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Article *in* Electrochimica Acta · May 2021

DOI. 10.1010/	J.electacta.2021.130300	

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Ni-Fe Alloy Nanostructured Electrodes for Water Splitting in Alkaline Electrolyser

Biagio Buccheri¹, Fabrizio Ganci¹, Bernardo Patella¹, Giuseppe Aiello¹, Philippe Mandin², Rosalinda Inguanta^{1, *}

¹Dipartimento di Ingegneria, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

²Université Bretagne Sud, IRDL UMR CNRS 6027, 56100 Lorient, France

*Corresponding author: rosalinda.inguanta@unipa.it

ABSTRACT

Electrochemical hydrogen produced by water splitting is an interesting energy carrier without CO₂ emission. The high energy required by electrolysers and the use of high-quality catalysts are certainly the most relevant problems to be solved. To overcome these problems, in this work, the opportunities offered by the employment of nickel-iron alloy nanostructured electrodes obtained by template electrosynthesis method have been investigated. Such electrodes consist of nanowire arrays with high surface area. To obtain different alloy compositions, the concentration of the elements in the deposition baths was appropriately tuned. The morphological and chemical characterizations have shown the formation of regular and uniform arrays of nanowires well anchored to the current collector. The experimental results obtained show that the composition of nanowires does not change linearly with the composition of deposition bath but in all the cases analysed, the electrodes were found to be richer in Fe. Nanostructured electrodes were studied as both cathodes and anodes in alkaline conditions, in

30 wt% KOH aqueous solution, at room temperature to determine the best alloy composition. Furthermore, mid- and long-term stability tests were conducted in galvanostatic condition. In all electrochemical tests, the electrodes that performed best are those with iron content of 78.95 at%. Particularly, the results are very promising for the oxygen evolution reaction, with a Tafel's slope of 40 mV and a potential of 1.532 V vs. RHE after 6 h at constant current of 50 mA cm⁻². Besides, preliminary tests in 0.5 M NaCl alkaline aqueous solution are also reported.

KEYWORDS: Alkaline Electrolyzer, Nanostructured Electrodes, Ni-Fe Alloy, HER, OER, Template Electrosynthesis.

1. INTRODUCTION

In order to decrease greenhouse gas emissions, the reduction of fossil fuels consumption is nowadays an objective of paramount importance to avoid possible irreversible climate change [1], considering that the global electricity consumption has been growing steadily in recent years. Furthermore, the policies of some nations, such as China [2,3] or the European states [4–6], are pushing for an increasingly electrified transport sector to reduce cities pollution. To cope with the growing demand for energy, it seems clear that the use of renewable energy sources (RES) is necessary. The energy produced from RES, especially solar and wind, is constantly increasing and it is estimated to be the only energy production sector with a positive increase in terms of energy produced in 2020 [7,8]. However, the problems related to the intrinsic uncertainty and non-programmability of RES are not resolved yet. To overcome these limits, many researchers are focused on developing efficient electrical energy storage (EES) systems [9]. Among the EES technologies, electrochemical systems appear to be the most promising, therefore, in recent years,

different types of batteries for stationary applications have been developed [10-12]. The main disadvantage of batteries remains the self-discharge, and the consequent loss of stored energy, which reduces their energy efficiency. Furthermore, battery power is usually difficult to modulate, making them unsuitable for variable use over time [13]. For this reason, the use of hydrogen as EES in the near future appears to be very valid and promising [14]. In fact, hydrogen is less affected by the aforementioned problems, such as load variation and energy storage times. The electrochemical production of hydrogen, through electrolyzers, is thus a viable strategy to exploit the surplus electricity coming from RES. The main issue of these electrochemical cells is the high energy required enable the water splitting reaction [15–17]. The greatest energy losses are due to electrodes overpotential [18], which strongly depend on electrodes and electrocatalysts [19]. Among electrolyzer technologies, polymer electrolyte membrane electrolyzer cell (PEMEC) has better performance with respect to alkaline electrolyzer cell (AEC) in term of hydrogen production for the same energy consumed [20]. However, PEMEC electrocatalysts are usually noble metals, such as Pt or IrO₂, making the cost of these devices prohibitive, especially for large-scale systems [21]. In fact, AECs require less noble electrocatalysts due to the more favourable kinetic conditions, in particular for the oxygen evolution reaction (OER) [22]. Due to its resistance to corrosion in alkaline solutions and its electrocatalytic properties, Ni-based materials are the most used as electrocatalysts in AECs [23-25]. The type of material employed as electrocatalyst may vary depending on whether it is to be used as a catalyst of hydrogen evolution reaction (HER) or of OER. For HER, Ni alloys are very suitable, since they prevent the formation of hydrides that deactivate the catalyst surface [26]. In particular, the best alloys are those with other transition metals, such as NiPd [27,28], NiMo [29-31], NiZn [32,33], or, even more evidently, with the metals of the iron group, such as NiCo [34-36] and NiFe [37]. In addition to the excellent electrocatalytic property and high chemical stability in alkaline media, the latter are known for their mechanical and magnetic properties [38–40], making them excellent materials in the field of microelectromechanics.

As regard OER, the typical electrocatalysts used are oxides or hydroxides of transition metals or their alloys[41,42]. Even in this case, iron-group metals appear to be the most studied material, with even alternative compositions, such as nitrides, phosphides, sulphides, or borides [25]. In the last decade, increasing attention has been focused on nanostructured materials [43–45], due to the improvement of all surface properties and the reduction of material used. Among the most evident effects of the use of nanostructures, the increase in electrocalytic properties has made it possible to achieve greater efficiencies in the electrochemical cells, thanks to lower energy losses. For example, Wu et al. [46] prepared NiFe double hydroxide nanosheets electrodes onto a zeolite imidazole framework material, obtaining an overpotential of 222 mV at 10 mA cm⁻² and a Tafel slope of 53 mV for OER in alkaline solution, lower values than commercial RuO₂. Ni-W arrow-like nanostructures were developed by Jameei Rad et al. [47] as good HER electrocatalyst with high and sharp active sites that facilitate the release of H₂ bubbles from the surface. Ternary NiCoP nanoparticles by Wang et al. [48] showed excellent performance for both HER and OER, reaching a current density of 10 mA cm⁻² at 1.64 V.

In this work, NiFe alloy nanowires (NWs) electrodes have been manufactured by template electrosynthesis method [49]. Different alloy compositions have been obtained by tuning Ni and Fe concentration in the deposition baths. After morphological and chemical characterization, NiFe NWs electrodes have been investigated for both HER and OER. Furthermore, pure Ni and Fe NWs electrodes have also been made for a better understanding of the performance of the alloys., Electrochemical tests were carried out in 30 wt% KOH aqueous solution at room temperature. In particular, mid- and long-term tests were conducted at constant current density for 6 and 125 h, respectively. In addition, the results of a preliminary test for OER in the presence of chlorine ions is also reported.

2. EXPERIMENTAL

2.1. Electrode fabrication.

All nanostructured electrodes were fabricated through a two-step electrodeposition method. The nanostructures were obtained by nanoporous polycarbonate membrane (Whatman) which acted as template. Membrane thickness and mean pore diameter were about 20 µm and 200 nm, respectively. The fabrication method is detailed in previous works [50,51]. Briefly, a thin layer of gold was sputtered onto a surface of the membrane to make it electrically conductive. On this surface, a Ni layer was electrodeposited via a potentiostatic deposition at -1.5 V vs. SCE (saturated calomel electrode, 0.241 V vs. SHE) for 9000 s using the typical Watt's bath (300 g dm⁻³ NiSO₄· $6H_2O$, 45 g dm⁻³ NiCl₂· $6H_2O$, 45 g dm⁻³ H₃BO₃). Being compact and about 80 μ m thick, this layer acts as a mechanical support and current collector (CC) for the nanostructures. The deposition solution of the NWs consists of the Watt's bath containing different concentrations of FeSO₄·7H₂O (Table 1). NWs electrodeposition was carried out by pulsed potential. The potential was switched between -1.3 V and -0.9 V vs. SCE for 100 cycles. The two potentials were maintained for 6 s for 4 s, respectively. As explained in [28,33], the selected potentials were preliminarily examined in order to obtain an inversion in the polarity of the current during deposition. This is necessary to continuously restore the composition of electrode/electrolyte surface and control the accumulation of hydrogen gas inside the template channels [52]. This last aspect is more important to control the morphology of the nanostructures, because the accumulation of hydrogen in the nanochannels can lead to the formation of nanotubes with lower mechanical resistance compared to NWs [53-55]. All electrodepositions were carried out at room temperature using a three-electrode cell with a Pt mesh as a counter-electrode and a SCE as a reference. The area of working electrode was about

 11 cm^2 and a fresh solution was utilized for each test. After NWs deposition, the polycarbonate membrane was etched in CH₂Cl₂ at room temperature. To ensure the total removal of the template, the etching was repeated 4 times using fresh solvent for each step.

2.2. Electrode Characterization.

A FEG-ESEM microscope (QUANTA 200 by FEI) was employed to investigate morphology and composition of nanostructured electrode. This system is equipped with Energy Dispersive Spectroscopy (EDS) probe, that was used to analyse to NWs, after their detachment from CC, and to calculate the average composition. Different areas of samples were exanimated to investigate the uniform NWs composition and morphology. RIGAKU X-ray diffractometer (D-MAX 25600 HK) was used for x-ray diffraction (XRD) analyses that were performed in the 20 range from 30° to 100° with a sampling width of 0.01° and scan speed of 0.0667° s⁻¹. The Nifiltered Cu K α radiation (λ = 0.154 nm) was employed and tube current and potential were set at 40 mA and 40 kV, respectively.

The electrochemical and electrocatalytic tests were carried out at room temperature in 30 wt% KOH aqueous solution using a three electrodes cell. Before the electrochemical and electrocatalytic tests, the electrodes were insulated to limit a geometrical area of 0.5 cm². A Ni sheet was employed as counter-electrode, and Hg/HgO (0.165 V vs. SHE) as reference. In the following, all potentials will be referred to the value of reversible hydrogen electrode (RHE, - 0.826 V vs. SHE) at pH 14. Cell Test System (Solartron, Mod. 1470 E) was used to perform the electrochemical characterization and the data were recorded by MultiStat Software. Each experiment reported in this work was repeated at last three times.

3. RESULTS AND DISCUSSUION

3.1. Morphological and chemical characterization.

Nanostructured alloys with different composition were obtained by tuning the concentration of Ni and Fe in the deposition bath. Hereafter, electrode names are referred to Fe composition, as reported in Table 1. Figure 1 shows the content of Fe in the NWs as function of Fe concentration in electrodeposition solution. Each point was obtained as an average value of the composition of different areas. In all the cases, despite the iron is the less noble metal, its content is higher than the bath concentration. This result is in agreement with literature data [56,57], in fact, the electrodeposition of iron alloys is known as anomalous co-deposition consisting in the preferentially deposition of the less noble metal with respect to the noble one, that complicates the control of the alloy composition [58]. Several possible mechanisms can be found to explain this behaviour [59,60], that as showed by Llavona et al. is enhanced when the electrodeposition is carried out into nanoporous template [52]. The most plausible mechanism for the anomalous co-deposition of iron alloys was proposed by Matlosz [60] who demonstrated that the inhibition of Ni deposition in the presence of Fe in due to the preferential adsorption of iron intermediate species on electrode surface. As demonstrated in [52,61] for electrodeposition carried out in nanochannels a higher blocking of electrode surface occurs, due to adsorbed iron species, leading to deposition of Fe-rich NWs. In particular, the Fe content is much higher than that obtained under the same conditions with a planar electrode. Moreover, as reported by the same authors, depending on the deposition voltage it can be verified that the NWs composition is different along their length. Contrarily, we have found that NWs, under all deposition conditions, have uniform composition along their length. This result agrees with the data of Llavona et al. [52], which show that, for potential values really similar to the two values we used in this work to perform the pulsed deposition, the NWs composition is quite homogeneous.

Electrode Name	Solution Concentration (at%)		NWs Composition (at%)	
	Ni	Fe	Ni	Fe
Fe 0.00	100.0	0.00	100.0	0.00
Fe 26.22	95.24	4.76	73.78	26.22
Fe 45.25	90.91	9.09	54.75	45.25
Fe 64.59	83.33	16.67	35.41	64.59
Fe 78.95	66.67	33.33	21.05	78.95
Fe 84.39	50.00	50.00	15.61	84.39
Fe 100.0	0.00	100.0	0.00	100.0

Table 1. NWs atomic composition



Figure 1. NiFe NWs composition as a function of Fe concentration in the electrodeposition bath.

EDS spectra of these NWs are shown in Figure 2. According to the average values reported in Figure 1, the Ni peaks decrease as the Ni concentration in solution decreases and, consequently, the Fe peaks increase. In the Fe 100.0 spectrum, there is a relevant O peak due or to the competitive deposition of Fe hydroxide that occurs during Fe electrodeposition [62,63] or to the oxidation of Fe in air, or to both.



Figure 2. EDS spectra of different NWs electrodes: black) Fe 0.00; green) Fe 45.25; blue) Fe 78.95; red) Fe 100.0.

In Figure 3, the XRD patterns of the different electrodes are shown. To better compare, also the pattern that of pure Ni NWs was reported. These consist of well crystalline α -Ni with face-centered cubic (fcc) structure (ICDD® (International centre of diffraction data) card no. 04-850). Using the Sherrer's equation [64], the mean grain dimension was calculated considering the wide at half height (FWHM) of the main peak located at about 44.8°, founding a value of 25 nm. In the cases of alloy electrodes, the peaks at about 43.88°, 50.88° 74.75° and 90,11 can be respectively indexed to (111), (200) (220) and (420) planes of the fcc Fe-Ni alloy (card no. 47-1405) [61,65–68]. Chang et al [66] found that with the increase of Fe, the alloy changes

from fcc phase to bcc. We did not find this behaviour in our electrodes but, in our case, the intensity of peak located at about 44° (111) is lower than intensity of 51° (200) peak. Thus, the alloys are preferentially oriented along the (200) plane. The grain sizes of alloys were calculated on the basis of the FWHM of this peak finding a value of about 30 nm for the alloys with a Fe content lower then about 65% and a value of about 40 nm for alloys more Fe-rich alloy. Thus, from these results it can be concluded that the deposition of NWs arrays of fcc Fe-Ni alloy (card no. 47-1405) was obtained. In the case of NWs of pure Fe (Fe100.00), the peaks in the pattern are located in almost the same position of those of pure Ni. The peaks of pure iron are not present (card no. 65-4899), but there is a slight shift and above all a drastic decrease in the height of the Ni peaks. This could be due to the fact that the Fe nanostructures are practically amorphous, and their presence shields the intensity of the Ni peaks.



Figure 3. a) XRD patterns and b) relative enlargement of the main diffraction peaks of NiFe NWs electrodes: black) Fe 0.00; green) Fe 45.25; blue) Fe 78.95; red) Fe 100.0.

In Figure 4, the SEM images of the nanostructured electrode with different composition were reported. In all cases, the shape of NWs appears cylindrical with a surface smooth and regular, also the typical NWs interconnections due to template pores are clearly visible. Furthermore, the current collector surface is uniformly covered by NWs, with a diameter of 220-250 nm and a length of approximately 7 μ m. As expected, the morphology is independent on the composition because is related only to the type and shape of nanoporous template.



Figure 4. SEM images of NiFe NWs electrodes: a) Fe 0.00; b) Fe 45.25; c) 78.95; d) Fe 100.0.

3.2. Electrodes electrochemical and electrocatalytic tests.

To carry out electrochemical and electrocatalytic characterizations of the electrodes, cyclic voltammetry (CV), quasi steady-state polarization (QSSP) and galvanostatic polarization have been performed.

By CVs at different scan rates, specific capacitance was evaluated by the double layer capacitance method [69,70]. The specific capacitance is directly proportional to the real electrode surface and allows to compare different electrodes with the same system. For this reason, together with the electrodes manufactured in this work, a Ni planar sheet was also tested. CVs were carried out in the non-Faradic potential interval between 0.925 and 1.025 V vs. RHE at scan rates of 20, 25, 30, and 35 mV s⁻¹, as shown in Figure S1. Figure 5 shows the anodic and cathodic current density differences at 0.975 V vs. RHE for each electrode as function of scan rate. The slope of the lines obtained from the linear regression represents the specific capacitance.



Figure 5. Specific capacitance of various electrodes evaluated by double layer capacitance method: violet) Ni Lamina; black) Fe 0.00; green) Fe 45.25; blue) Fe 78.95; red) Fe 100.0.

As expected, specific capacitance of each nanostructured electrode is at least 5-7 times higher than a planar electrode. Thus, the nanostructured electrodes have a very high real surface area compared to planar electrode.

To estimate electrocatalytic electrodes behaviour, QSSP tests were carried out for both HER and OER. The scanned potential interval was 0.7 V with a scan rate of 0.1667 mV s⁻¹. For both reactions, the scanned range was chosen close to the thermodynamic potential, which corresponds to 0 V and 1.23 V vs. RHE for HER and OER, respectively. Particularly, for cathodic QSSP tests, the potential interval was scanned from -0.1 to 0.6 V vs. RHE, while for anodic QSSP tests, it was scanned from 1.1 V to 1.8 V vs. RHE. Figures 6a and 6b show the linear range of potential as function of the logarithmic current density (in absolute value) for cathodic and anodic QSSP, respectively. To compare the results obtained for these alloys with other electrodes, the same procedure of fitting reported in previous works [33,36] was executed. The QSSP curves were fitted with Tafel's equation (1)

$$\eta = a + b \log i \tag{1}$$

where *a* and *b* parameters are related to the exchange current density and to the Tafel's slope of the curve, respectively. In Table 2 the values of the parameters obtained from the fitting of the experimental curves, in addition to the R-square value referred to each fitting, were reported. As for the HER, b absolute values of the alloy electrodes are lower than pure Ni (Fe 0.00) and pure Fe (Fe 100.0). However, the values are higher than the values previously obtained with the NiCo alloy [36], which to date has been the nano-structured alloy with the best performance we have manufactured and tested. Table 2 shows that the slope values for HER are close to 120 mV, indicating that the rate determining step of the reaction is the Volmer stage [71].

For the OER, all the electrodes showed excellent performances, in terms of Tafel's slope. The best electrode was Fe 78.95 that has a slope value of 40 mV. This result is similar to others obtained with NiFe alloy electrodes [72,73].

The good electrocatalytic behaviour of nanostructured electrodes can be imputable to the very high electrochemical active surface area, according to the results reported in Figure 5, that ensures a very high number of active sites for HER and OHR. Thus, as reported by Darband et al. [74], electrodes with NWs morphology have higher electrocatalytic activity compared to bare ones. Moreover, the super aerophobic surface of NWs, guarantees a rapid separation of gas bubbles from the surface [75] and thus



Figure 6. Linearity range of (a) cathodic QSSP for HER and (b) anodic QSSP for OER at - 0.1667 mV s⁻¹ scan rate in 30 wt% KOH aqueous solution at room temperature.

	HER			OER		
Electrode	a (V)	b (V)	$R^{2}(\%)$	a (V)	b (V)	$R^{2}(\%)$
Fe 0.00	-0.596	-0.153	99.64	1.638	0.060	99.92
Fe 45.25	-0.579	-0.129	99.56	1.512	0.042	99.92

Table 2. Fitted Tafel's parameters for HER and OER.

Fe 78.95	-0.547	-0.116	99.69	1.515	0.040	99.90
Fe 100.00	-0.525	-0.130	99.75	1.559	0.042	99.93

To evaluate the behaviour at high current densities, galvanostatic-step polarizations were carried out for both HER and OER. The tests were conducted with a multi current step procedure consisting in a stepwise increase of current, each lasting 300 s for each step, from 10 to 500 mA cm⁻² (10, 20, 50, 100, 200, 500). Figures 7a and 7b show electrode potential as function of current density for HER and OER, respectively. Each point in the graphs corresponds to the average value of the electrode potential during the step. In the case of HER, the curves are all close to each other except for Fe 100.0, which showed the better performance. At -100 mA cm⁻², Fe 100.0 potential was -0.529 V vs. RHE, while Fe 78.95 potential was -0.478 V vs. RHE, therefore with a difference of 51 mV. In the case of OER, Fe 45.25 and Fe 78.95 performed better than pure element electrodes. In particular, at 100 mA cm⁻², Fe 78.95 potential was 1.598 V vs. RHE, which means an overpotential of 0.368 V, while Fe 100.0 potential was 1.665 V vs. RHE.



Figure 7. Galvanostatic-step polarizations for (c) HER and (d) OER in 30 wt% KOH aqueous solution at room temperature.

To study the stability over time, constant current density mid-term tests were carried out for 6 h at -50 mA cm⁻² and 50 mA cm⁻² for HER and OER, respectively. Figures 8a and 8b show the electrode potential as function of time. Each point in the graphs corresponds to a potential averaged over 1800 s. The results showed good stability over time, especially for OER. In HER case, Fe 78.95 performed well with final potential of -0.477 V vs. RHE with a loss of 30 mV in 6 h, while Fe 0.00 recorded a final potential of -0.535 V vs. RHE with a loss of 54 mV. As expected, the electrode potential of Fe 100.0 decreases over time. This is due to a modification of the electrode because of corrosion reactions [76].



Figure 8. Constant current density mid-term stability test for (a) HER at -50 mA cm⁻² and (b) OER at 50 mA cm⁻² in 30 wt% KOH aqueous solution at room temperature.

Also, in the OER case, Fe 78.95 was found to be the most stable and the best performing. In fact, after 6 h, the final potential was 1.532 V vs. RHE with a loss of only 10 mV from the start of the test. For these reasons and for those reported above, Fe 78.95 was evaluated as the best composition of the NiFe alloy for overall water splitting in alkaline solution.

A further investigation was carried out on these electrodes to verify their long-term stability. The results of 125 h long galvanostatic tests were reported in Figures 9a and 9b for HER and OER, respectively. Each point in the graphs corresponds to a potential averaged over 4 h. Fe 78.95 shows a stable trend during the whole-time span of the test, with an overall loss of 6 mV, which can be expressed as an hourly drop of 0.048 mV h⁻¹. In the case of OER, the test was carried out both in 30% w/w KOH solution and in the same solution also containing 0.5 M of NaCl. The choice of using sodium chloride was made to simulate the possible use of these electrodes in sea water, where the presence of chlorine can lead to the hypochlorite ion formation at the anode (Eq. 2) and consequently corrode the electrode more quickly [77].

$$20H^{-} + Cl^{-} \hookrightarrow 0Cl^{-} + H_2O + 2e^{-}$$
 E°= 1.714 V vs. RHE (2)

For test without NaCl, the potential remained below 1.6 V vs. RHE, with final value of 1.573 V vs. RHE and an overall variation of 30 mV, with an hourly loss quantifiable in 0.24 mV h^{-1} .



Figure 9. Constant current density long-term stability test: for a) HER at -50 mAcm⁻² and (b) OER at 50 mAcm⁻² at room temperature.

In the presence of NaCl, the potential loss during the 125 h is slightly higher, equal to 52 mV, particularly concentrated in the first hours of the test. However, even in this case, the electrode

potential remained below 1.6 V vs. RHE, i.e., lower than the hypochlorite formation potential. Consequently, it is possible to conclude that there is no formation of hypochlorite and the current is attributable to OER, as reported in [78] where similar conditions were adopted.

The electrodes used for the long-term tests were further analysed by SEM analysis to evaluate the mechanical and chemical stability. Figure 10a shows Fe 78.95 electrode after 125 h of HER at -50 mA cm⁻². The electrode appears different from what was observed in the Figure 4c, some damages are clear visible with some fallen wires. On the contrary, as shown in Figure 10b, Fe 100.0 morphology is completely changed, due to a modification of the electrode because of corrosion reactions [76]. This explains the electrocatalytic behaviour during the mid- and long-term duration conditions, previously reported.



Figure 10. SEM images after long-term stability of a) Fe 78.95 and b) Fe 100.0 at -50 mA cm⁻² in 30 wt% KOH aqueous solution at room temperature.



Figure 11. SEM images after long-term stability of Fe 78.95 at 50 mA cm⁻² in a) 30 wt% KOH aqueous solution and b) 30 wt% KOH + 0.5 M NaCl aqueous solution at room temperature.

In Figures 11a and 11b, Fe 78.95 morphologies are shown after long-term tests of OER at 50 mA cm⁻² in 30% w/w KOH solution without and with 0.5 M NaCl, respectively. In both cases, the nanostructures are perfectly intact and appear as-prepared, as shown in Figure 4. This result is very promising, especially in the case of the solution with chlorine ions, because it would allow the application of these electrodes with the use of sea water. In the case of Fe 100.0 (Figure S2) the morphology is quite different of as-prepared electrodes with the formation of NWs bundles having a rough surface due to passive film [76]. The formation of bundles suggests that under oxygen evolution the Fe NWs have a poor mechanical stability and consequently they tend to collapse. In order to compare the results obtained in this work with those obtained in previous works and with reference data from the literature, the most significant values art reported in Table 3.

 Table 3. Comparison of performance of various electrocatalysts (TW: this work)

Electrocatalysts	Reaction	KOH solution	Tafel slope (mV)	Current density (mA cm ⁻²)	Potential at current density (V vs. RHE)	Ref.

Ni strip	HER	30 % w/w	-142			[50]
Ni NŴs	HER	30 % w/w	-118	-10	-0.250	[50]
Ni NWs + Pd NPs	HER	30 % w/w	-120			[50]
Ni _{0.05} Co _{0.95} NWs	HER	30 % w/w	-105	-10	-0.231	[36]
NiZn NWs 50-50	HER	30 % w/w	-104	-10	-0.276	[33]
NiW NWs 33-67	HER	30 % w/w	-111	-10	-0.291	[33]
Ni-Fe(OH) _x /NF	HER	1 M	-135	-10	-0.170	[79]
NiFe LDH/NF	HER	1 M	-138	-10	-0.250	[80]
Fe 0.00	HER	30 % w/w	-153	-10	-0.290	TW
Fe 100.0	HER	30 % w/w	-130	-10	-0.265	TW
Fe 78.95	HER	30 % w/w	-116	-10	-0.315	TW
NiFe LDH/ZIF-67	OER	1 M	53	10	1.452	[46]
NiCoP NPs	OER	1 M	52	10	1.54	[48]
Ni _{0.05} Co _{0.95} NWs	OER	30 % w/w	88	10	1.501	[36]
Ni-Fe(OH) _x /NF	OER	1 M	47	50	1.527	[79]
Ni _{2.85} Fe _{0.15} (NO ₃) ₂ (OH) ₄	OER	1 M	121	10	1.579	[81]
NiFe 1:0.5	OER	1 M (NaOH)	81	10	1.507	[82]
FeNi/NiFe2O4@NC	OER	1 M	60	10	1.546	[83]
nNiFe LDH/NGF	OER	0.1 M	45	10	1.567	[84]
Fe 0.00	OER	30 % w/w	60	10	1.518	TW
Fe 100.0	OER	30 % w/w	42	10	1.475	TW
Fe 78.95	OER	30 % w/w	40	10	1.435	TW

4. CONCLUSIONS

In this research, the template electrosynthesis method has been employed for the fabrication of NiFe alloy nanostructured electrodes. To obtain different alloy compositions, NWs electrodeposition bath concentration was varied by tuning the amount of Fe. After the template removal, chemical and morphological characterizations were carried out by EDS, XRD and SEM analyses. From EDS analysis, the well-known anomalous deposition of Fe has been confirmed. In fact, NWs compositions are richer in Fe compared to Fe concentration in the deposition bath. These electrodes were studied both as cathodes and anodes for water electrolysis in alkaline conditions. Electrochemical and electrocatalytic characterizations were carried out in 30 wt% KOH aqueous solution at room temperatures. In particular, CV, QSSP and galvanostatic tests were conducted to investigate the electrodes behaviour to both HER and OER. Anodic QSSP tests reported very good results for electrodes containing Fe, and Fe 78.95 was the best with a Tafel slope of 40 mV. However, less promising results came from cathodic

the QSSPs, for which the electrodes performed worse than the other nanostructured alloys that we have previously investigated. To better analyse the stability of the electrodes under the evolution of both gasses, mid- and long-term galvanostatic test were carried out at 0.05 A cm⁻² current density for 6 and 125 h, respectively. Fe 78.95 showed excellent stability, performing hourly drops of 0.048 and 0.24 mV h⁻¹ for HER and OER, respectively.

Furthermore, preliminary stability test was carried out in alkaline solution also containing 0.5 M NaCl to simulate seawater condition. We found that the presence of chlorine does not seem to affect the stable functioning of the electrode in the short or long term.

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