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Cu-integrated NiFe nanofoams synthesised by one-step dynamic hydrogen bubble template electrodeposition for enhanced hydrogen evolution in alkaline electrolysis

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Nanostructured foams (nanofoams) can be synthesised by one-step dynamic hydrogen bubble template (DHBT) electrodeposition as sustainable, high-performance, and competitive electrodes for the hydrogen evolution reaction (HER) in alkaline electrolysis (AEL). This work shows the progressive integration of 0.5 to 33% of Cu content in a NiFe (~50/50) framework to produce tri-metallic NiFeCu nanofoams with improved HER activity. The electrochemical HER activity of the nanofoams was studied by linear sweep voltammetry (LSV), Tafel analysis and chronoamperometry (for longevity assessment). The morphology, composition, real surface area and crystalline structure of the nanofoams were characterised by scanning electron microscopy, energy-dispersive spectroscopy, confocal laser scanning microscopy and X-ray diffraction. The NiFe nanofoam without Cu content exhibited overpotentials of -170 and -260 mV at -10 and -50 mA cm⁻², respectively, while the integration of Cu to produce the NiFeCu_{2.0} nanofoam resulted in improved overpotentials of -110 and -180 mV, respectively. After 60 h of continued chronoamperometric ageing, both the NiFe and NiFeCu_{2.0} electrodes exhibited robust longevity under harsh HER conditions, retaining 92% of the electrochemical activity when assessed by potentiodynamic LSV measurement, while the current during the chronoamperometry was approximately 60%. The difference between these two retention figures is thoroughly discussed in relation to resistive and mass-transport phenomena under the sustained hydrogen evolution.

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Introduction

Considering the current landscape of the energy transition, energy demand and consumption are increasing due to population growth and global electrification. Renewables have demonstrated greater resilience than fossil fuels in response to global geopolitical events, which cause fluctuations in worldwide energy demand. However, renewables are inherently intermittent: the energy supply does not correlate linearly with the energy demand. This emphasises the necessity of energy storage and conversion processes capable of maintaining a continuous energy supply. Energy conversion technologies transform the energy surplus into more versatile and practical energy carriers that can be utilised beyond the power grid. Among these, hydrogen production *via* electrolysis stands out as a particularly valuable solution, enabling the storage of excess electricity in a clean, transportable, and flexible form.¹

Over the past few years, hydrogen has experienced consistent growth, with production capacity increasing by approximately 5 Mt of H₂ from 2021 to 2024. Electrolysis contributes only a small share of the total hydrogen production, emphasising the urgent need to decarbonise this industry. Among the diverse electrolysis technologies, alkaline electrolysis (AEL) and proton exchange membrane electrolysis (PEM, also known as polymer electrolyte membrane) stand out with the highest installed capacities, with solid-oxide electrolysis (SOE) representing a less pronounced share. AEL maintains the highest share of deployed electrolysis compared to the other electrolysis technologies, which can be justified by its more flexible scale-up, simpler instrumentation and equipment design, and the use of more economical and abundant materials, resulting in lower costs and the highest market maturity.²

It is necessary to improve and optimise AEL into efficient systems that operate robustly under excess and intermittent renewable energy while being competitive with other electrolysis systems and meeting sustainability objectives.³ The development of novel and highly active electrodes impacts the overall performance of the electrolyser by defining and optimising the kinetics and mechanisms of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Two research

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vectors arise concerning electrode design: the development of high surface area 3D architectures and the integration of differently active transition metals in alloyed or composite electrode compositions to create more favourable mechanistic pathways. These strategies are aimed towards increasing the specific surface area (SSA), which is otherwise unoptimized by the conventional perforated plates used by the AEL industry.⁴ Moreover, this also results in enhanced intrinsic activity of the active material, eliminating the use of scarce precious metals like Pt.⁵

Transition metals are considered an alternative to noble-metal-based catalysts since they are more abundant and less expensive. Ni stands out among catalytic benchmark metals (e.g., Pt, Pd, Au, Ir, and Ru) with its low binding energy for the adsorption of hydrogen atoms onto the catalyst surface.^{6,7} The incorporation of other transition metals into Ni-based frameworks improves the overpotential towards lower absolute values,^{8,9} while simpler Ni electrodes exhibit higher energy demand to kickstart the hydrogen evolution process.¹⁰ In our previous work,¹¹ we reported nanostructured NiFe foams (nanofoams) synthesised by dynamic hydrogen bubble template (DHBT) electrodeposition as improved HER catalysts, with approximately 50% of Ni content replaced by the more abundant and economic Fe, exhibiting a highly porous cauliflower-like nanostructure. The use of DHBT electrodeposition is industrially relevant because of its lower cost and favourable scalability compared with conventional techniques used to produce 3D architectures, such as electrospinning,¹² 3D printing,¹³ surface treatments, and sacrificial templates.^{14,15} These techniques are often overshadowed by the thermodynamically intensive steps and costly sacrificial templates used in the synthesis processes.¹⁶

The ability of some transition metals to form nanofoams by the DHBT process is attributed to their deposition kinetics (reduction rates) and crystalline properties. For example, the reduction rates of Ni, Fe and Cu are more favourable under the intensive cathodic regimes of the HER than those of other metals like Ru and Mo. Therefore, while Ni, Fe and Cu easily deposit alongside the intense hydrogen release that creates the necessary template characteristic of DHBT, Ru and Mo are more prone to form uniform coatings.^{17,18} The crystallography of the metals also plays an important role in determining the formation of nanofoams. For example, metals that possess face-centered cubic (fcc) lattices (like Ni and Fe) often manifest more uniform isotropic growth around hydrogen bubbles.¹⁹ In contrast, metals with body-centered cubic (bcc) lattices (like Mo and W) exhibit anisotropic growth that inhibits pore formation around hydrogen bubbles.²⁰ Both DHBT and HER reactions require electricity to reduce the metallic ions and trigger water electrolysis, respectively. This energy requirement can be met by coupling the synthesis process with renewable energy sources, a popular and well-established integration for systems like AEL.²¹ Therefore, Ni-based electrodes incorporating certain transition metals, like Fe and Cu, represent a sustainable and viable strategy for the development of novel cathodes with the potential for large-scale applications that can only be enabled using low-cost and more abundant materials.

Having established the bi-metallic NiFe framework, while Fe is associated with enhanced charge transfer and stabilisation of intermediates involved in the gas evolution reaction mechanisms, Cu has the potential to improve the conductivity and to restructure the surface of the nanofoam towards enhanced HER.⁹ Cu is an economic metal like Fe, but with enhanced corrosion resistance,²² resulting in high versatility when integrated in multi-metal electrode compositions.²³ The work of Younus *et al.*²⁴ reported tri-metallic Ni-Co-Cu electrodes with superior structural integrity, improved charge transfer and a durability of 95% after 120 h, compared to bi-metallic Ni-Co and pure Cu electrodes. In another study,²⁵ the addition of Cu in Ni-Mo-O_x and Mo-O_x systems was shown to significantly increase the surface area and improve water adsorption by enhancing electrode hydrophilicity. These improvements are associated with the formation of dendritic structures that can potentially increase the surface area of the active material. According to Mehrabi *et al.*,²⁶ these dendrites are readily formed under diffusion-limited electrodeposition conditions, such as those promoted by the DHBT process. This dynamic behaviour of Cu results in coexisting oxidation states (e.g., Cu²⁺ and Cu⁺) in related Cu-containing HER electrodes, which are proposed to provide active sites that tune the hydrogen binding energy and stabilise the catalyst during hydrogen evolution.²⁷ Confirmation of these oxidation states in the NiFeCu nanofoam electrodes reported in this work would require X-ray photoelectron spectroscopy (XPS) outside of the scope of the present characterisation (see the Conclusions section). The incorporation of Cu into multi-metal systems, like the Nb-Ti-Fe-Cu electrodes explored by Xu *et al.*,²⁸ intensifies the coexistence of different Cu phases, rearranging the nanostructure towards optimised adsorption energies of intermediate species of the HER process.

In this work, we explore the progressive integration of Cu into previously reported NiFe nanofoams¹¹ and discuss how the NiFeCu nanofoam can be used to optimize the electrochemical HER activity, highlighting the influence of Cu dendrites on the nanofoam's integrity, morphology and resulting electroactivity.

Materials and methods

Reactants

The deposition electrolytes were prepared from a base of ammonium chloride (NH₄Cl, Sigma-Aldrich, ≥99.5 wt%), citric acid (C₆H₈O₇, Carl Roth, ≥99.0 wt%), nickel chloride (NiCl₂·6H₂O, Carl Roth, ≥98.0 wt%), iron chloride (FeCl₃·6H₂O, Carl Roth, ≥99.0 wt%) and variable compositions of copper chloride (CuCl₂·2H₂O, Carl Roth, ≥99.0 wt%). The electrochemical activity for the HER was assessed in alkaline media prepared with potassium hydroxide (KOH, Carl Roth, ≥85.0 wt%).

Electrode synthesis

The synthesis was conducted in an electrochemical cell assembled with a 3D stainless steel (SS) substrate as the cathode and a Pt plate as the anode. The substrate and Pt electrodes were connected to an energy source (BX PRECISION® model 1688B). Different depositions were conducted under

Table 1 Ratio of Ni, Fe and Cu in the prepared electrolytes for nanofoam deposition

Electrode	% Ni	% Fe	% Cu
NiFe	60.0	40.0	0.0
NiFeCu _{0.5}	59.7	39.8	0.5
NiFeCu _{1.0}	59.4	39.6	1.0
NiFeCu _{1.5}	59.1	39.4	1.5
NiFeCu _{2.0}	58.8	39.2	2.0
NiFeCu _{5.0}	57.0	38.0	5.0
NiFeCu ₁₀	54.0	36.0	10.0
NiFeCu ₂₀	48.0	32.0	20.0
NiFeCu ₃₃	40.2	26.8	33.0

galvanostatic conditions of -1.0 A cm^{-2} , using a geometric deposition area of 1.54 cm^2 and a deposition duration of 50 s. The NiFeCu nanofoams were identified by the percentage of Cu in their respective deposition electrolyte as NiFeCu_{%Cu}. For example, NiFeCu₂₀ refers to the NiFeCu nanofoam produced using a deposition electrolyte containing 20% Cu of the total metal composition, with the remaining 80% being divided between Ni (60%) and Fe (40%). Because Cu deposits much faster than Ni and Fe,²⁹ the initial nanofoams were made with very small amounts of Cu in the electrolyte. Then, the Cu percentage was gradually increased up to 33% to reach a 1 : 1 : 1 ratio of Ni, Fe and Cu in the deposition electrolyte. The following Cu concentrations were prepared: 0.5, 1.0, 1.5, 2.0, 5.0, 10, 20 and 33% Cu, resulting in the following electrodes: NiFeCu_{0.5}, NiFeCu_{1.0}, NiFeCu_{1.5}, NiFeCu_{2.0}, NiFeCu_{5.0}, NiFeCu₁₀, NiFeCu₂₀, and NiFeCu₃₃, respectively. Table 1 provides the nominal atomic ratio of Ni, Fe and Cu for each of the prepared deposition electrolytes.

Electrochemical tests

All electrochemical tests were conducted with a potentiostat (Gamry Interface 1000 Potentiostat/Galvanostat/ZRA, Gamry Instruments). Linear sweep voltammetry (LSV) and chronoamperometry (CA) studies were performed at room temperature and pressure in alkaline media of 30 wt% KOH (pH = 14.7). The presented LSV plots were not corrected for iR drop. LSV tests were performed at a scan rate of 1 mV s^{-1} from the OCP to $-1.4 \text{ V vs. Hg/HgO}$ and later converted to the reversible hydrogen electrode (RHE) reference according to eqn (1). CA tests were performed at $-1.4 \text{ V vs. Hg/HgO}$ for 60 h (uninterrupted), to assess the longevity of the electrodes for the HER, respectively.

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \text{ V} + 0.059 \times \text{pH} \quad (1)$$

Tafel analysis

An analytical treatment of the LSV plots grounded on the Tafel analysis was conducted to determine key electrochemical parameters for comparison and assessment of the HER activity. A standardised algorithm was applied to the LSV plots of all samples and an illustrative example is available in Fig. S1 of the SI, alongside a theoretical explanation of the mathematical

determination of the Tafel slope and the HER onset. The primary parameters determined by the Tafel analysis are as follows:

- η_{10} – overpotential [V] at -10 mA cm^{-2} .
- η_{50} – overpotential [V] at -50 mA cm^{-2} .
- b – Tafel slope [mV dec^{-1}].
- j_0 – exchange current density [mA cm^{-2}].
- R_{ω} – resistance at high current densities [Ω].
- n_e – number of exchanged electrons during the HER.

R_{ω} is a practical parameter derived from the linearity ruled by Ohm's law, as adapted in eqn (2), where the current (I [A]) and the potential establish the slope of the LSV in the high-current region of the plot.

$$I = \frac{E}{R_{\omega}} \quad (2)$$

n_e is determined from the standard relation of the Tafel slope given by eqn (3).

$$b = \frac{2.303RT}{\alpha n_e F} \quad (3)$$

where α is the charge-transfer coefficient of 0.5 and F is Faraday's constant of 96485 C mol^{-1} .

Physico-chemical characterisation

The morphology and pore distribution of the electrodes were characterised by optical microscopy (Leica DM 2700 M from Leica Microsystems) and scanning electron microscopy (SEM) (Phenom Desktop SEM from Thermo Fisher Scientific). The chemical composition of the synthesised electrodes was also identified and quantified by energy-dispersive spectroscopy (EDS) coupled with SEM. The presence of dissolved metals in test electrolytes was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

To identify structural and crystalline properties of the electrodes, X-ray diffraction (XRD) was performed using a Bruker D8 ADVANCE diffractometer equipped with a LYNXEYE XE-T detector operating in 1D mode and a Cu $K\alpha$ radiation source of $1.5418 \text{ \AA}$. The instrument operated in a 2θ range of 10 to 80° with a step size of 0.02° and a duration of 10 s per step.

Confocal laser scanning microscopy (CLSM) (broadband confocal Leica TCS SP5 from Leica Microsystems) was used in this work to determine the real surface area of the NiFe and the NiFeCu_{2.0} nanofoams. A helium–neon (HeNe) laser was used for measurements at a visible light wavelength of 633 nm (red light) at 15% of the total intensity of the laser, with the samples immersed in water (refractive index, n_i of 1.33). All CLSM images were processed with the LAS X Office software from Leica Microsystems and Fiji open-source software and are made available in the SI.

Results and discussion

Morphological analysis by SEM

Low concentrations of Cu in the deposition electrolyte resulted in the cauliflower-like porous nanostructures, which were the subject of study in our previous work.¹¹ The formation of the

cauliflower structure is particularly predominant for the NiFeCu_{0.5} and NiFeCu_{1.0} nanofoams (Fig. 1b and c) suggesting that, under these conditions, the Cu percentage provided in the deposition electrolyte was not sufficient to change the morphology of the NiFe nanofoams. It is important to note that the pore distribution of the NiFeCu_{0.5} and NiFeCu_{1.0} electrodes reveals a higher scarcity of pores in comparison to bi-metallic nanofoams. On the other hand, the NiFeCu_{1.5} nanofoam (Fig. 1d) shows novel dendritic-like structures piercing out from the surface of the nanofoam, while the inner region of the pores retains the cauliflower structure. This dendritic trend is further intensified for the NiFeCu_{2.0} electrode (Fig. 1e) covering the entirety of the outer regions of the nanofoam (unlike the dendrites of NiFeCu_{1.5}) and diverging in further ramifications along the axis of the dendrites, like pine trees. The dendritic structure occurs due to diffusion-limited aggregation, a deposition phenomenon (and model) that occurs when Cu is deposited faster than it can diffuse from the bulk deposition electrolyte. Consequently, Cu forms a protrusion on the substrate surface that favours the further deposition of Cu on-site instead of the surroundings of the protrusion, causing a needle-like structure that ultimately achieves a crystallinity threshold and forms a dendrite. The work of Yang *et al.*³⁰ comprehensively explained the growth dynamics of Cu, delving into the simulation of the diffusion-limited aggregation model and establishing a dependence between dendrite growth and the concentration of Cu ions in the deposition electrolyte. This characteristic dendritic growth of Cu was the target of the work of Ferreira *et al.*³¹ where the dendritic growth dynamics were guided by myelin surfactant assemblies. The NiFeCu_{2.0} electrode also highlights larger pores when compared to the electrodes produced with 0.5 to 1.5% Cu, attributed to growth expansion caused by the dendrites.

Furthermore, increasing Cu content resulted in the extensive growth of the dendrites, completely covering the inner and outer regions of the pores. Fig. 1f shows the NiFeCu_{5.0} nanofoam, revealing a forest-like distribution of the dendritic structures observed for the other NiFeCu nanofoams, a morphology that prevails for 10% Cu content and exhibits denser and less organised dendritic structures, which overshadow the porous surface with the bulk formation of the active material (Fig. 1h and i).

Chemical composition analysis by EDS

EDS analysis was performed to confirm that the formation of the tri-metallic nanofoams was successful and consistent with the % Cu content of the deposition electrolytes. The homogeneity of NiFe was a subject of study in our previous work on the optimisation of NiFe nanofoams,¹¹ while the homogeneity of the NiFeCu nanofoams can be observed in Fig. S4 and S5. The available EDS maps indicate homogeneous tri-metallic distributions across the detection areas. The detected contents of Ni, Fe and Cu are presented in Fig. 2, where a comparison with the 50/50 composition of the previously produced NiFe nanofoam is also presented.

As observed, the NiFeCu nanofoams synthesised with 0.5 to 1.5% Cu content effectively resulted in an average deposited Cu content of 5.7%. The amount of deposited Cu continues to increase up to a maximum of 53.5%, surpassing Ni and Fe, individually. Fig. 2 also shows the variation of the Ni : Fe ratio with increasing Cu content, as small amounts of Cu are shown to favour deposition of Ni compared to Fe, returning to the near 50/50 ratio for the NiFeCu_{2.0} electrode (Ni : Fe = 0.97) and then decreasing substantially for the highest Cu concentrations, maintaining an average ratio of 0.54. This indicates that the electrodeposition of Fe becomes more favourable than that of

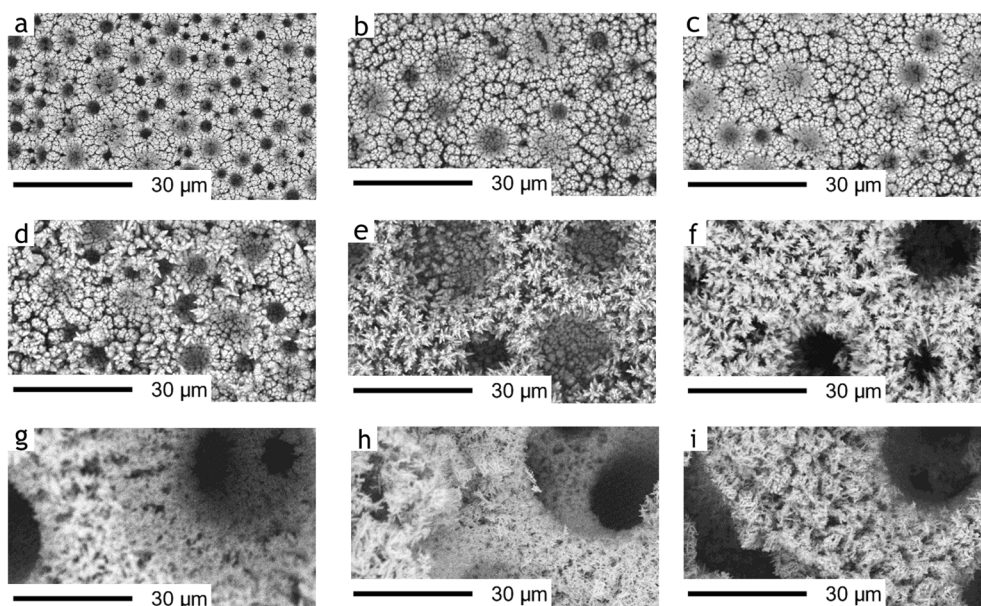


Fig. 1 SEM images of the (a) NiFe, (b) NiFeCu_{0.5}, (c) NiFeCu_{1.0}, (d) NiFeCu_{1.5}, (e) NiFeCu_{2.0}, (f) NiFeCu_{5.0}, (g) NiFeCu₁₀, (h) NiFeCu₂₀ and (i) NiFeCu₃₃ nanofoams.

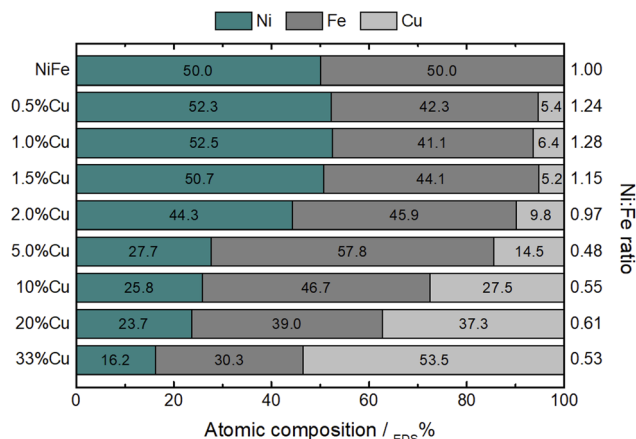
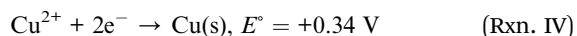
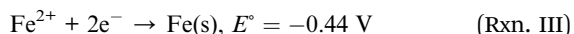
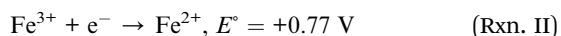
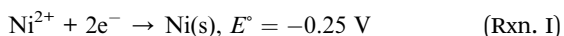
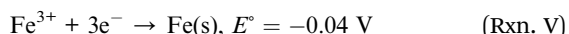


Fig. 2 EDS chemical composition of NiFeCu nanofoams and respective Ni : Fe ratios.

Ni when Cu content increases past a $\sim 5\%$ Cu threshold. The behaviour of this electrodeposited ternary system can be explained by the thermodynamic and kinetic properties of Ni, Fe and Cu, and the operating conditions of the DHBT electrodeposition. DHBT electrodeposition requires highly negative potentials to enable hydrogen evolution, which heavily impacts the deposition behaviour of the metals. Considering the standard potentials (E°) [V] of the metals (Ni(II), Fe(III) and Cu(II)), the following reactions occur:



(Rxn. I) to (Rxn. IV) represent the individual deposition steps for each metal, with iron having an extra step ((Rxn. II) and (Rxn. III)) due to its additional oxidation state. The overall reaction from Fe(III) to Fe(s) is defined by (Rxn. V).



According to the respective E° of the metals, Cu should be the metal that deposits at a higher rate, followed by Fe, and then by Ni. Fe is also prone to form hydroxides before depositing in its metallic form,³² but due to the acidic pH of the deposition electrolyte (promoted by the addition of citric acid as a complexing agent) and the highly cathodic regime of electrodeposition by DHBT, Fe is expected to deposit favourably in comparison to Ni.³³ Regarding the favourable deposition of Fe over Ni with increasing Cu content (*i.e.*, EDS results, Fig. 2), this phenomenon could be attributed to the crystalline synergy between Fe and Cu that competes with Ni deposition and alters the morphological properties of the ternary material (*e.g.*, grain structure).³⁴

Crystalline structure by XRD

XRD analysis (Fig. 3) was performed on the selected cathodes to assess the influence of Cu-integration on the NiFe framework.

As observed in Fig. 3, the diffraction patterns of NiFe and NiFeCu_{2.0} highlight a similar structural framework, with subtle differences induced by the integration of Cu. The XRD pattern for NiFe revealed diffraction peaks at 2θ values of 15.6° , 44.2° , 50.9° (with a shoulder at 51.5°) and 74.7° , corresponding to the Miller indices (hkl) of (003), (111), (200) and (220), respectively. The (003) index is consistent with NiFe LDH basal planes,^{35,36} while the other indices represent the non-basal reflections of an fcc structure, often attributed to Ni and Ni-rich alloys.^{37,38} NiFeCu_{2.0} reveals diffraction peaks at 2θ values of 14.0° , 43.9° , 50.9° and 74.6° , corresponding to the same (hkl) indices determined for the NiFe nanofoam. NiFeCu_{2.0} highlights diffraction peaks slightly shifted towards lower angles, associated with the Cu incorporation into the NiFe fcc structure which causes lattice expansion while maintaining the poor crystallinity observed. Using Bragg's law applied to the (111) index, the lattice parameters of the NiFe nanofoam were determined to be $a = 3.549 \text{ \AA}$ and $a = 3.572 \text{ \AA}$ for the NiFeCu_{2.0} electrode, corresponding to a lattice expansion of $+0.023 \text{ \AA}$ (approximately $+0.65\%$), supporting the earlier peak-shift observations. The coexistence of fcc and amorphous scaffolds agrees with the defect-rich structure common to materials electrodeposited *via* DHBT.³⁹

Electrochemical activity and Tafel analysis

Fig. 4a and b present the LSV and Tafel plots of the NiFeCu electrodes, alongside the activity of the NiFe electrode (previously assessed for DHBT electrodeposition in 2D plates¹¹) to assess the electrochemical influence of Cu content on the HER. A clear enhancement in HER activity is shown in the LSV plots, with more negative j achieved as Cu percentage increases, as seen in Fig. 4a. This trend is followed throughout the NiFeCu electrodes up to NiFeCu₁₀, with the following electrodes showcasing nuanced performances that indicate a threshold of Cu's electrochemical contribution. The Tafel slopes, observed in

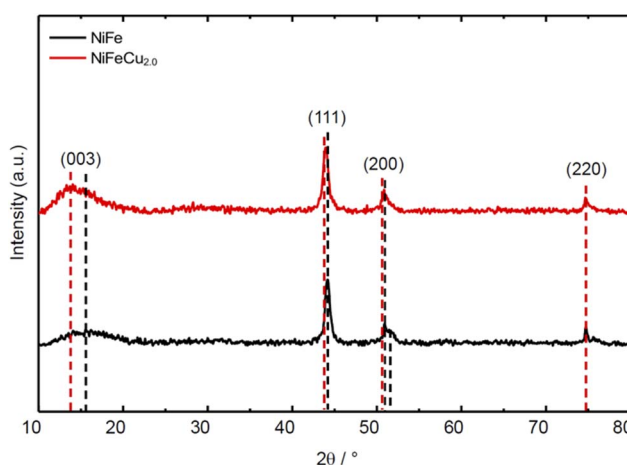


Fig. 3 XRD patterns of NiFe and NiFeCu_{2.0} nanofoams.

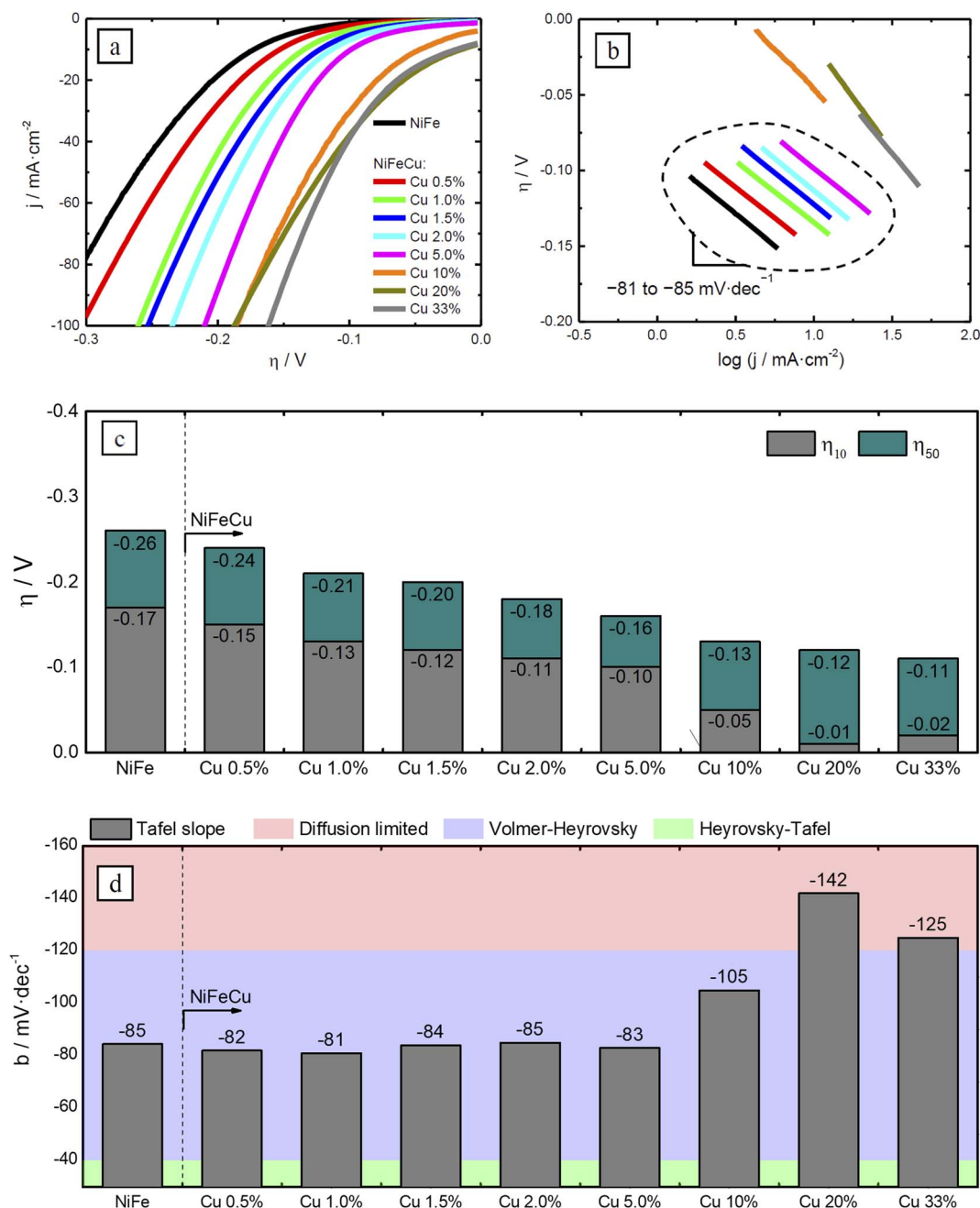


Fig. 4 Electrochemical data of the NiFe and NiFeCu electrodes: (a) LSV plots and (b) respective Tafel slopes; (c) overpotentials; and (d) b values.

Fig. 4b, highlight electrodes of similar HER mechanisms for all electrodes, given the near-parallel behaviour of the slopes. Coherent with the previous observations from the LSV plots, the Tafel plots present distinct results for NiFeCu electrodes produced between 10% and 33% Cu, highlighting steeper slopes. Fig. 4c presents the data concerning the η under referenced conditions. Both $|\eta_{10}|$ and $|\eta_{50}|$ values decreased with increasing Cu integration, with the trend becoming less straightforward for the nanofoams at Cu content between 10 and 33%.

The values of b presented in Fig. 4d show that the HER mechanisms are seemingly retained despite the addition of Cu,

with an average $|b|$ value of $\approx 83 \text{ mV dec}^{-1}$, similar to that of NiFe ($|b| = 85 \text{ mV dec}^{-1}$) indicating a similar HER. This behaviour only changes for the NiFeCu₁₀ electrode, highlighting a degradation of around 20 mV dec^{-1} , while retaining a Volmer-Heyrovsky limited HER. However, the NiFeCu₂₀ and NiFeCu₃₃ electrodes present worse slopes, surpassing Volmer step's -120 mV dec^{-1} threshold and changing the reaction mechanism to diffusion-limited HER. It is also to be noted that the nanofoams produced with 10 and 33% Cu display small cathodic currents detected near 0 V vs. RHE. These currents are likely attributable to uncompensated resistance and capacitive/double-layer effects typically persistent in high surface area and highly

porous electrodes,^{40,41} which, for the stated Cu content where this was observed, are consistent with the bulkier morphologies detected for these nanofoams. Fig. 5a–c present additional electrochemical results derived from the Tafel analysis, namely the values of j_0 , R_w and n_e for all nanofoams.

Fig. 5a shows that the j_0 values maintain the order of magnitude shown for the NiFe electrode (0.10 mA cm^{-2}), with a maximum achieved by NiFeCu₂₀ (7.7 mA cm^{-2}). In addition to the increase in j_0 with Cu content, the NiFeCu nanofoams present smaller values of R_w (Fig. 5b) compared to NiFe and slightly decreasing values of n_e (Fig. 5c). This trend reflects the role of Cu in improving the conductivity of the tri-metallic nanofoams, which is associated with Cu donating electrons to Ni and Fe, thereby facilitating the adsorption/desorption

processes they promote,⁴² while higher Cu content yields a decrease of exchanged electrons. Thus, Cu acts as a facilitator for the HER, enhancing activity rates of Fe and Ni; however, at higher Cu yields, its own poor water-dissociation and hydrogen-adsorption kinetics dominate the process⁴³ and overshadow the Ni-Fe activity, hindering the overall HER performance. This supports the argument that moderate Cu incorporation exhibits a clear improvement of the electrical yield of the electrodes (lower $|\eta|$ and R_w and higher j_0), whereas higher amounts of Cu, particularly in the range of 10% to 33% Cu, are detrimental to the HER charge transfer efficiency (higher $|b|$ and lower n_e).

This electrochemical analysis can be correlated with and supported by previous SEM and EDS results. The SEM images of NiFeCu electrodes (Fig. 1a–i) evidenced the formation of bulkier

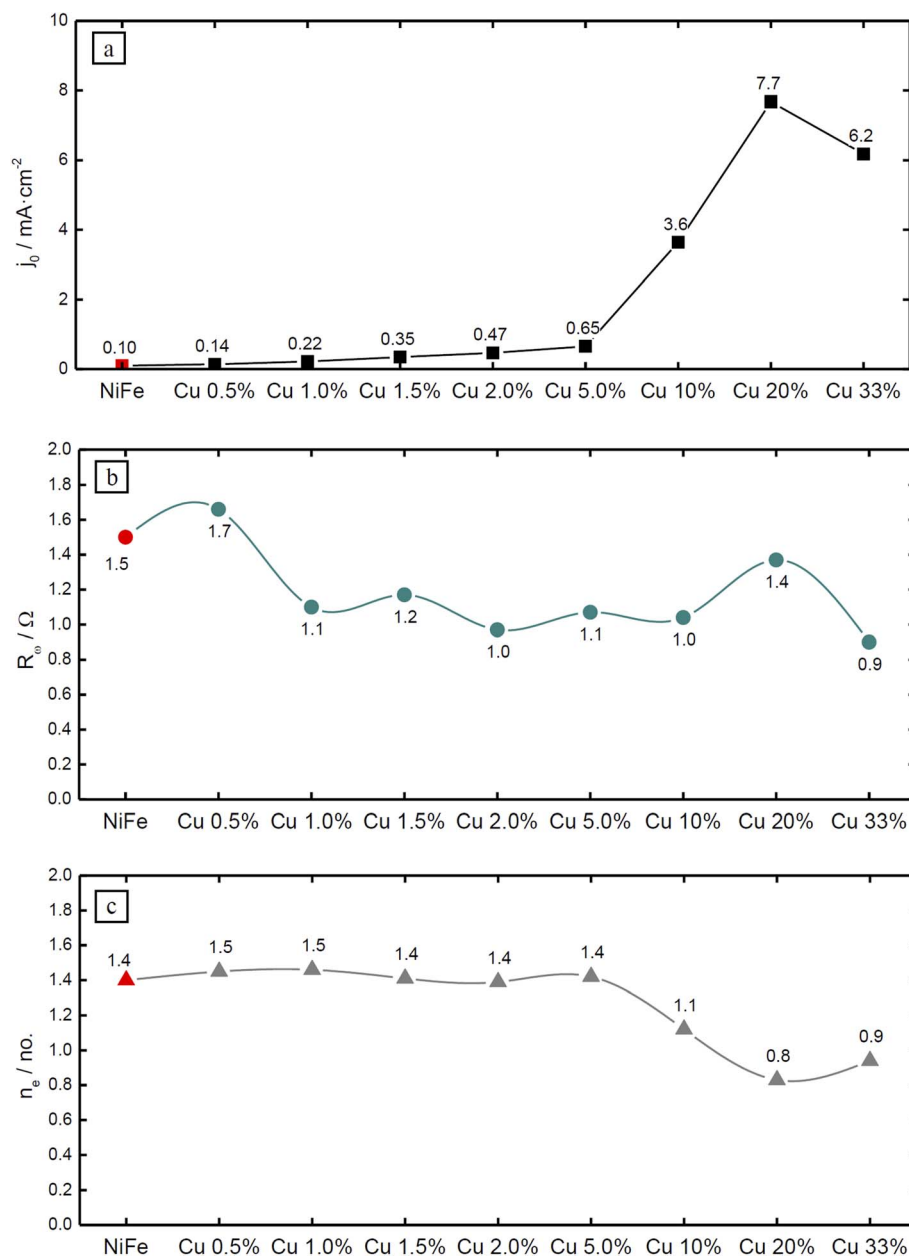


Fig. 5 Electrochemical data of the NiFeCu nanofoams: (a) j_0 , (b) R_w and (c) n_e .

nanofoms for 10% to 33% Cu, suggesting that the incorporation of high Cu contents in the NiFe framework may have caused a detrimental influence on the morphology of the nanofoms, resulting in the loss of active sites and the formation of less active Cu phases.⁴⁴ These results reveal the significance of lower Cu content (0.5% to 5.0%) in improving the electrochemical HER activity while maintaining structural stability, compared to higher Cu contents.

The NiFeCu_{2.0} electrode (Fig. 1e) defines the threshold of Ni : Fe ratio stability (Fig. 2), ensuring a limit to the reproducible deposition of the already established bi-metallic structure while introducing promising electrochemical improvements without the degradation of the electroactivity associated with higher Cu yields. This marks a shift in the deposition behaviour of the NiFe framework which, accompanied by the electrochemical observations highlighted by Fig. 4d (retention of the -85 mV dec^{-1} Tafel slope), makes NiFeCu_{2.0} the most attractive candidate for further study. The NiFeCu_{2.0} nanofoam also exhibited a remarkable improvement in HER activity when compared to the NiFe nanofoam, as seen in Table 2.

The NiFeCu_{2.0} nanofoam improved the overpotentials by 60 mV for η_{10} and 80 mV for η_{50} , all compared to the NiFe nanofoam. The Tafel slope was retained at -85 mV dec^{-1} , therefore preserving the Volmer–Heyrovsky mechanism. Other performance metrics were also improved with the use of 2% Cu: a fivefold increase in j_0 , the retention of n_e , and the improvement of R_w . This electrochemical improvement is consistent with a 78% increase in the real surface area of NiFeCu_{2.0} relative to the NiFe nanofoam, as determined by CLSM (Fig. S2 and S3). Therefore, the surface-area expansion induced by dendritic Cu incorporation provides an extrinsic improvement alongside the intrinsic improvements discussed above.

Table 3 compares the η_{10} and b results of NiFeCu_{2.0} with the reported values for the state-of-the-art cathodes based on transition metals (same family as the NiFeCu_{2.0} nanofoams) and noble metals (ultimate HER benchmarks). Based on the surface analysis and the electrochemical studies, the novel NiFeCu_{2.0} nanofoam delivered promising results for its application as a functional HER cathode. This comparison therefore indicates competitive activity among the reported literature presented. However, direct ranking is limited by differences in electrolyte used, temperature, substrate type and scan rates.

These findings, based on surface and electrochemical analysis, establish the NiFeCu_{2.0} nanofoam as a successful optimisation result derived from the NiFe framework, revealing that small quantities of Cu introduced into the deposition electrolyte can lead to a remarkable improvement of electrode activity

Table 3 Comparison of NiFe and NiFeCu_{2.0} with state-of-the-art cathodes

Electrode	η_{10}/V	$b/\text{mV dec}^{-1}$	References
NiFe	−0.17	−85	This work
NiFeCu	−0.11	−85	This work
NiPS ₃	−0.41	−103	45
Ni foam	−0.22	−130	46
MnCoNiO _x	−0.20	−114	8
Cu–Ni ₃ S ₂ /Ni	−0.19	−87	47
Co/WC/NC	−0.18	−98	48
IrNPs	−0.12	−32	45
Pd/CeO ₂ /N	−0.08	−44	49
PtRu/CNT	−0.05	−48	49
Pt/C	−0.05	−37	50

for the HER. NiFeCu_{2.0} was selected for further characterisation by longevity studies.

Longevity study

The electrochemical activity of NiFe and NiFeCu for the HER process was determined before and after the CA test, as shown in Fig. 6a. The LSV and Tafel plots are depicted in Fig. 6b and c, respectively. From these plots, both overpotentials (Fig. 6d) and b values (Fig. 6e) were determined.

The ageing by CA (Fig. 6a) shows a progressive degradation of the current over the duration of the test. As observed for the NiFe nanofoam, the initial high-current response of -125 mA cm^{-2} decreased to -90 mA cm^{-2} in the first 2 h. Following this decline, it increased to -115 mA cm^{-2} and then ultimately decreased to -75 mA cm^{-2} at the end of the CA, suggesting dynamic participation of active sites facing bubble accumulation or surface transformation. According to the CA results, the NiFe electrode exhibited around 60% retention. The NiFeCu_{2.0} nanofoam revealed a similar retention of 61%. Nevertheless, at the end of ageing, NiFeCu exhibited a final j higher than that of NiFe, retaining its superiority in current yield. It is important to note that at the end of the ageing test, part of the NiFe and NiFeCu_{2.0} electrodes were noticeably uncovered by the electrolyte. This was due to experimental limitations, which did not include electrolyte regeneration during the test, which resulted in the intensive HER process to evaporate the electrolyte due to the Joule effect⁵¹ and, consequently, expose part of the electrode surface. As the measured current is proportional to the electrode area actively participating in the reactions, a reduction of the submerged area will provoke a reduction in the measured

Table 2 Electrochemical data of the NiFe and NiFeCu_{2.0} nanofoams^a

Electrode	η_{10}/V	η_{50}/V	$b/\text{mV dec}^{-1}$	$j_0/\text{mA cm}^{-2}$	R_w/Ω	$n_e/\text{no.}$
NiFe	-0.17 ± 0.01	-0.26 ± 0.01	-85 ± 3	0.10 ± 0.01	1.5 ± 0.1	1.4 ± 0.0
NiFeCu _{2.0}	-0.11 ± 0.01	-0.18 ± 0.01	-85 ± 7	0.47 ± 0.34	1.0 ± 0.1	1.4 ± 0.1

^a Reported measurements performed in triplicate ($n = 3$) for NiFe and NiFeCu_{2.0} to assess nanofoam reproducibility. Values are reported as mean $\pm$ standard deviation. Remaining compositions (0.5 to 33% Cu, excluding 2% Cu) represent single depositions.

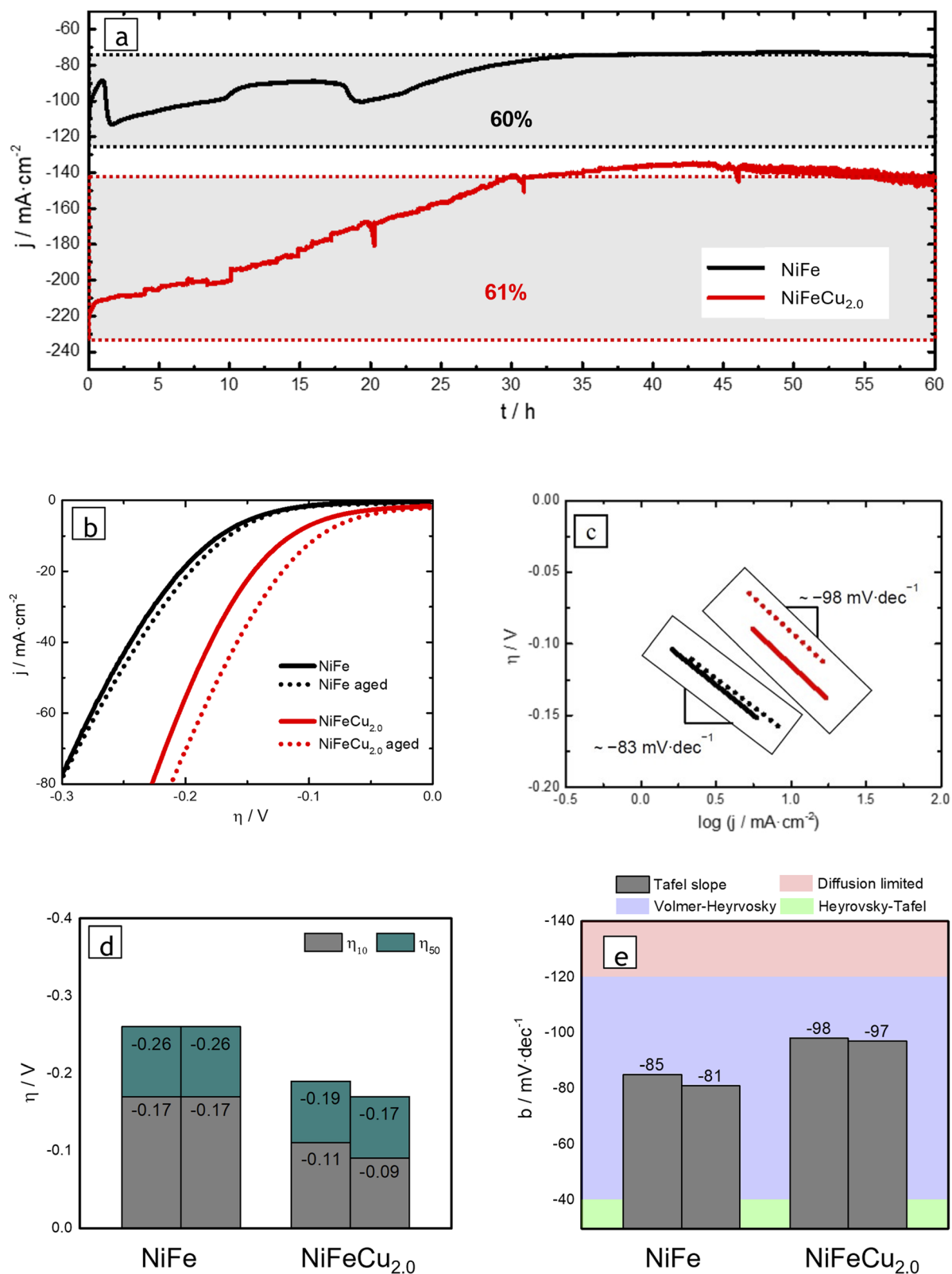


Fig. 6 Electrochemical data of NiFe and NiFeCu electrodes before and after (a) 60 h of the CA test; (b) LSV plots and (c) respective Tafel slopes; (d) overpotentials; and (e) b values.

current during the CA test.⁵² This limitation was addressed by normalising the CA curves to a gradual surface-area decrease from the area submerged at the start of the CA to the surface

area effectively submerged at its end. Specifically, the submerged area was measured before and after the 60 h test with the currents pertinently rescaled, assuming a linear and

time-proportional decrease across the CA test. Considering the fact that the submerged area was not monitored continuously across the test, the correction is to be regarded as a first-order approximation. The curves presented in Fig. 6a show the corrected current retained over time.

While Fig. 6a demonstrates hydrogen evolution hindered by the degradation of the cathode activity, the LSVs obtained for fresh and aged NiFe and NiFeCu electrodes (Fig. 6b) present a positive evolution, indicating *in situ* activation further supported by the near-parallel Tafel plots (Fig. 6c). The results presented in Fig. 6d show unchanged overpotentials for NiFe and an improvement of around 20 mV for NiFeCu. The *b* values (Fig. 6e) demonstrate a significant retention of the reaction mechanism, with residual improvements for both electrodes (Δb of 4 and 1 mV dec⁻¹). Table 4 shows the *j* values measured by CA and LSV, at the start and the end of ageing tests and the respective losses.

As evidenced in Table 4, the *j* values retrieved by CA and LSV measurements have distinct differences, with significantly greater degradation observed in CA (~40% *j* loss) compared to LSV (~8% *j* loss), while also highlighting that both electrodes exhibit identical activity loss in the same measurement mode. This comparison demonstrates that potentiostatic measurements induce greater activity deterioration than potentiodynamic conditions. It is well reported that prolonged operation at a fixed potential accelerates resistance-inducing mechanisms like the accumulation of hydrogen bubbles and electrode-electrolyte surface saturation.^{53,54} In contrast, these effects are significantly mitigated during LSV where the measurement potential is reached more briefly and dynamically. Therefore,

while a CA test is a reliable ageing procedure for simulating operating conditions near-identical to a real industrial AEL setting, it does not provide accurate information concerning the true catalytic state of the aged electrode. Bubble accumulation and electrolyte saturation are phenomena that occur at the long-term steady-state of CA and overshadow a considerable portion of *j* due to their highly resistive nature.⁵⁵ The contribution of these resistive phenomena was estimated to be approximately ~32% (difference between CA and LSV loss in Table 4, which isolates non-catalytic degradation), meaning that around a third of the degraded HER activity of the electrode is not associated with catalytic degradation. This figure should be regarded as an order-of-magnitude estimate instead of a precise separation, considering that the approximation assumes that the catalytic and mass-transport contributions are additive and independent, simplifications that could be potentially deconvoluted and validated by techniques such as electrochemical impedance spectroscopy (EIS).

This inference of 32% is supported by the similar values of *j* at the start of the CA and the LSV plots for NiFe (−127 and −145 mA cm⁻², respectively) and for NiFeCu_{2.0} (−233 and −249 mA cm⁻², respectively), which indicate comparable intrinsic activity at the start of ageing followed by a greater discrepancy of final *j* values, the latter attributed to a contribution from non-catalytic effects (around 32%). These observations could be further strengthened by performing CA with forced convection (*e.g.*, using a rotating disk electrode) or conducting intermittent forced bubble clearing during the test. Therefore, according to the LSV results (Table 4), both electrodes exhibit a retention of 92%. Concerning the effect of Cu in the NiFe framework, the results suggest that its integration had no negative impact on the longevity of the electrode. A comparison of the NiFe and NiFeCu electrodes with the reported literature is presented in Table 5.

The electrodes reported in this work are well placed within the upper echelon of reported durability results among transition-metal-based electrodes and their composites. As observed in Table 5, ageing studies commonly take place in a reference electrolyte of 1 M KOH. Conversely, NiFe and NiFeCu_{2.0} were tested under harsher conditions, subject to HER duration (60 h) in very alkaline electrolyte (KOH 30 wt%, ~6 M), which is a more conventional electrolyte concentration in the industrial AEL

Table 4 Values of *j* at −1.4 V vs. Hg/HgO at the start/end of CA and LSV tests

Electrode	<i>j</i> /mA cm ⁻² by CA at −1.4 V ^a			<i>j</i> /mA cm ⁻² by LSV at −1.4 V ^a		
	Before	After	Loss	Before	After	Loss
NiFe	−127	−74.9	−41%	−145	−133	−8.3%
NiFeCu _{2.0}	−233	−141	−40%	−249	−229	−8.0%

^a Potential measured vs. the Hg/HgO reference electrode.

Table 5 Comparison of longevity results with the reported HER literature

Electrode	Electrolyte	Ageing	Retention ^a /%	References
NiFe	KOH 30 wt%	CA, 60 h	92 ^b	This work
NiFeCu _{2.0}	KOH 30 wt%	CA, 60 h	92 ^b	This work
NiMoS ₂ /Ni/MoS ₂	1 M KOH	CA, 150 h	95	56
NiS ₂ /MoS ₂ -CeO ₂ /LDH	1 M KOH	CA, 160 h	95	57
Pt-NiFeO _x H _y /NiFe-LDH	1 M KOH	CA, 24 h	73	58
Ru-O-Mo/Ru/MoO ₂	1 M KOH	CP, 40 h	>95	59
S-Co ₂ P	1 M KOH	CA, 20 h	>95	60
N-NiCoP _x	1 M KOH	CA, 100 h	94	60

^a Some retention values are estimated based on reported current/potential results over the test range of the respective article. Retentions shown as “>95%” represent studies that claimed negligible, minimal and residual activity losses without retention quantification. ^b Post-ageing current retention was determined by LSV measurements before and after CA ageing.

Table 6 Electrochemical HER data of the cathodes before and after ageing

Electrode	$j_0/\text{mA cm}^{-2}$	R_{ω}/Ω	$n_e/\text{no.}$
NiFe	0.095	1.6	1.4
NiFe aged	0.092	2.1	1.5
NiFeCu	0.68	1.3	1.2
NiFeCu _{2.0} aged	1.1	1.6	1.2

setting. Though full comparative parity with the referenced literature is not possible due to the wide variety of operating conditions used within the field, some industrially interesting variables associated with the more realistic KOH concentration may have influenced the longevity study, such as the increased electrolyte viscosity, bubble diffusion dynamics and impact of greater ionic conductivity. Industrial benchmarks are also reported in longevity studies that last a few thousands of hours (1000 to 6000 h) and operate at very high j values (300 to 1000 mA cm^{-2}), usually in intermediate scaled-up testing setups.^{61,62}

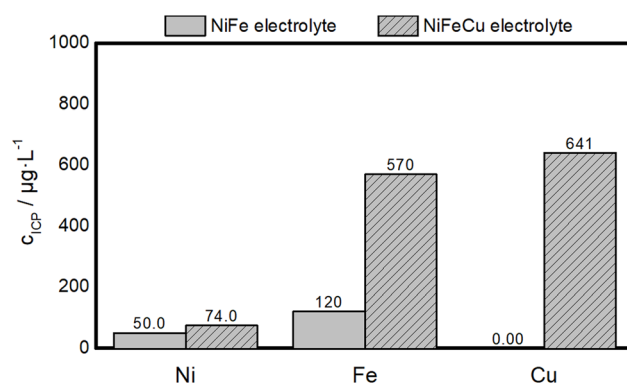
The stability of the NiFe and NiFeCu_{2.0} electrodes was further analysed using additional electrochemical activity results (j_0 , R_{ω} , and n_e), presented in Table 6, before and after ageing.

As supported by Table 6, the long-term stability of the NiFe nanofoam is demonstrated by similar values of j_0 and n_e , with a slightly more resistive R_{ω} . This represents negligible variations and is consistent with the near-overlapping LSV plots. The NiFeCu_{2.0} electrode highlights identical values, apart from an enhancement of j_0 from 0.68 to 1.1 mA cm^{-2} .

To further understand and complete the study of the electrode transformations provoked by ageing, the weight variation of the electrodes was determined and presented in Table 7 by comparing the nanofoam mass (m) [mg].

As observed in Table 7, the integrity of the nanofoams was significantly preserved, with NiFe gaining approximately 1% and NiFeCu_{2.0} losing a bit less than 2% of its mass. These results indicate that the nanofoams have robust integrity for intensive hydrogen evolution. Mass loss can be attributed to the formation of oxides–hydroxides and dissolution of metals in the ageing electrolyte. Therefore, ICP-OES analysis was used to detect and quantify the concentration of dissolved metals (c_{ICP}) [$\mu\text{g L}^{-1}$] during ageing. The results of the analysis of the used electrolyte are presented in Fig. 7.

Fig. 7 highlights that the presence of dissolved metals in the electrolyte used for NiFe and NiFeCu_{2.0} was $<1 \text{ mg L}^{-1}$ for all

**Fig. 7** Concentration of dissolved metals by ICP-OES of the KOH electrolyte used in NiFe and NiFeCu ageing, respectively.

elements. These results demonstrate that both cathodes have strong structural and chemical stability despite minimal leaching facing an aggressive long-term HER regime. Therefore, both nanofoams exhibited promising durability for long-term industrial AEL operation.

Conclusions

This work has demonstrated the progressive integration of Cu in a NiFe framework to enhance the electrochemical activity for the HER. The outcome of this strategy was a NiFeCu nanofoam cathode with improved catalytic activity. It was shown that NiFeCu trimetallic nanofoams can be accomplished while retaining the one-step DHBTP process, resulting in uniform and homogeneous distribution of the constituting elements. Notable thresholds were detected for Cu incorporation into the NiFe framework. Stable NiFeCu nanofoams can be produced with improved activity up to 2.0% Cu integration and with only a small mass change after ageing. The modified NiFeCu_{2.0} electrode exhibited improved overpotentials and a lower R_{ω} value when compared to the NiFe nanofoam.

The longevity assessment of the NiFe and NiFeCu_{2.0} nanofoams was performed over 60 h of continuous CA testing. The electrodes demonstrated strong structural stability with negligible mass loss, which was corroborated by ICP results that highlighted low levels of leaching. Potentiodynamic measurements provided a more accurate and representative assessment of the catalytic performance, whereas the lower retentions observed under potentiostatic conditions (CA) were attributed to resistive mass-transport phenomena (e.g., bubble accumulation and electrolyte saturation). The longevity studies thereby highlight the robustness of the NiFeCu_{2.0} electrode under highly aggressive HER operating conditions.

Although not within the scope of this work, the use of EIS analysis was identified as an interesting technique to complement and deconvolute the charge-transfer and solution resistance study across the NiFeCu nanofoams. XPS characterisation is also proposed as future work to address the identification of the oxidation states of Cu, Ni and Fe for a mechanistic study grounded on the present findings.

Table 7 Weight variation of the nanofoams^a of NiFe and NiFeCu cathodes

Nanofoam	m/mg (pre-ageing)	m/mg (aged)	Var.
NiFe	10.551	10.609	+0.93%
NiFeCu _{2.0}	12.499	12.275	−1.79%

^a These values do not account for the substrate weight.

NiFe and NiFeCu_{2.0} exhibited identical retentions, with NiFeCu_{2.0} achieving more favourable overpotentials in the long-term compared to NiFe at the expense of slightly more metal leaching. In conclusion, NiFeCu_{2.0} was found to be a remarkable evolution of the NiFe nanofoam with a minimal addition of Cu, improving the HER activity due to the dendritic-like porous nanostructure while retaining identical and competitive HER longevity.

Conflicts of interest

There are no conflicts to declare.

Abbreviations

AEL	Alkaline electrolysis
PEM	Proton exchange membrane electrolysis
SOE	Solid-oxide electrolysis
HER	Hydrogen evolution reaction
SSA	Specific surface area
DHBT	Dynamic hydrogen bubble template
fcc	Face-centered cubic
bcc	Body-centered cubic
SS	Stainless-steel
XPS	X-ray photoelectron spectroscopy
LSV	Linear sweep voltammetry
CA	Chronoamperometry
RHE	Reversible hydrogen electrode
SEM	Scanning electron microscopy
EDS	Energy-dispersive spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
XRD	X-ray diffraction
CLSM	Confocal laser scanning microscopy
<i>hkl</i>	Miller indices
EIS	Electrochemical impedance spectroscopy

Data availability

The data for this article, including the raw datasets related to linear sweep voltammetry, chronoamperometry and X-ray diffraction plots are available in the Zenodo repository at <https://doi.org/10.5281/zenodo.18851345>, whose files can be accessed and downloaded *via* this link. The available data consist of raw exports with no conversions, smoothing, filtering, or baseline corrections, and directly correspond to the plots and analyses in the manuscript.

Supplementary information (SI): (i) detailed methodology applied for the Tafel analysis of all samples, specifically a standardised algorithm for slope determination; (ii) additional figures and surface area determination in the scope of the CLSM results; (iii) chemical composition detection maps for all studied samples in the scope of EDS results. See DOI: <https://doi.org/10.1039/d6ta02065h>.

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