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Article

Hydrogen and Oxygen Evolution on Flexible Catalysts Based on Nickel-Iron Coatings

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Abstract: Electrolysis of water is one of low-cost green hydrogen production technologies. The challenge is designing and developing low-cost and high-activity catalysts. Herein, we present a strategy to fabricate flexible electrocatalysts based on nickel-iron (NiFe) alloy coatings. NiFe coatings were plated on the flexible copper-coated polyimide surface (Cu/PI) using the low-cost and straightforward electroless metal plating method and morpholine borane as a reducing agent. It was found that Ni₉₀Fe₁₀, Ni₈₀Fe₂₀, Ni₆₀Fe₄₀, and Ni₃₀Fe₇₀ coatings were deposited on the Cu/PI surface, then the concentration of Fe²⁺ in the plating solution was 0.5 mM, 1 mM, 5 mM, and 10 mM, respectively. Morphology, structure, and composition of Ni_xFe_y/Cu/PI catalysts have been examined using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and inductively coupled plasma optical emission spectroscopy (ICP-OES), whereas their activity has been investigated for hydrogen evolution (HER) and oxygen evolution (OER) reactions in 1 M KOH using linear sweep voltammetry (LSVs). It was found that the Ni₈₀Fe₂₀/Cu/PI catalyst exhibited the lowest overpotential value of −202.7 mV for the HER to obtain a current density of 10 mA cm^{−2} compared to Ni₉₀Fe₁₀/Cu/PI (−211.9 mV), Ni₆₀Fe₄₀/Cu/PI (−276.3 mV), Ni₃₀Fe₇₀/Cu/PI (−278.4 mV), and Ni (−303.4 mV). On the other hand, the lowest OER overpotential (344.7 mV) was observed for the Ni₆₀Fe₄₀/Cu/PI catalyst to obtain a current density of 10 mA cm^{−2} as compared with the Ni₃₀Fe₇₀ (369.9 mV), Ni₈₀Fe₂₀ (450.2 mV), Ni₉₀Fe₁₀ (454.2 mV) coatings, and Ni (532.1 mV). The developed Ni₆₀Fe₄₀/Cu/PI catalyst exhibit a cell potential of 1.85 V at 10 mA cm^{−2}. The obtained catalysts seem to be suitable flexible catalysts for HER and OER in alkaline media.

Keywords: nickel; iron; morpholine borane; electroless metal plating; water splitting; hydrogen evolution; oxygen evolution

1. Introduction

The search for novel and optimized energy storage and usage technologies is accelerating rapidly. In order to be considered for implementation, these technologies must satisfy three principal criteria: they must be efficient, reliable and inexpensive. Among these technologies, electrochemical energy is emerging as a clear front-runner, offering significant potential for advancement. The production of clean hydrogen via electrolytic water splitting represents a viable and efficient approach, with hydrogen being considered an optimal substitute for traditional fossil fuels [1–3]. The electrochemical water splitting process involves two half-reactions: the hydrogen evolution reaction (HER), which occurs at the cathode, and the oxygen evolution reaction (OER), which occurs at the anode electrode. The slow kinetics of these reactions represents a significant challenge that must be

addressed. The efficiency of this process can be markedly enhanced through the strategic use of carefully selected catalysts [4]. Advancements in electrocatalysts, in particular those with reduced overpotential and enhanced durability, have the potential to contribute to an improvement in the efficiency of HER/OER processes. Precious metal-based materials, such as Pt for HER and Ir/RuO_x or their alloys for OER, have been identified as the most effective catalysts for water splitting. However, there are still some challenges to be addressed, particularly in terms of cost and availability, which could affect their large-scale applications.

A variety of non-noble transition metal-based (TM) catalysts has been developed as an alternative to the high-cost but effective noble metal-based catalysts [5–7]. Systems, based on iron and nickel, have been demonstrated to have considerable potential for the overall splitting of water. For example, heterostructures of Fe-Ni₃S₂/Ni₂P [8], Fe-doped nickel-based phosphides [9], Ni/NiFe-Pyro@IF [10], amorphous Ni-Fe-P alloys with varying phosphorous concentrations [11] have demonstrated impressive electrocatalytic activity with respect to both OER and HER processes. However, the intrinsic electrocatalytic effectiveness of the majority of current catalysts has yet to be fully realised, primarily due to a number of challenges, including low activity, low conductivity, poor stability and high aggregation. The electrochemical performance of Ni-Fe catalysts has been enhanced on numerous occasions through the utilisation of non-metallic elements, including sulfur [12], phosphorus [12], boron [13], and selenium [14], among others. The incorporation of additional heteroatoms with varying atomic radii and electronegativities into the catalyst can lead to further changes in the electronic structure of the material surface, thereby speeding the overall water splitting process [11].

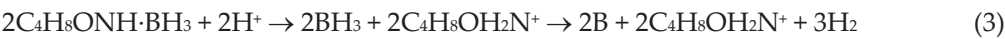
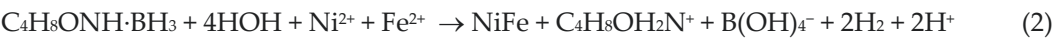
In many cases, the selection of an appropriate substrate represents a key strategy for enhancing catalyst performance. For example, the use of high-conductive nickel [15,16] iron [10] or both nickel-iron [12,17] foams not only improve the conductivity of the material, but also significantly increases the electrochemical active surface area of the catalyst. Furthermore, cost-effective carbon-based substrates, including carbon cloth [18,19], carbon nanotubes [19], carbon nitrides [20], graphitic carbon [21], and graphite felt [22], can also be employed for this purpose. However, the use of unmodified pristine carbonaceous materials has been observed to result in reduced activity, particularly at the anodic reaction, due to their susceptibility to oxidative degradation at higher anodic polarisations. In such circumstances, polyimide (PI), which represents a class of conducting polymers, emerges as a potentially more suitable candidate for the substrate due to its favorable electronic conductivity, excellent oxidative stability in both strong acids and alkalis, flexibility, and low cost [23]. Recently, the polyimide-carbon nanotube (PI-CNT) film has been referenced as a promising substrate for a flower-like Co-Ni alloy catalyst, which has demonstrated a notable enhancement in the catalyst's OER performance. This was characterised by a low overpotential and a rapidly increasing current density [24]. Another high-performing OER catalyst was developed by immobilizing iridium (Ir) single atoms on a PI support, exhibiting high mass activity on a carbon paper electrode while simultaneously achieving outstanding stability with negligible decay for 360 hours [25]. Furthermore, a reduced graphene oxide-polyimide/carbon nanotube film decorated with NiSe nanoparticles was used directly as a HER electrocatalyst without further treatments, which exhibited well-defined HER catalytic activity [26]. Meanwhile, FeNi₃/Fe₃O₄ hybrid NPs anchored to laser-induced graphene (LIG) electrodes directly patterned on both sides of an inexpensive polyimide film showed exceptional performance in water splitting [27].

It is important to note that the use of TM-based catalysts in devices is only possible with the use of polymeric binders such as Nafion. This presents a significant limitation for commercial applications, as it increases electrical resistance, decreases the active area of the catalyst and reduces the efficiency of electrocatalyst binding to the conductive support [28]. Typically, fine-grained catalytic NPs are mixed with a polymer binder (Nafion), conductive fillers and a solvent to form an ink and then sprayed onto the conductive electrodes. However, this frequently results in sparse accumulation or distribution of catalysts. It is therefore of particular importance to consider the use of PI supports for the development of catalysts [23,29]. This work presents a strategy for the fabrication of flexible electrocatalysts based on NiFe alloy coatings on copper-coated low-cost

polyimide surfaces (Cu/PI) using a simple, and straightforward electroless metal plating method with the aim of using them as anode/cathode catalysts for hydrogen production by water splitting.

2. Results and Discussion

Production of green hydrogen via water electrolysis is widely investigated and the main research is focused on the search and development of an efficient and low-cost materials with high activity for hydrogen and oxygen evolution reactions. Many materials like Pt-based catalysts, non-noble metal catalysts are created. In this study we present a strategy to fabricate flexible electrocatalysts based on nickel-iron coatings. As flexible substrate we use polyimide coated with a copper film. PI is lightweight, flexible, resistant to heat and chemicals. Ni_xFe_y coatings were deposited on the Cu surface by a simple electroless metal plating method using morpholine borane (MB) as a reducing agent. The reactions occurring during the NiFe coatings deposition are the oxidation of the reducing agent – MB (Equation (1)) and the cathodic reduction of NiFe (Equation (2)) and boron (B) (Equation (3)):



In order to obtain the NiFe coatings with different contents of Ni and Fe, the plating baths were used where concentrations of glycine, nickel sulfate, ethylenediaminetetraacetic acid, and sodium malonate were kept constant, whereas the concentration of iron sulfate ranged from 0.5 mM to 10 mM. The plating bath operated at a temperature of 60 °C for one hour. The composition of the coatings was analyzed by ICP-OES. The data obtained are shown in Table 1. By varying the concentration of iron sulfate in the plating bath, we deposited the NiFe coatings with different compositions – the content of Ni varied from 90 to 30 at.% and iron – from 10 to 70 at.%. As can be seen, when Ni₉₀Fe₁₀, Ni₈₀Fe₂₀, Ni₆₀Fe₄₀, and Ni₃₀Fe₇₀ coatings were deposited on the Cu/PI surface, the concentration of Fe²⁺ in the plating solution was 0.5 mM, 1 mM, 5 mM, and 10 mM, respectively.

Table 1. Composition of the deposited Ni_xFe_y coatings determined by ICP-OES analysis.

Sample	Metal loading in the coatings, mg cm ⁻²			Element, at. %		Coating denoted as
	Ni	Fe	Ni+Fe	Ni	Fe	
No. 1	0.4805	0.9060	1.3865	34.60	65.30	Ni ₃₀ Fe ₇₀
No. 2	0.6305	0.4521	1.0826	58.24	41.76	Ni ₆₀ Fe ₄₀
No. 3	2.9040	0.6995	3.6035	80.60	19.40	Ni ₈₀ Fe ₂₀
No. 4	2.3400	0.2695	2.6095	89.70	10.30	Ni ₉₀ Fe ₁₀

Figure 1 shows the dependence of the deposited Fe and Ni content in the NiFe coatings on the concentration of FeSO₄ in the plating solution. It can be seen that by increasing the Fe²⁺ concentration up to 10 mM, the deposited Ni content decreases and the Fe content increases. In addition, further increases in the Fe²⁺ concentration in the plating solution result in lower Fe content and higher Ni content in the NiFe coating. The plating rate for the Ni₉₀Fe₁₀, Ni₈₀Fe₂₀, Ni₆₀Fe₄₀, and Ni₃₀Fe₇₀ coatings was approximately 2.6, 3.6, 1.1, and 1.4 mg cm⁻² h⁻¹, respectively.

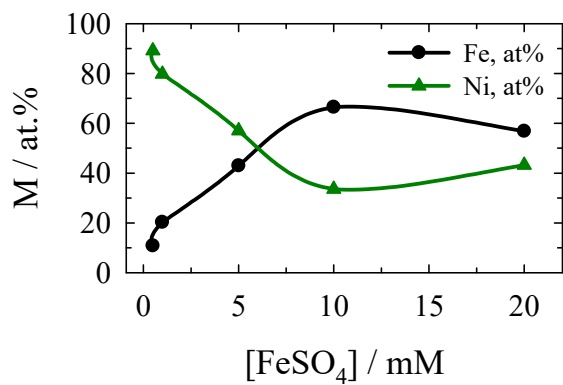
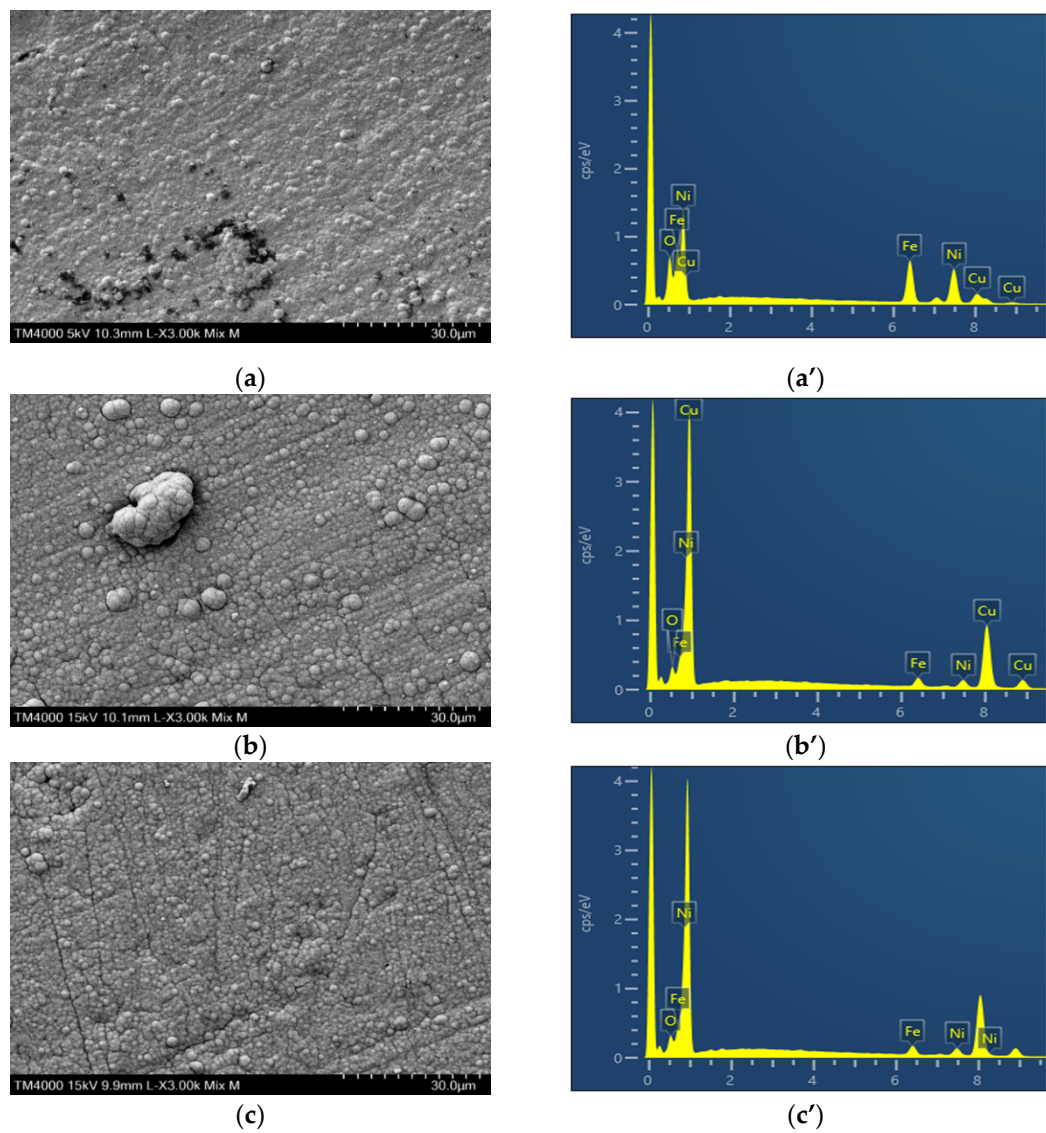


Figure 1. The content of deposited Fe and Ni in NiFe coatings as a function of the concentration of FeSO₄ in the plating solution.

The morphology and composition of the Ni_xFe_y coatings were characterized using SEM and EDX analysis (Figure 2). From the SEM views, it can be seen that NiFe produces a layer of granular nickel-iron particles up to two hundred nanometers in size (Figure 2a–d). Energy dispersive X-ray analysis confirms the presence of nickel and iron in all coatings (Figure 2a’–d’).



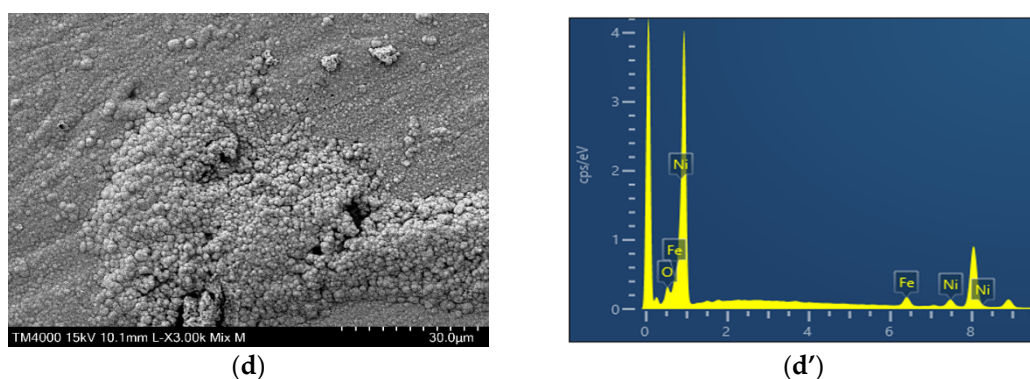


Figure 2. SEM images of $\text{Ni}_{90}\text{Fe}_{10}$ (a), $\text{Ni}_{80}\text{Fe}_{20}$ (b), $\text{Ni}_{60}\text{Fe}_{40}$ (c), and $\text{Ni}_{30}\text{Fe}_{70}$ (d) coatings and the corresponding EDX spectra (a'-d').

XRD patterns of the Ni_xFe_y coatings obtained are shown in Figure 3. The peaks at about 43.6° , 50.7° and 74.3° can be respectively indexed to the (111), (200) and (220) planes of the fcc Fe-Ni alloy (JCPDS card No. 47-1405), respectively (Figure 3). For example, in the case of $\text{Ni}_{30}\text{Fe}_{70}$, with the higher Fe content, the additional peak at 45.2° is seen in the XRD pattern which can be indexed to the (110) plane of the bcc Fe-Ni alloy (JCPDS card no. 37-0474).

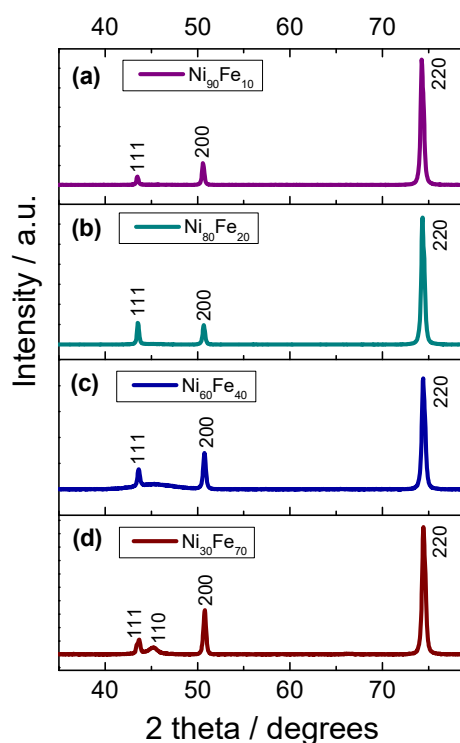


Figure 3. XRD patterns of different Ni_xFe_y coatings.

It can be seen that between 10 at.% Fe and 40 at.% Fe (Figure 3a-c), the fcc structure predominates, with the presence of the (111), (200) and (220) fcc peaks. Increasing the Fe content up to 70 at.% in the coating results in the appearance of the bcc (110) contribution, while the fcc (111) remains predominant in the XRD pattern (Figure 3d).

Hydrogen evolution was investigated on the obtained catalysts in an N_2 -deaerated 1 M KOH solution. The HER polarization curves on the different $\text{Ni}_x\text{Fe}_y/\text{Cu}/\text{PI}$ catalysts are shown in Figure 4a.

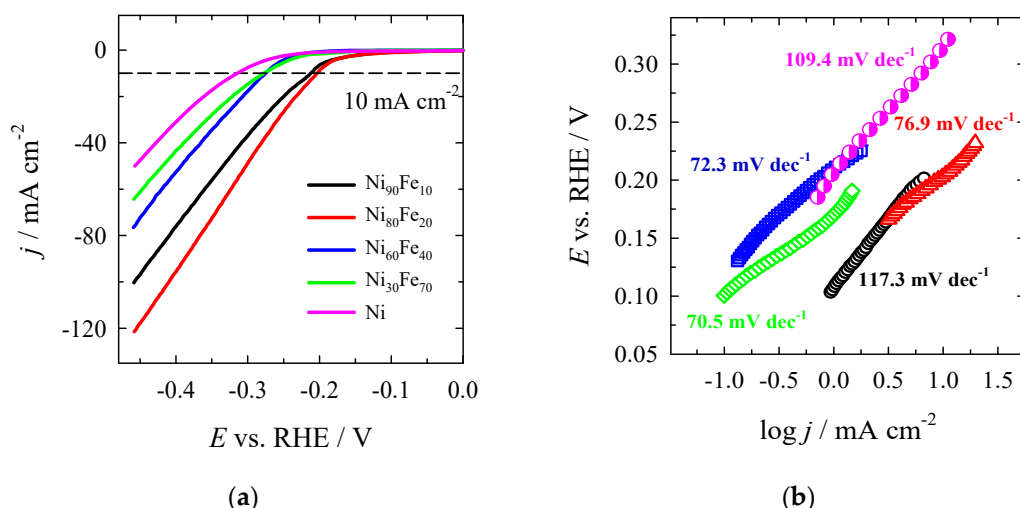


Figure 4. (a) HER polarization curves of Ni, Ni₉₀Fe₁₀, Ni₈₀Fe₂₀, Ni₆₀Fe₄₀, and Ni₃₀Fe₇₀ catalysts in N₂-saturated 1 M KOH solution at a potential scan rate of 2 mV s⁻¹; (b) The corresponding Tafel slopes for each catalyst.

Data given in Table 2 show that among the investigated catalysts, the lowest onset potential (E_{onset}) of -0.0928 V exhibits the Ni₈₀Fe₂₀ catalyst compared to the Ni₉₀Fe₁₀, Ni₃₀Fe₇₀, and Ni₆₀Fe₄₀. In addition, this catalyst shows the highest current density at -0.45 V (Figure 4a) and the lowest overpotential of -202.7 mV to achieve the current density of 10 mA cm^{-2} . The reaction kinetics and mechanism of the as-prepared catalysts can be evaluated based on Tafel slopes determined from the following equation (Equation (4)) [30]:

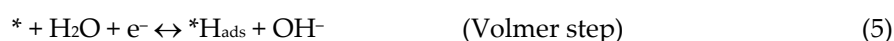
$$\eta = b \cdot \log j/j_0 \quad (4)$$

Table 2. Electrochemical performance of Ni and the deposited Ni_xFe_y coatings for HER in alkaline media.

Sample	E_{onset} , V at $j = -1 \text{ mA cm}^{-2}$	η_{10^*} , mV	Tafel slope, mV dec^{-1}
Ni	-0.1722	-303.4	109.4
Ni ₉₀ Fe ₁₀	-0.1081	-211.9	117.3
Ni ₈₀ Fe ₂₀	-0.0928	-202.7	76.9
Ni ₆₀ Fe ₄₀	-0.2113	-276.3	72.3
Ni ₃₀ Fe ₇₀	-0.1710	-278.4	70.5

* Overpotential at 10 mA cm^{-2} .

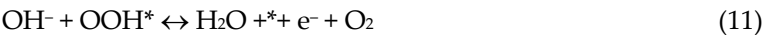
η is the overpotential, b is the Tafel slope, j is the experimental current density, and j_0 is the exchange current density. The plot of η versus $\log j$ represents the Tafel slope. It is widely accepted that HER proceeds by either the Volmer–Heyrovsky or Volmer–Tafel mechanisms, and in alkaline media, it involves three main steps as shown in Equations (5)–(7) [31]:



H_{ads} denotes the H_2 adsorbed to the metal sites, where $*$ represents the metal sites. The theoretical Tafel slopes in the aforementioned reaction steps are 120 mV dec^{-1} , 40 mV dec^{-1} , and 30 mV dec^{-1} , respectively. The corresponding Tafel plots for NiFe catalysts are shown in Figure 4b. The calculated

Tafel slopes were in the range from ca. 70 to 117 mV dec⁻¹, indicating that HER might occur through the Volmer–Heyrovsky mechanism – which is for water molecules or H₂ to adsorb onto an electrode to generate MH_{ads} species. The most promising composition of NiFe is Ni 80 at.% and Fe 20 at.% for efficient HER.

The oxygen evolution reaction in an alkaline medium can be represented by Equations (8)–(11) [32–34]:



where * denotes the electrocatalyst’s adsorption site, similarly, during OER, the adsorbed intermediates are OH*, O*, and OOH*. The first step of the OER process, denoted by Equation (8), is the electrosorption of OH⁻ onto the active sites of the catalyst’s surface. Higher oxidation state metal species are more susceptible to adsorb OH⁻, accelerate the multielectron transportation process, and, hence, can therefore enhance the OER process [32,34]. The data of oxygen evolution measurements on the investigated catalysts are shown in Figure 5 and Table 3. As can be seen from the LSVs recorded on Ni and different Ni_xFe_y catalysts in a 1 M KOH solution, the lower onset and overpotential values at 10 mA cm⁻² were obtained on the Ni_xFe_y catalysts containing a lower content of Ni – 60 and 30 at.% and higher content of iron – 40 and 70 at.% (Figure 5a).

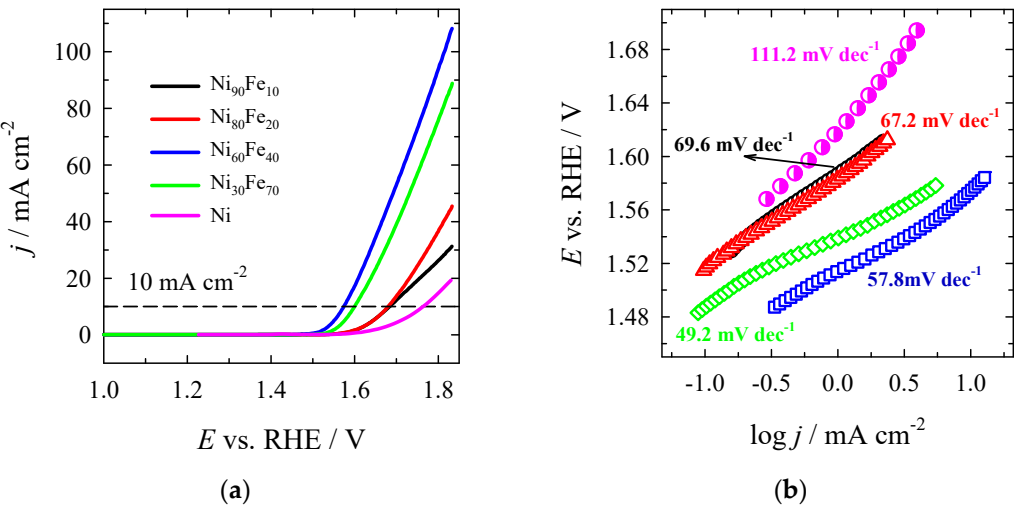


Figure 5. (a) OER polarization curves of Ni, Ni₉₀Fe₁₀, Ni₈₀Fe₂₀, Ni₆₀Fe₄₀, and Ni₃₀Fe₇₀ catalysts in N₂-saturated 1 M KOH solution at a potential scan rate of 2 mV s⁻¹; (b) The corresponding Tafel slopes for each catalyst.

Table 3. Electrochemical performance of Ni and the deposited Ni_xFe_y coatings for OER in alkaline media.

Sample	<i>E</i> _{onset} , V at <i>j</i> = 1 mA cm ⁻²	η _{onset} , mV	<i>E</i> , V at <i>j</i> = 10 mA cm ⁻²	η _{10*} , mV	Tafel slope, mV dec ⁻¹
Ni	1.6163	386.3	1.7621	532.1	111.2
Ni ₉₀ Fe ₁₀	1.5868	356.8	1.6842	454.2	69.6
Ni ₈₀ Fe ₂₀	1.5829	352.9	1.6802	450.2	67.2
Ni ₆₀ Fe ₄₀	1.5162	286.2	1.5747	344.7	57.8
Ni ₃₀ Fe ₇₀	1.5390	309.0	1.5999	369.9	49.2

* Overpotential at 10 mA cm⁻².

The increase of iron content in the Ni_xFe_y coatings results in a higher activity for oxygen evolution as compared with the coatings containing a lower content of iron and a higher content of nickel. The most promising composition of NiFe is Ni 60 at.% and Fe 40 at.% for efficient OER. The current density of 10 mA cm^{-2} was reached at this catalyst with an overpotential of 344.7 mV, indicating superior catalytic activity and favorable OER kinetics. The low Tafel slope values of approximately $49.2\text{--}69.6 \text{ mV dec}^{-1}$ for NiFe catalysts showed that the oxygen evolution proceeds more easily compared with the pure Ni catalyst ($111.2 \text{ mV dec}^{-1}$).

To confirm the bifunctional activity of the developed catalysts for HER and OER in alkaline media, the both cathodic (HER) (Figure 4a) and anodic (OER) (Figure 5a) polarization curves were replotted and are given in Figure 6a.

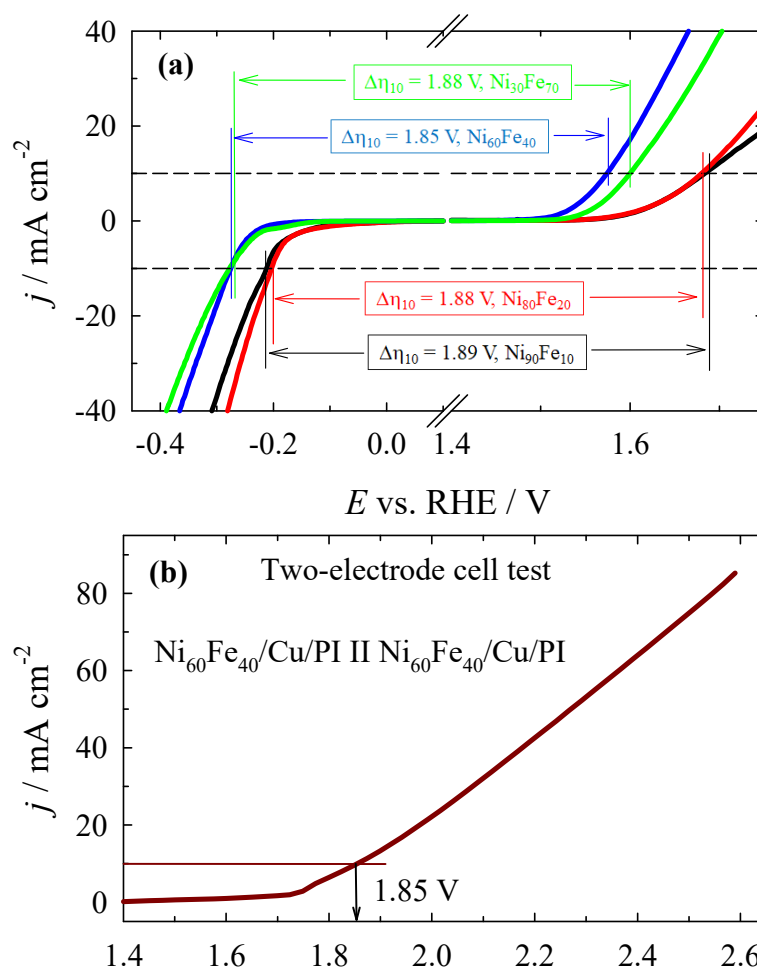


Figure 6. (a) Predicted bifunctional activity of Ni_xFe_y catalysts: values of full-cell potential $\Delta\eta_{10}$ calculated from the difference between overpotential values (η_{10}) at $\pm 10 \text{ mA cm}^{-2}$ obtained from the corresponding HER and OER LSVs in Figures 4a and 5a. (b) LSV curve for $\text{Ni}_{60}\text{Fe}_{40}/\text{Cu}/\text{PI}$ as both anode and cathode electrocatalytic water splitting in 1 M KOH solution.

The potential difference ($\Delta\eta_{10}$) between HER and OER current density of $\pm 10 \text{ mA cm}^{-2}$ ($\eta_{10}^{\text{OER}} - \eta_{10}^{\text{HER}}$) for $\text{Ni}_x\text{Fe}_y/\text{Cu}/\text{PI}$ catalysts represent an expected full-cell potential window. The calculated values of full-cell potential $\Delta\eta_{10}$ delivered from the corresponding HER and OER polarization curves are 1.85 V for $\text{Ni}_{60}\text{Fe}_{40}/\text{Cu}/\text{PI}$, 1.88 V for $\text{Ni}_{30}\text{Fe}_{70}/\text{Cu}/\text{PI}$ and $\text{Ni}_{80}\text{Fe}_{20}/\text{Cu}/\text{PI}$, and 1.89 V for $\text{Ni}_{90}\text{Fe}_{10}/\text{Cu}/\text{PI}$ (Figure 6a). The obtained values suggest the potential application of catalysts for a practical overall water splitting (OWS) device in an alkaline electrolyte, employing the same electrode materials as both the anode and the cathode. The overall catalytic performance in a two-electrode alkaline electrolyzer cell configuration was also carried out by using the same $\text{Ni}_{60}\text{Fe}_{40}/\text{Cu}/\text{PI}$ catalyst as both the anode and the cathode - $\text{Ni}_{60}\text{Fe}_{40}/\text{Cu}/\text{PI} \parallel \text{Ni}_{60}\text{Fe}_{40}/\text{Cu}/\text{PI}$. The developed $\text{Ni}_{60}\text{Fe}_{40}/\text{Cu}/\text{PI}$ electrode exhibit a cell potential of 1.85 V at 10 mA cm^{-2} (Figure 6b) compared to other cell potential

values reported in the literature - Ni-Fe/Cu||Ni-Fe/Cu (1.83 V) [11] and NiO@CNTR||NiO@CNTR (1.81 V) [35] as well as is comparable with the Pt/C||IrO₂ (1.71 V) and Pt/C||Pt/C (1.83 V) [36]. The calculated energy efficiency of the Ni₆₀Fe₄₀/Cu/PI cell is 66.5%. Moreover, the turnover frequency (TOF) is important indicator for the determination of the intrinsic activity of the catalysts. Herein, the TOF values were calculated to evaluate the intrinsic OER performance of the prepared Ni_xFe_y/Cu/PI catalysts at an overpotential of 600 mV. The TOF value of Ni₆₀Fe₄₀/Cu/PI catalyst was observed as 14.9 s⁻¹ at an overpotential of 600 mV, which significantly outperforms that of Ni₃₀Fe₇₀/Cu/PI (9.3 s⁻¹), Ni₉₀Fe₁₀/Cu/PI (1.9 s⁻¹), and Ni₈₀Fe₂₀/Cu/PI (1.8 s⁻¹), indicating high intrinsic properties of this catalyst. The results of our study offer insights into the future design of flexible composite electrocatalysts for sustainable hydrogen production. Furthermore, the suggested strategy allows to produce low-cost, scalable, and self-standing electrocatalysts with efficient water splitting activity and stability.

3. Materials and Methods

3.1. Chemicals

Nickel sulfate (NiSO₄·7H₂O, >98%, Chempur), iron sulfate heptahydrate (FeSO₄·7H₂O, 97%, Chempur), morpholine borane (MB, C₄H₈ONH·BH₃, 97%, Alfa Aesar), glycine (NH₂CH₂COOH, 99%, Chempur), ethylenediaminetetraacetic acid (EDTA, 99%, Reachem), sodium malonate (CH₂(COONa)₂, 97%, Merck), palladium chloride (PdCl₂, 59.5%, Alfa Aesar), copper sulfate pentahydrate (CuSO₄·5H₂O, 98%, Chempur), sulfuric acid (H₂SO₄, 98%, Chempur), polyimide (PI) film of 0.125 mm thickness (DuPont™ Kapton® HN, GoodFellow).

3.2. Electroless Plating of NiFe Coatings on Polyimide Coated with Cu Film

Before electroless plating of NiFe coatings, the PI surface was pre-treated by using adhesion/activation pretreatment procedures as described in detail in refs. [37,38]. The Cu layer was electroplated from CuSO₄ and H₂SO₄ solution at a current density of 1 A dm⁻² for 45 minutes. Then, the NiFe coatings with different contents of Ni and Fe were deposited on the Cu-coated PI surface using the electroless metal plating and morpholine borane as the reducing agent. Figure 6 shows the scheme of the plating process of Ni_xFe_y on Cu/PI.

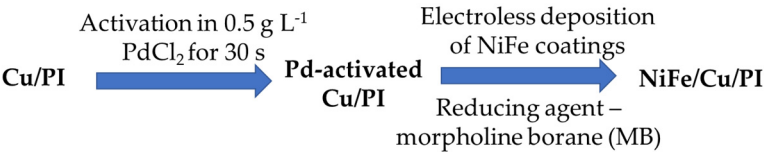


Figure 6. The scheme of the plating process of NiFe on Cu/PI.

Briefly, the Cu/PI surface was activated with Pd²⁺ ions by immersion it in a 0.5 g L⁻¹ PdCl₂ solution for 30 s, then rinsed with deionized water and placed in a freshly prepared electroless plating solution. The composition of the electroless plating solution and the deposition parameters of the coatings are given in Table 4.

Table 4. Composition of the electroless plating solution and plating parameters of NiFe coatings on Cu/PI surface.

Sample	Composition of plating solution, M						Plating conditions		
	NiSO ₄	MB	NH ₂ CH ₂ COOH	FeSO ₄	EDTA	CH ₂ (COONa) ₂	pH	T, °C	t, min
No. 1				0.01					
No. 2	0.14	0.2	0.2	0.005	0.05	0.1	7	60	60
No. 3				0.001					
No.4				0.0005					

In all cases, the pH of the plating solutions was 7 (measured at room temperature). The plating bath was operated at a temperature of 60 °C for 60 min (Table 4). Concentrations of glycine, nickel sulfate, ethylenediaminetetraacetic acid, and sodium malonate were kept constant, whereas the concentration of iron sulfate was different.

3.3. Characterization of Coatings

The composition of the NiFe coatings deposited on the Cu surface was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The Ni and Fe loadings in the coatings were determined using an Optima 7000DV ICP spectrometer (PerkinElmer, Shelton, CT, USA).

The surface morphology of the samples and the distribution of elements were analyzed using a TM4000Plus scanning electron microscope with an AZetecOne detector (Hitachi, Tokyo, Japan).

The XRD patterns of the investigated samples were measured using an X-ray diffractometer D2 PHASER (Bruker, Karlsruhe, Germany). The measurements were performed in the 2θ range of 10–90°.

3.4. Electrochemical Measurements of HER and OER

The performance of the synthesized samples was evaluated using a PGSTAT100 potentiostat/galvanostat (Metrohm Autolab B. V., Utrecht, The Netherlands). A standard three-electrode cell was used, where the working electrode was NiFe/Cu/PI with a geometric surface area of 2 cm². The reference and counter electrodes were Ag/AgCl (3 M KCl) and glassy carbon (GC), respectively. Linear sweep voltammograms (LSVs) were recorded in an N₂-saturated 1 M KOH solution at a scan rate of 2 mV s⁻¹. For comparison, a Ni foam electrode (2 cm²) was used. All reported potential values were referred to the reversible hydrogen electrode (E_{RHE}) according to the following Equation (12):

$$E_{\text{RHE}} = E_{\text{measured}} + 0.059 \cdot \text{pH} + E_{\text{Ag/AgCl (3 M KCl)}} \quad (12)$$

where $E_{\text{Ag/AgCl (3 M KCl)}} = 0.210 \text{ V}$.

The HER and OER current densities presented in this paper have been scaled to the geometric area of the catalysts.

Two-electrode water electrolysis cell was constructed using two the same Ni₆₀Fe₄₀/Cu/PI electrodes as the anode and the cathode. Energy efficiency of the cell was calculated using the following equation:

$$\eta_{\text{electrolyzer}} = E_{\text{th}}/V_{\text{e at } j} \quad (13)$$

where $E_{\text{th}} = 1.23 \text{ V}$; $V_{\text{e at } j}$ is the input voltage required to drive the electrolysis at the current density of interest. The energy efficiency calculated in this study was obtained at $j = 10 \text{ mA cm}^{-2}$.

The turnover frequency (TOF) value was calculated using the following Equation (14) [39]:

$$\text{TOF} = j \times A / 4 \times F \times n \quad (14)$$

where j is the current density at an overpotential of 600 mV, A is the geometric surface area of the electrode, F is the Faraday constant (96,485 C mol⁻¹), 4 is the number of electrons transferred in the OER, and n is the number of moles of all metal ions calculated from the ICP-OES results.

4. Conclusions

In this study, we highlighted a promising strategy to fabricate cost-effective and flexible catalysts for electrochemical water splitting devices. NiFe coatings containing different contents of Ni and Fe have been plated on the flexible copper-coated polyimide surface using the low-cost and straightforward electroless metal plating method and morpholine borane as a reducing agent. It was found that the most promising catalysts for HER and OER are Ni₈₀Fe₂₀/Cu/PI and Ni₆₀Fe₄₀/Cu/PI catalysts, respectively. The Ni₈₀Fe₂₀/Cu/PI catalyst exhibited the lowest overpotential value of -202.7 mV for the HER to obtain a current density of 10 mA cm⁻², while the lowest OER overpotential (344.7

mV) was observed for the Ni₆₀Fe₄₀/Cu/PI catalyst to obtain a current density of 10 mA cm⁻². It was found that a cell potential of 1.85 V at 10 mA cm⁻² was achieved by employing the developed flexible Ni₆₀Fe₄₀/Cu/PI catalyst as the anode and the cathode (Ni₆₀Fe₄₀/Cu/PI || Ni₆₀Fe₄₀/Cu/PI). The exploration of the bifunctional electrocatalysts for overall water splitting by Ni_xFe_y deposited on Cu-coated polyimide provide insights into the future design of composite electrocatalysts for the production of hydrogen via the electrochemical water splitting.

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