrolyte interface and the use of nanostructured-based electrodes leads to better electrode features (Ganci et al., 2021; Patella et al., 2022). This approach has been used for both OER and HER by developing nanowires (NWs), nanotubes (NTs) and nanoparticles (NPs) based electrodes, confirming that the high surface area of these electrodes leads to better electrode performances (Haase et al., 2022; Liu et al., 2020).

Transitional metals such as nickel, cobalt, iron, tungsten and molybdenum are good catalysts for both HER and OER (Laursen et al., 2012). Among them, nickel has excellent properties for both HER and OER, in terms of cost, overpotential, and stability.

In the last years, the fabrication of nickel-based alloys has been exploited. Many different alloys have been developed, such NiMo, NiZn, NiW, NiFe (Hong et al., 2015; Nairan et al., 2019; Sakita et al., 2018; Zhang et al., 2018). In our previous work, we developed nickel-iron nanowires alloys (NiFe NWs) by electrodeposition into a polycarbonate template and used it as both anode and cathode in an alkaline electrolyzer (Buccheri et al., 2021). Particularly, the NWs composition was varied by changing the composition of the electrodeposition bath and different alloys with different Ni/Fe ratios were tested. We found that all the alloy works better than pure Ni NWs and Fe NWs for HER and the alloy with 78.95% of iron has the best performance.

In this work, we have modified these NWs adding sulfur (NiFeS NWs) and tested for HER. The objective of this work was to find out the effect of adding sulfur to the NiFe NWs alloy for HER. Indeed, the presence of sulfur in NiFe gives outstanding properties to the alloy. Jiang et al. developed a FeNiS₂ NS/rGO electrode and used it for OER in an alkaline solution and found that their alloy works even better than a standard RuO₂ electrode (Jiang et al., 2018). Yu et al. synthesized NiFeS micro-flower based electrodes and found that the alloy has an overpotential of 198 mV vs RHE to produce 10 mA cm⁻² and it has a very high stability over time (Yu et al., 2017). Tang et al. characterized hierarchical NiFeS/CoS and used it for both OER and HER finding a very low overpotential of 150 and 170 mV for HER and OER at 50 mA cm⁻², respectively (Tang et al., 2021). In this work, we have obtained a ternary alloy of NiFeS by electrodeposition into the pores of a polycarbonate membrane obtaining vertically standing NWs. NWs have a mean diameter of about 220 nm and a length of about 13 µm. This morphology offers a very high surface area to the electrolyte allowing to obtain lower overpotential. Moreover, NWs are hydrophobic and thus the detachment of gas bubbles, produced during both OER and HER, occurs very easily and thus the regeneration of catalytic sites is a fast process.

The electrode was characterized by EDS, confirming the presence of the ternary alloy. The electrode surface area was analyzed by calculating the electrochemical surface area (ECSA) and results showed that the ternary alloy has a higher ECSA of about 20% compared to the binary alloy of NiFe NWs. Finally, the NiFeS NWs were tested for HER at different applied current densities (Galvanostatic step) and by applying a current density of 50 mA cm⁻² for 3 hours. The results of these experiments showed a very low electrode overpotential and a very satisfying mid-term stability.

2. Experimental

2.1 Electrode fabrication and characterization

NiFe and NiFeS NWs were obtained by a two-step method based on template synthesis. Particularly, a nanoporous polycarbonate membrane (mean pore diameter of 220nm) was used as the template. To make it conductive, the polycarbonate template was gold sputtered with a thin layer of gold. On the same membrane side, a nickel layer was electrodeposited applying a constant potential of -1.5 V vs SCE for 1.5 hours. Electrodeposition was carried out using a Cell Test System (Solartron, Mod. 1470 E). The electrodeposition solution was the nickel Watt's bath (300 g/L of NiSO₄ 6 H₂O, 45 g/L NiCl₂ 6H₂O and 45 g/L of H₃BO₃).

This nickel layer, about 20 µm thick, acts both as the current collector and as the mechanical support for the NWs. Then, NWs were deposited on the other side of the membrane using the same solution for current collector deposition modified with 125 g/L of FeSO₄ 7H₂O, 10 g/L of sodium thiosulphate (Na₂S₂O₃) to obtain the ternary alloy. The solution pH was modified by 1M NaOH at pH 4.2. During electrodeposition, inside the template occurs

a change in solution composition, due to the deposition of NiFeS, and the formation of H₂ bubbles, due to the concurrent hydrogen evolution reaction. To avoid these effects, the deposition was carried out by pulsed potential electrodeposition switching between -0.5 V and -1.3 V vs SCE for 60 cycles. Each potential was maintained for 6s and 4s, respectively. Those potentials were selected to obtain a positive current during the reverse polarization to restore the solution composition and release the gas bubbles. In this way, uniform and compact NWs with a homogeneous composition on the entire length were obtained. Electrochemical depositions were carried out at room temperature, using a platinum mesh and an SCE as counter and reference electrodes, respectively. Each deposition was carried out using a fresh solution. After NWs electrodeposition, the polycarbonate membrane was etched in pure chloroform. Particularly, each electrode was etched 4 times for 5 minutes each using a fresh CH₃Cl solution. NWs morphology was characterized using a FEG-ESEM microscope (QUANTA 200 by FEI) while NWs composition was analyzed using an Energy Dispersive Spectroscopy (EDS). Each electrode was analyzed in different areas to prove their uniformity.

2.2 Electrochemical measurements

The as-prepared electrodes were insulated with a geometrical area of 0.6 cm². Electrochemical tests were carried out at room temperature using 30% KOH aqueous solution as electrolyte. A Ni foil was used as counter electrode and a Hg/HgO as reference electrode. The potentials were then referred to the reversible hydrogen electrode (RHE, -0.826 V vs SHE) at pH 14. Electrochemical measurements were carried out using a Cell Test System (Solatron, Mod. 1470 E). Each experiment was carried out in triplicate. Electrochemical surface area (ECSA) was evaluated by CVs at different scan rate evaluating the double layer capacitance. CV tests were carried out in the potential interval from 0.89 to 1.09 V vs RHE and the difference between the anodic and cathodic branches at 0.975 V vs RHE was plotted against the scan rate. To compare the ECSA of the NiFeS NWs, the same test was carried out using a Ni sheet and NiFe NWs.

3. Results and discussions

3.1 Electrode synthesis and characterization

In our previous work, we optimized the deposition of NiFe NWs by varying the iron composition of the deposition bath. The NWs composition was evaluated using ICP-MS and we found that NWs were richer in iron nevertheless the Ni/Fe ratio of the deposition bath. This result is due to the anomalous electrodeposition of Fe. After an optimization process, the NiFe NWs deposition was optimized to obtain the best performances for HER. In this work, the same deposition bath was modified adding 10 g/L sodium thiosulphate to incorporate sulfur into the atomic lattice of NWs. For this reason, the pulse potential deposition parameters were slightly modified compared to NiFe NWs synthesis. Particularly, the pulse duration and forward potential were not modified while the reverse pulse was modified from -0.9 to -0.5 V vs SCE. Figure 1a shows the recorded current density during the pulse potential deposition and the corresponding potential wave. As it is possible to see, during the forward polarization a stable current density of about -13 mA cm⁻² was obtained. During the reverse polarization, an inversion of the polarity of current density was obtained (lower than +1 mA cm⁻²). This inversion is essential to obtain stable and uniform NWs because it allows to:

- a) restore the composition of the solution inside the membrane pores;
- b) allow the release of hydrogen bubbles produced inside the pores.

In this way, the NWs composition is uniform in the entire NWs length. In addition, the nanotube formation, which has a low mechanical resistance, is prevented because hydrogen accumulation in the nanochannels was avoided. These assumptions were confirmed by the SEM images of Figures 1b-d where uniform (see low magnification SEM image, Figure 1b-c), stable and vertically standing NWs (see high magnification SEM image, Figure 1d) are clearly visible.

The electrode composition was then analyzed by EDS analysis, shown in Figure 1e. The peaks of Iron, Nickel and Sulfur are identified, demonstrating the deposition of the ternary alloy. No other peaks were detected, thus the formation of the pure alloy was obtained. Further physical-chemical characterization of the electrode will be carried out to fully characterize it.

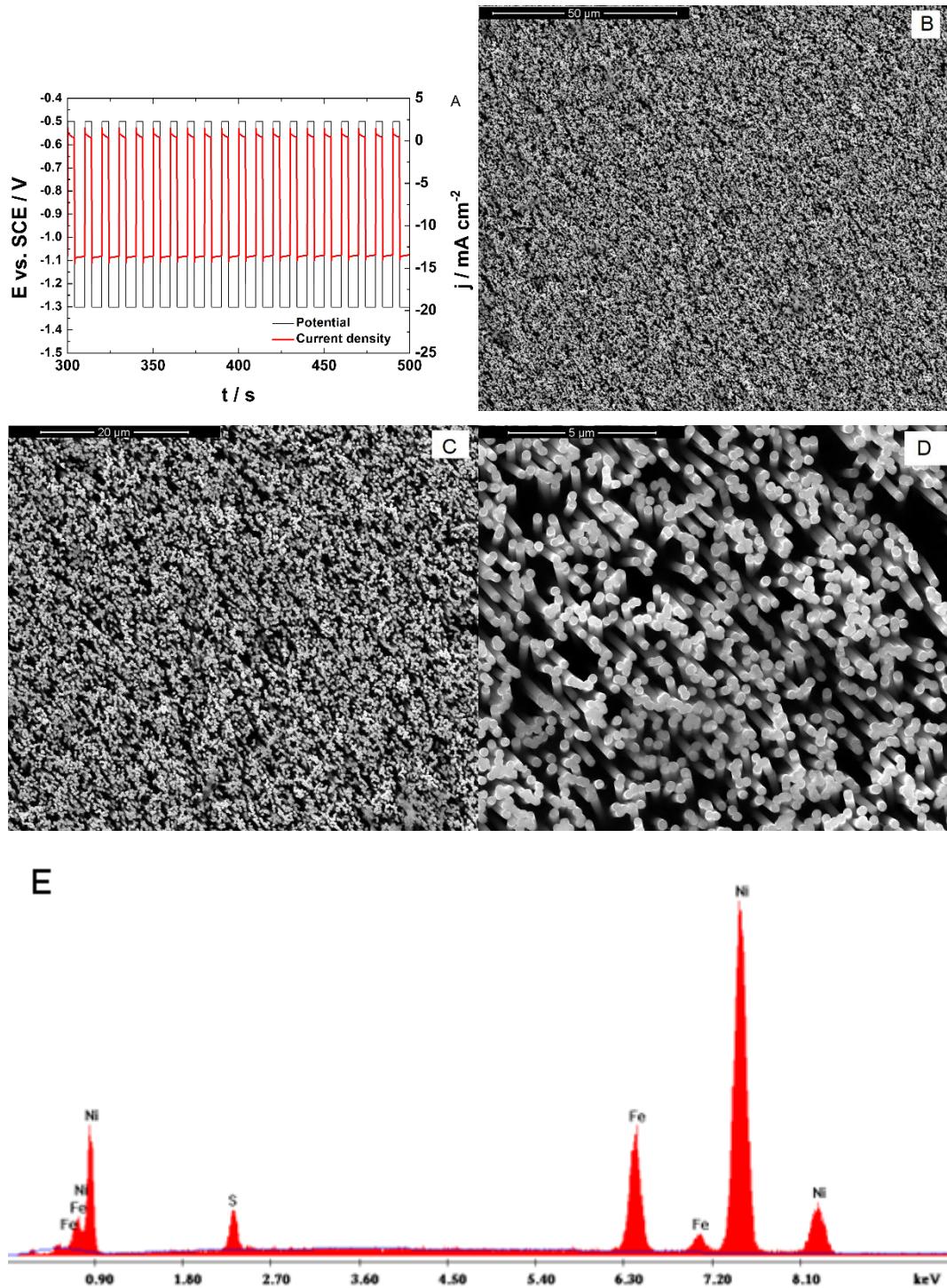


Figure 1 A) Applied potential (black) and measured current density (red) during NiFeS electrodeposition and B,C,D) corresponding SEM images at different magnitudes, E) corresponding EDS analysis

The electrochemical surface area of the electrode was studied evaluating the double-layer capacitance. CVs were carried out at different scan rates using the as-prepared NiFeS NWs, and also for comparison, the NiFe NWs and a planar nickel foil were tested. Results of these tests showed that NWs-based electrodes (both NiFe and NiFeS NWs) have an ECSA 7 times higher than the planar nickel foil, due to the nanostructured morphology. Comparing NiFe NWs and NiFeS NWs, the ECSA of NiFeS NWs increases of 20% showing that the presence of sulfur increases the roughness of NWs and thus increases the catalytic properties of the electrode.

The catalytic properties of the NiFeS NWs for HER were evaluated in a three-electrodes cell where the nanostructured electrode acts as working electrode while the nickel foil is the counter electrode, and a 0.1M NaOH Hg/HgO is the reference electrode. Electrodes were tested using a 30% KOH as the electrolyte solution. The galvanostatic step test is shown in Figure 2a. These tests consist of a stepwise increase of current from 10 to 500 mA cm⁻² and each step lasted 300 seconds. Each point of Figure 2a represents the average of the measured potential. The increase of the applied current density leads to a higher electrode potential and at 50 mA cm⁻² the electrode potential is -0.278 V vs RHE. To test the electrode mid-term stability, -50 mA cm⁻² was applied for 3 hours. Figure 2b shows the potential over time (each point represents the mean value over 30 minutes). The electrode potential changes from -266 mV to -275 mV during those 3 hours, with a linear increase of about 3.8 mV h⁻¹. The long-term stability of the electrode will be tested in future work but this result suggests that the electrode is stable and can be efficiently used to produce hydrogen in an alkaline electrolyzer.

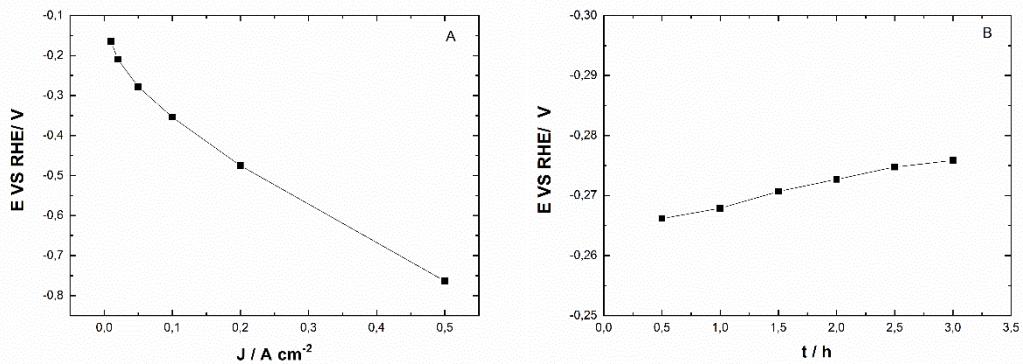


Figure 2 A) Quasi steady state polarization and B) mid-term stability at -50 mA cm⁻² of NiFeS NWs

4. Conclusions

In this work, we have synthesized a ternary alloy of NiFeS with a nanostructured morphology, using a template-assisted electrodeposition method. The nanostructured electrode was characterized by SEM showing that it is made of vertically standing NWs with a mean diameter of 220 nm and a length of about 13 μm. The composition of NWs was evaluated by EDS analysis, confirming the presence of the ternary alloy. The as-prepared electrode was used as a cathode in an alkaline electrolyzer showing very good performance. Further studies are in progress to build a lab-scale electrolyzer integrated with properly designed power electronic converters.

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