

Article

Enhanced Performance of Gold Nanoparticle-Modified Nickel–Iron Coatings for Sodium Borohydride Electrooxidation

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Abstract

The Ni-Fe coatings modified with AuNPs were deposited on the flexible copper-coated polyimide (Cu/PI) surface using electroless metal plating, while the galvanic displacement technique was applied to modify the surface of NiFe coatings by a small content of AuNPs in the range of $16.5 \mu\text{g}_{\text{Au}} \text{cm}^{-2}$. AuNPs of a few nanometers in size were deposited on the NiFe/Cu/PI surface by immersing it in a solution containing AuCl_4^- ions. The electrooxidation of sodium borohydride was evaluated in a 1 M NaOH solution containing 0.05 M of sodium borohydride using cyclic voltammetry, chronoamperometry, and chronopotentiometry. In addition, the performance and stability of the NiFe/Cu/PI and AuNPs-NiFe/Cu/PI catalysts were evaluated for potential use in a direct $\text{NaBH}_4\text{-H}_2\text{O}_2$ fuel cell. The NiFe coating modified with AuNPs demonstrated significantly higher electrocatalytic activity towards the oxidation of sodium borohydride as compared to bare Au or unmodified NiFe/Cu/PI. Furthermore, it exhibited a superior power density of 89.7 mW cm^{-2} at room temperature and operational stability under alkaline conditions, while the NiFe anode exhibited 73.1 mW cm^{-2} . These results suggest that the AuNPs-modified NiFe coating has great potential as a material for use in direct borohydride fuel cells (DBFCs) applications involving the oxidation of sodium borohydride.

Keywords: gold nanoparticles; sodium borohydride; electrooxidation; electroless metal plating; galvanic displacement; fuel cells



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1. Introduction

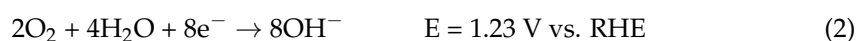
Hydrogen has emerged as a potentially promising source of energy due to its clean and energy-efficient characteristics. It is regarded as a potential candidate for future implementation as an energy carrier [1]. Nevertheless, significant challenges persist in the domains of hydrogen storage and transport due to its low density and safety concerns [2]. Hydrogen-rich compounds, including sodium borohydride (NaBH_4), which possesses a substantial hydrogen content of 10.6 wt% and an energy density of 9.3 Wh g^{-1} [3], have emerged as a compelling candidate for carbon-free energy applications. This is attributable to its high energy density, environment-friendly profile, ease of handling in both liquid and solid phases, and abundant availability [4]. Due to these properties, NaBH_4 has been the focus of extensive research as a prospective fuel for DBFCs, which possess a high theoretical

cell voltage of 1.64 V [5,6]. The utilization of DBFCs in a wide range of applications is enabled by the aforementioned advantages. These applications include portable electronic devices, aerospace power systems, and other sectors that require short-term energy supply solutions [7]. DBFC functions through two fundamental half-cell reactions. The anodic half-reaction involves the borohydride oxidation reaction (BOR), while the cathodic half-reaction corresponds to the oxygen reduction reaction (ORR). The detailed electrochemical reactions are provided in the following Equations: (1)–(3) [8].

Anodic Reaction (BOR)—Oxidation of NaBH_4 :



Cathodic Reaction (ORR)—Oxygen Reduction Reaction:



Overall Cell Reaction:



However, the BOR generally exhibits a high overpotential, which considerably restricts the output voltage of DBFCs. Therefore, it is imperative to rationally design BOR electrocatalysts to enhance their catalytic performance in order to optimize the overall efficiency of these fuel cells [9]. Conventional noble metal catalysts, including Pt [10], Ru [11], Pd [12], Au [13], and their alloys integrated with non-precious metals, such as PtCo/ Co_3O_4 nanosheets [14], Pd–Sn [15], Ni@Au [16], and Cu@Ag [17,18], have been extensively explored as electrocatalysts for the BOR. However, the high cost and limited abundance of noble metals pose substantial barriers to their large-scale application. It has been demonstrated that the BOR on gold (Au) proceeds via an eight-electron transfer mechanism, as Au functions as an efficient electrocatalyst for BOR rather than merely facilitating hydrolysis. However, the significantly high cost of Au poses a substantial obstacle to the commercialization of DBFC technology. Consequently, contemporary research endeavors are progressively concentrating on methodologies to reduce Au utilization in the formulation of anode catalysts, while preserving or amplifying their catalytic efficiency [19,20].

Given these circumstances, there is an urgent need to develop alternative, cost-effective electrocatalysts that demonstrate superior performance in the BOR. Recently, there has been an increasing focus on low-cost transition metals. These metals possess unfilled 3d orbitals, which favor the adsorption of BH_4^- species. This property renders them promising candidates as primary components in BOR electrocatalyst design [21–23]. Three-dimensional transition metals are distinguished by their inherent abundance, minimal cost, and advantageous theoretical catalytic properties. Among these elements, Fe [24], Co [25], Ni [26], and Zn [25,27] have been the focus of extensive research. The incorporation of these transition metals into noble metal-based catalysts has demonstrated effectiveness in two primary areas: the reduction in material costs and the enhancement of overall catalytic performance. Geng et al. investigated the potential of Ni–Pt/C as an anode catalyst for DBFCs, demonstrating its remarkable catalytic activity and stability for the BOR compared to Ni/C alone [28]. Duan et al. similarly reported that Cu–Pd/C bimetallic nanoparticles not only achieve catalytic performance comparable to that of Pd/C but also offer reduced material costs and enhanced electrocatalytic activity in alkaline media [29]. The findings indicate that the incorporation of 3d transition metals into noble metal-based catalysts can result in significant enhancements in catalytic performance.

Venugopal and colleagues conducted a comprehensive examination of the water–gas shift reaction, employing a series of catalysts composed of Au-M (M = Ag, Bi, Co, Cu, Mn, Ni, Pb, Ru, Sn, Ti) supported on Fe₂O₃. The study's results indicated that the catalytic activity of the Ni- and Ru-modified catalysts surpassed that of the unmodified Au/Fe₂O₃ system. The enhanced performance of the Au–Ru system was predominantly attributable to the intrinsic activity of each metal, with minimal synergistic interaction. In contrast, the Au–Ni catalyst exhibited enhanced activity, which was predominantly attributed to synergistic effects between Au and Ni, as well as between Au and the Fe₂O₃ support. Electronic (chemical) interactions contributed to this effect, to a certain extent [30]. Motivated by these observations, the objective of this study is to design, synthesize, and evaluate the activity of gold nanoparticles (AuNPs)-decorated NiFe coating on a flexible copper-coated polyimide (Cu/PI) surface for BOR. The electrocatalytic performance of the AuNPs-decorated NiFe coating for the BOR was comprehensively assessed in an alkaline medium using cyclic voltammetry (CV), chronoamperometry (CA), and chronopotentiometry (CP).

2. Materials and Methods

2.1. Chemicals

Polyimide (PI) film of 0.125 mm thickness (DuPont™ Kapton® HN, GoodFellow), cobalt sulfate (CoSO₄·7H₂O, 98%, Chempur, Piekary Śląskie, Poland), sodium sulfide (Na₂S·9H₂O, 99.99%, Sigma-Aldrich, Taufkirchen, Germany), palladium chloride (PdCl₂, 59.5%, Alfa Aesar, Ward Hill, MA, USA), copper sulfate pentahydrate (CuSO₄·5H₂O, 98%, Chempur, Piekary Śląskie, Poland), iron sulfate heptahydrate (FeSO₄·7H₂O, 97%, Chempur, Piekary Śląskie, Poland), nickel sulfate (NiSO₄·7H₂O, >98%, Chempur, Piekary Śląskie, Poland), glycine (NH₂CH₂COOH, 99%, Chempur, Piekary Śląskie, Poland), ethylenediaminetetraacetic acid (EDTA, 99%, Rechem, Mississauga, Canada), sodium malonate (CH₂(COONa)₂, 97%, Merck, Darmstadt, Germany), morpholine borane (MB, C₄H₈ONH·BH₃, 97%, Alfa Aesar, Ward Hill, MA, USA), sulfuric acid (H₂SO₄, 98%, Chempur, Piekary Śląskie, Poland), sodium hydroxide (99%, Chempur, Piekary Śląskie, Poland), sodium borohydride (NaBH₄, 99%, Merck, Darmstadt, Germany).

2.2. Fabrication of NiFe and AuNPs-Modified NiFe

This study presents a simple, two-step approach for fabricating Au nanoparticle-modified NiFe catalysts. The first step involves electroless NiFe deposition on flexible, copper-coated polyimide (Cu/PI). The second step involves spontaneous Au displacement from the HAuCl₄ solution. The flexible substrate used is a polyimide (DuPont™ Kapton®, Goodfellow Cambridge Limited, Huntingdon, UK). PI is non-conductive, so its surface was pre-treated by using adhesion/activation pretreatment procedures as described in reference [31]. A thin, conductive CoS layer was formed on the PI surface using the SILAR method. Then, a Cu layer was electrodeposited on the CoS/PI surface. Finally, the NiFe coating was deposited on the Cu/PI using the following procedures:

- Activation of Cu/PI by dipping it in a 0.5 g L^{−1} PdCl₂ solution for 1 min, followed by rinsing with deionized water.
- Electroless plating of the NiFe coating onto the activated Cu/PI with Pd by immersing it in an electroless plating solution containing 0.14 M NiSO₄, 1 mM FeSO₄, 0.05 M EDTA, 0.1 M CH₂(COONa)₂, 0.2 M MB, and 0.2 M NH₂CH₂COOH (pH 7). The bath operated at 60 °C for 1 h.

The AuNPs were deposited on the prepared NiFe/Cu/PI electrode via the galvanic displacement technique [32]. The NiFe/Cu/PI electrode was immersed in 1 mM HAuCl₄ for 1 min, followed by rinsing with deionized water and drying. Figure 1 shows a general fabrication scheme of the catalysts.

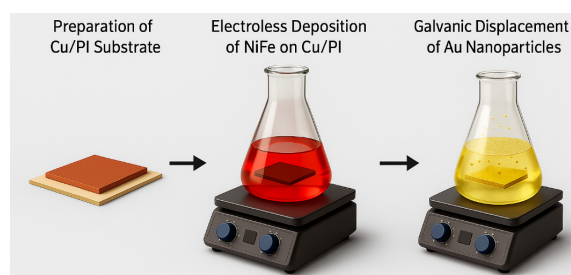


Figure 1. Fabrication scheme of the NiFe and AuNPs-NiFe catalysts.

2.3. Characterization of Materials

The surface morphology and elemental composition of the catalyst were evaluated using an SEM-focused ion beam facility (Helios Nanolab 650, FEI, Eindhoven, The Netherlands) equipped with an EDX spectrometer (INCA Energy 350 X-Max 20, Oxford Instruments, Oxford, UK).

The XRD patterns of the prepared materials were measured using a SmartLab X-ray diffractometer (Rigaku, Tokyo, Japan), which was equipped with a 9 kW rotating Cu anode X-ray tube. The grazing incidence (GIXRD) method was used in the 2θ range of $15\text{--}90^\circ$. The angle between the parallel X-ray beam and the specimen surface (ω angle) was adjusted to 0.5° . Phase identification was performed using the PDXL software package (Rigaku) and the ICDD powder diffraction database PDF-4+ (2022 release).

The composition of the prepared catalysts was determined using an ICP optical emission spectrometer Optima700DV (Perkin Elmer, Waltham, MA, USA).

2.4. Electrochemical Measurements

The BOR was investigated using a potentiostat/galvanostat PGSTAT100 (Metrohm Autolab B. V., Utrecht, The Netherlands). A conventional three-electrode cell was used for electrochemical measurements. The NiFe/Cu/PI and AuNPs-NiFe/Cu/PI catalysts with a geometric area of 2 cm^2 were employed as working electrodes. An Hg_2Cl_2 (3.5 M KCl) electrode was used as a reference, Pt sheet with a geometric area of 4 cm^2 was used as a counter electrode. For comparison, the bare Au electrode with a geometric area of 0.636 cm^2 was used. Cyclic voltammograms (CVs) were recorded at a potential scan rate of 10 mV s^{-1} from the open-circuit potential value in the anodic part up to $+0.6\text{ V}$ unless otherwise stated in a 1 M NaOH solution containing NaBH_4 concentration of 0.05 M at a temperature of 25°C . Chronoamperometry test was carried out at a constant potential value of -0.2 V for 10 h, while chronopotentiometry test was carried out at a constant current density of 10 mA cm^{-2} versus the geometric area of the investigated catalysts for 10 h.

All reported potential values are referred to as “SCE”.

2.5. Fuel Cell Test Experiments

Direct experiments were conducted on a $\text{NaBH}_4\text{--H}_2\text{O}_2$ fuel cell employing NiFe and AuNPs-NiFe catalysts, with an anode with a geometric area of 1 cm^2 . A Pt sheet was used as the cathode. These were placed on either side of the middle container. The anodic and cathodic compartments of the fuel cells were separated by means of a Nafion N117 membrane. The anolyte utilized was an alkaline mixture of 1 M NaBH_4 and 4 M NaOH, while the catholyte was a solution of 1.5 M HCl and 5 M H_2O_2 . Each cell compartment was filled with 100 mL of freshly prepared electrolyte. The current densities presented were then normalized with respect to the geometric area of the catalysts. Electrochemical measurements were assessed using a Zennium workstation (ZAHNER-Elektrik GmbH

& Co. KG, Kronach, Germany). Cell polarization curves were recorded at temperatures ranging from 25 to 55 °C.

3. Results and Discussion

In this study we present a strategy to fabricate flexible electrocatalysts based on Ni-Fe coatings modified with AuNPs. As flexible substrate we use polyimide which is lightweight, flexible, resistant to heat and chemicals. MB was chosen as a reducing agent for depositing the NiFe coating because it is a relatively mild, stable, less explosive and toxic, and environmentally friendly alternative to traditional reducing agents like hydrazine (N_2H_4) or NaBH_4 . In addition, MB is also stable in solution, which allows for a longer plating bath life. Figure 2a–c present SEM views of the NiFe coating at different magnifications. The surface exhibits a cauliflower-like morphology, with individual grains or clusters that appear tightly packed together. The grains are irregularly shaped and separated by grain boundaries. The coating is dense and continuous, indicating good substrate coverage.

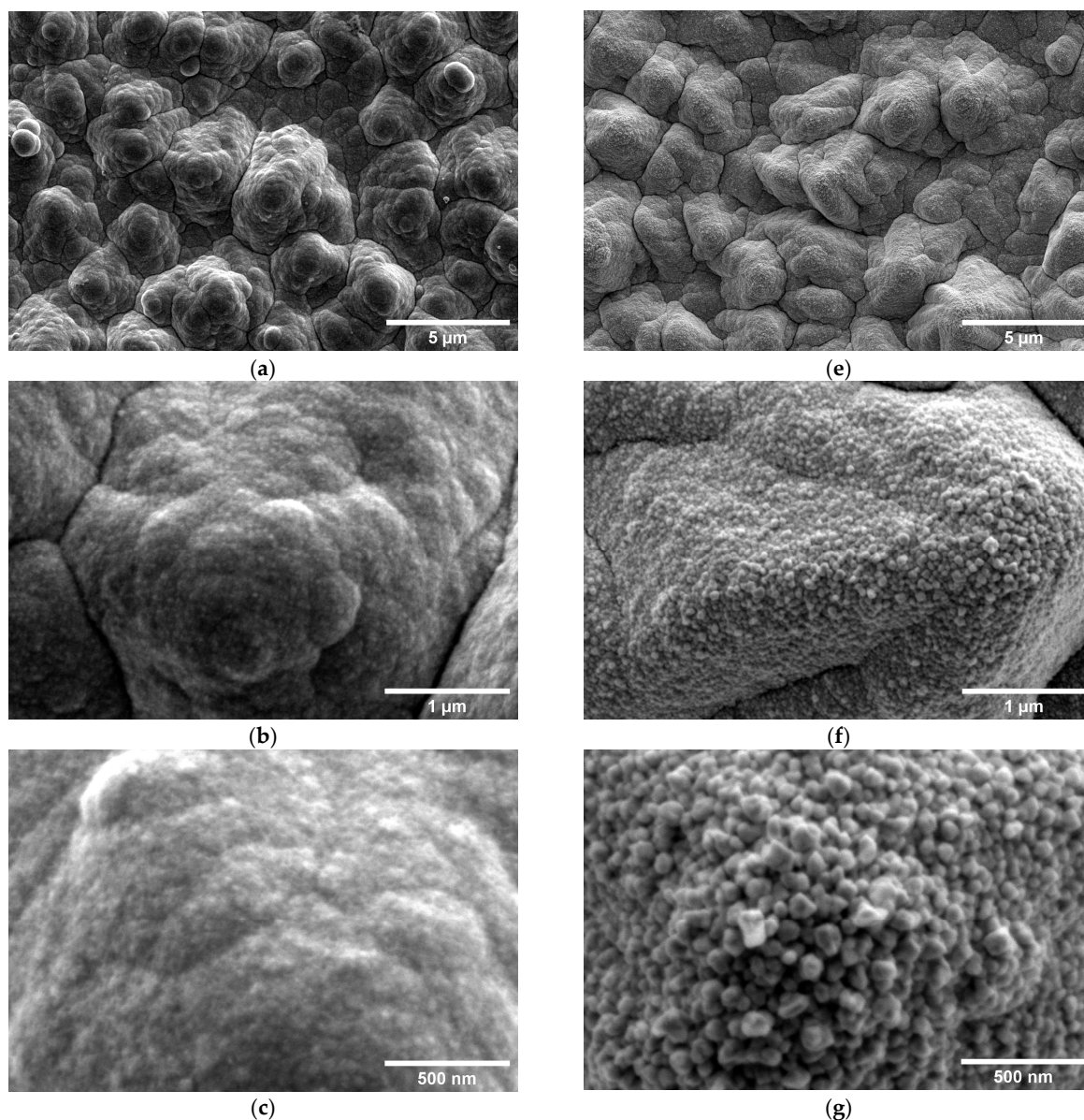


Figure 2. Cont.

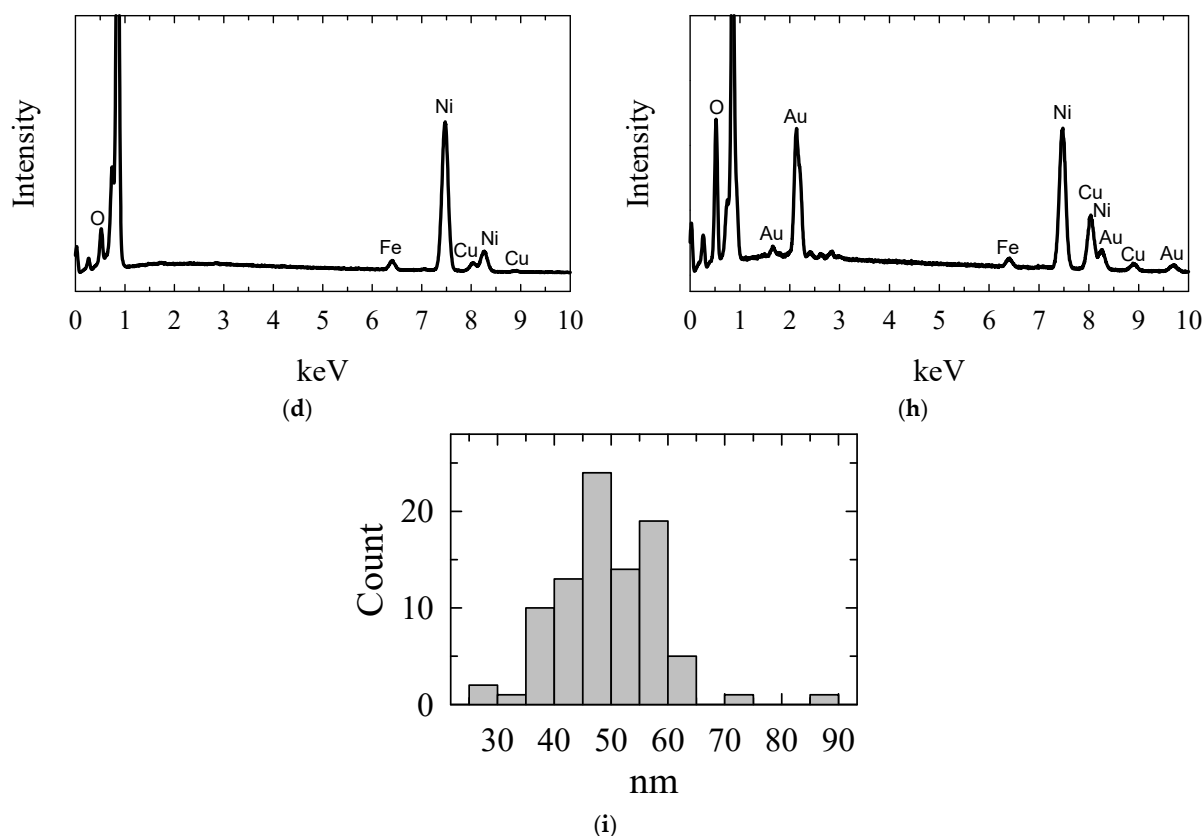


Figure 2. SEM images of the NiFe (a–c) and AuNPs-NiFe (e–g) catalysts deposited on the Cu/PI surface. (d,h) The corresponding EDX spectra. (i) Particle distribution histogram of AuNPs-NiFe/Cu/PI.

AuNPs were deposited on the NiFe coating by immersing it in a gold-containing solution for 1 min. This simple procedure is known as galvanic displacement, whereby a noble metal is deposited through the oxidation of a precursor metal adlayer deposited on the substrate at open-circuit potential [32]. SEM images of the prepared AuNPs-modified NiFe coating at different magnifications are shown in Figure 2e–g. As with the previous images (Figure 2a–c), the structure retains a cauliflower-like morphology, indicating that the deposition of AuNPs did not damage the base layer. The modification of the NiFe coating by Au via galvanic displacement occurs by deposition of small Au nanoparticles with diameters ranging from 40 to 60 nm (Figure 2i), which are close one to other and later coalesce or grow into a more continuous film. The individual grains or clusters appear rounded and densely packed, suggesting a uniform deposition process. Furthermore, the surface is highly structured, roughened, and nanoparticle-rich (Figure 2f,g).

Figure 2d,h show the energy dispersive X-ray (EDX) spectra corresponding to the NiFe and AuNPs-NiFe catalysts, respectively. These spectra confirm the presence of Ni, Fe and Au in both catalytic materials. The composition of the deposited NiFe and AuNPs-NiFe catalysts was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The summarized data are given in Table 1.

Table 1. The data of the composition of the prepared catalysts by ICP-OES analysis.

Catalyst	Element, at%		
	Au	Ni	Fe
NiFe	-	96	4
AuNPs-NiFe	5	93	2

The results showed that the NiFe coating deposited on Cu/PI contained approximately 96 at% of Ni and 4 at% of Fe, while the AuNPs-NiFe catalyst contained 93 at% of Ni, 2 at% of Fe, and 5 at% of Au. Additionally, the Au loading was approximately $16.5 \mu\text{g cm}^{-2}$.

X-ray diffraction was used to evaluate the crystal structure of the materials under investigation. Figure 3a shows the XRD patterns for NiFe/Cu/PI. The peaks at 2θ values of 43.29° , 50.43° , 74.13° , 89.92° , and 95.17° correspond to the (111), (200), (220), (311), and (222) planes, respectively, and confirm the cubic lattice of Cu. All the XRD peaks are in good agreement with the standard pattern for pure face-centered cubic planes of Cu (PDF card no. 00-004-0836).

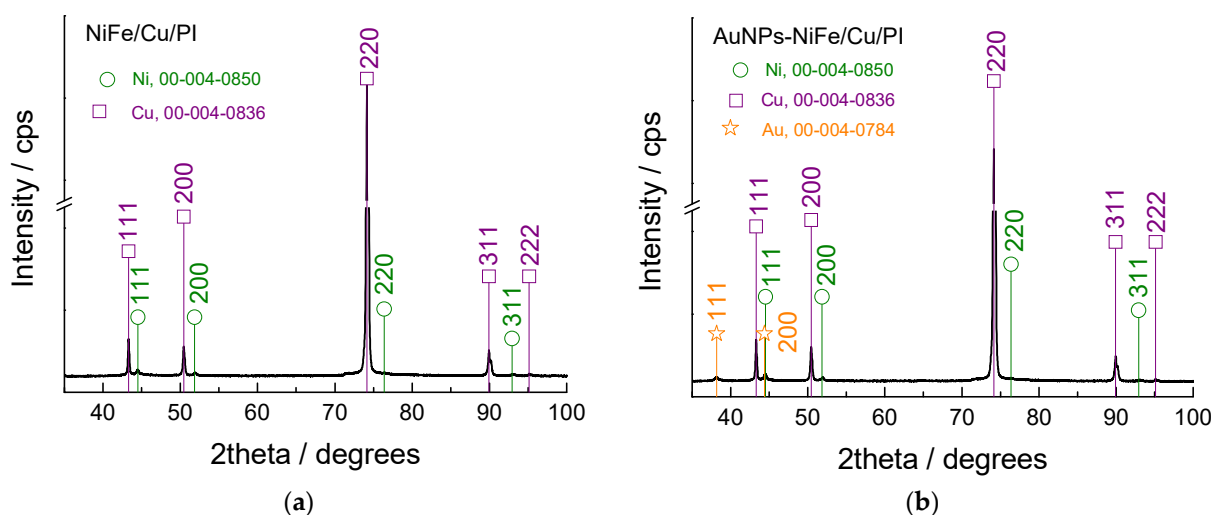


Figure 3. XRD patterns of NiFe/Cu/PI (a) and AuNPs-NiFe/Cu/PI (b). Peaks positions are indicated according to database PDF4+ data card: Ni—card. no. 00-004-0850, Cu—card. no. 00-004-0836, and Au—card. no. 00-004-0784.

The XRD peaks at 2θ values of 44.42° , 51.94° , 76.37° , and 92.97° , correspond to the (111), (200), (220), and (311) planes, respectively. These are attributed to the cubic lattice of Ni, according to the pure face-centered cubic plane of Ni (PDF card. no. 00-004-0850). Furthermore, the peaks at approximately 43.29° , 50.43° , and 74.13° overlap with the Cu XRD peaks and can be indexed to the (111), (200), and (220) planes of the fcc Fe-Ni alloy (JCPDS card no. 47-1405) [33]. In the case of AuNPs-NiFe, the additional XRD peaks at 2θ values of 38.12° and 44.45° can be indexed to the (111) and (200) planes of fcc Au (PDF card no. 00-004-0784) (see Figure 3b).

The electrocatalytic properties of bare Au, NiFe, and AuNPs-modified NiFe coatings towards sodium borohydride oxidation were investigated using cyclic voltammetry. Figure 4 shows the oxidation of borohydride on a bare Au electrode (a), an unmodified NiFe electrode (b and c), and an AuNPs-modified NiFe electrode (d). The solid lines in Figure 4b,d represent the CVs recorded in a background solution containing 1 M NaOH. Figure 4e,f show bar columns of current densities and potential values, respectively, under peak A for the bare Au and AuNPs-NiFe catalysts.

In the case of the bare Au catalyst, a broad anodic peak A is evident at a potential of -0.36 V within the positive potential scan, as illustrated in Figure 4a. This oxidation peak has been attributed to the direct oxidation of BH_4^- ions, as depicted in Equation (1) [34]. Moreover, a broad oxidation wave extending up to 0.4 V is concomitant with the oxidation of reaction intermediates on the partially oxidized gold surface. In the reverse scan, a sharp peak B is observed at ca. 0.27 V (Figure 4a). The potential exhibited a peak at 0.27 V , followed by a plateau in the potential region from 0.0 to -0.6 V , which corresponds to the oxidation of adsorbed species such as BH_3OH^- or other borohydrides formed as

intermediates during the oxidation of BH_4^- ion in the forward scan [34]. However, the BOR current densities on the bare Au electrode decrease in subsequent scan cycles (Figure 4a). This can probably be due to the formation of intermediates adsorbed on the electrode in the electrocatalytic process, so the poisoned surface of the electrode diminished the electrocatalytic activity of the bare gold electrode [34].

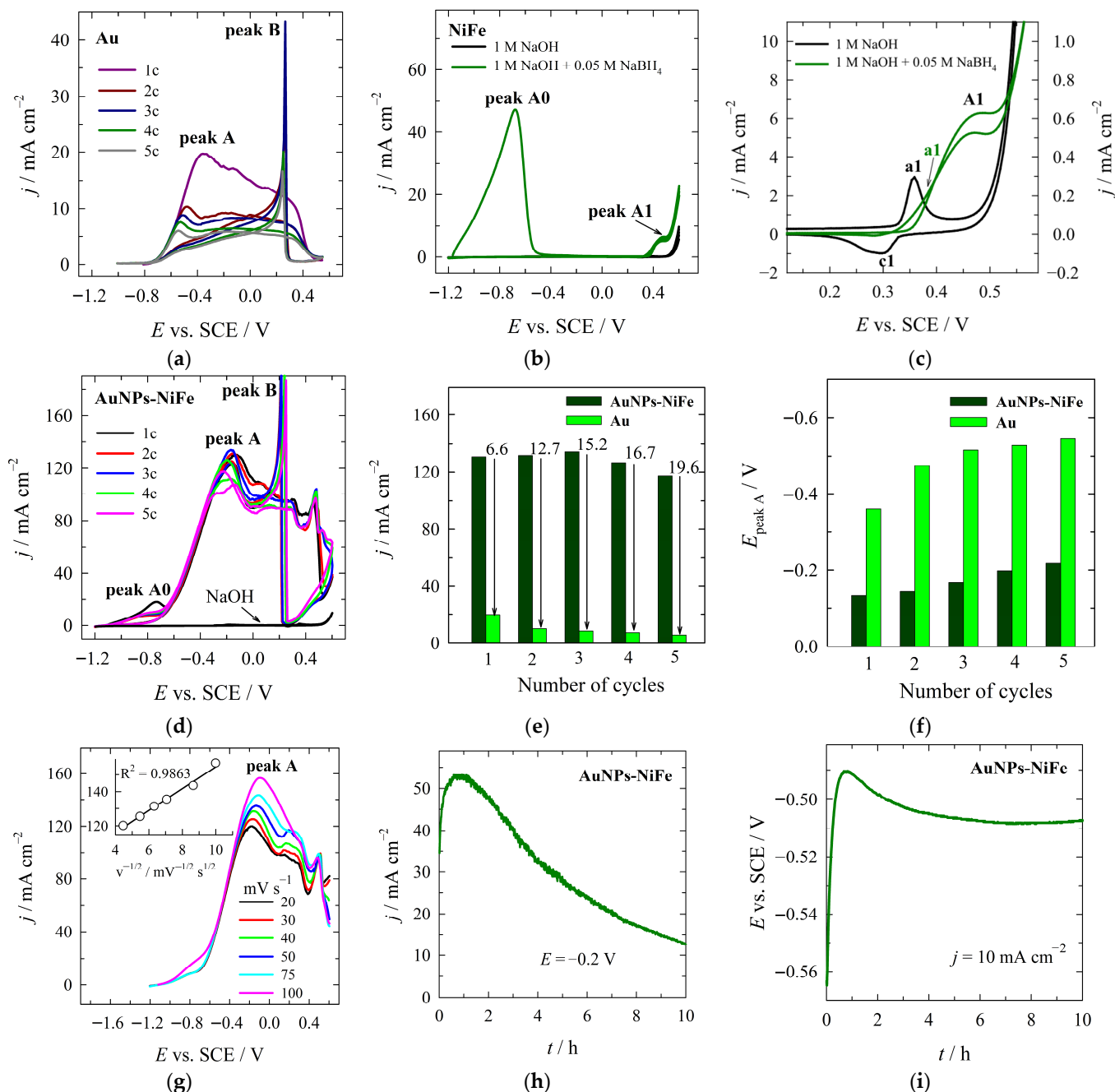


Figure 4. CVs of Au (a), NiFe (b,c), and AuNPs-NiFe (d) catalysts recorded in 0.05 M NaBH_4 + 1 M NaOH and 1 M NaOH (b–d) at 10 mV s^{-1} . (c) presents the CVs for NiFe at lower potential window. Bar columns of current densities (e) and potential values (f) under peak A for the bare Au and AuNPs-NiFe catalysts. (g) LSVs of AuNPs-NiFe recorded in 0.05 M NaBH_4 + 1 M NaOH at different potential scan rates. (h) shows CA curve recorded on AuNPs-NiFe at a constant potential of -0.2 V for 10 h. (i) shows CP curve recorded at a current density of 10 mA cm^{-2} for 10 h.

In the case of the NiFe catalyst, two oxidation peaks (A0 and A1) are visible in the cyclic voltammogram (Figure 4b). The first peak, which occurs at low overpotentials, may be

related to the oxidation of hydrogen generated by sodium borohydride hydrolysis [34,35], while the second peak A1, which occurs at potentials greater than 0.4 V, may be related to the direct oxidation of sodium borohydride. Figure 4c shows similar CVs to those presented in Figure 4b, but in the lower potential region. The black line presents the CV of NiFe recorded in a 1 M NaOH background solution, while the green line shows the CV recorded in a NaBH₄ solution at NiFe. During an anodic scan of NiFe in the background solution, an anodic peak (a1) at 0.36 V is observed. In the reverse scan, a cathodic peak (c1) is detected, which is assigned to the Ni²⁺/Ni³⁺ redox process [36]. In the case of the CV of NiFe in a 1 M NaOH solution containing 0.05 M NaBH₄ (Figure 4c, green line), the peak a1 is hardly distinguishable, followed by the appearance of a peak A1 at a more positive potential value of 0.48 V vs. SCE are observed. The current density of the anodic peak A1 was so large that the anodic peak a1 became ill-defined (Figure 4c). It can therefore be concluded that the oxidation of NaBH₄ took place after the oxidation of Ni(OH)₂ to NiOOH [37–40]. The Ni²⁺/Ni³⁺ redox couple acts as a catalyst for the oxidation of NaBH₄. Moreover, no anodic peaks were observed at negative potential values during subsequent anodic scans on this catalyst, indicating that the surface of the NiFe catalyst is inactive and does not catalyze the direct oxidation of BH₄[−] ions at higher potentials. This is due to passivation caused by the formation of Ni(hydr)oxide(s) [39,41], or possibly the poisoning of the catalyst surface by strongly adsorbed intermediates generated during BH₄[−] ion oxidation [34].

In contrast, the BOR on the AuNPs-modified NiFe catalyst proceeds in the same manner as on the bare Au electrode (see Figure 4a,d). The BOR starts at an electrode potential value of approximately −0.70 V on the Au electrode and −0.66 V on the AuNPs-NiFe catalyst. This is followed by broad oxidation peaks A, which are related to direct borohydride oxidation and are observed at −0.36 V and −0.13 V, respectively. As can be seen in Figure 4a,d, the potential values of the first anodic peak A on the AuNPs-NiFe catalyst are shifted by 0.22 V towards positive potential values compared to the bare Au electrode (Figure 4e). During the long-term potential cycling for AuNPs-NiFe between ca. −1.2 and +0.6 V for 5 cycles (Figure 4d), between −1.0 and +0.5 V for Au electrode (Figure 4a), and between ca. −1.2 and +0.6 V for NiFe (Figure 4b), the significantly higher BOR currents were obtained on the AuNPs-modified NiFe coating compared to the bare Au and unmodified NiFe electrodes, exhibiting increased catalytic properties of this catalyst. Therefore, sharp peaks B in the negative scan at the AuNPs-NiFe catalyst are observed at ca. +0.20 V (Figure 4d). Furthermore, the BOR current densities recorded on the AuNPs modified NiFe exhibits ca. 6.6 (first cycle) and 19.6 (fifth cycle) times higher current densities compared with those at the bare Au electrode (Figure 4e). Furthermore, during the long-term potential scanning, the potential values of peak A shift towards more negative potential values for the bare Au and AuNPs-NiFe catalysts, indicating the high activity of the AuNPs-NiFe and Au electrodes (Figure 4f). The deposition of a small amount of AuNPs significantly enhances the activity of the NiFe catalyst for the BOR. The enhanced oxidation currents of the AuNPs-NiFe catalyst can be attributed to the electrocatalytic properties of gold and metal particles, and gold–metal alloy formation [42,43]. Modification by AuNPs is implicated in higher catalytic activity due to providing active sites or improving charge transfer. Additionally, the AuNPs can improve the chemical stability of the coating and, therefore, increase electrical conductivity.

Figure 4g shows LSVs recorded on the AuNPs-NiFe catalyst in 0.05 M NaBH₄ + 1 M NaOH solution at different scan rates. As can be seen, the current density of peak A increases with an increase in the scan rate, indicating that the BOR is diffusion-controlled.

The chronoamperometric response of the AuNPs-NiFe catalyst was investigated in a 0.05 M NaBH₄ + 1 M NaOH solution at a constant potential of −0.2 V for 10 h (see Figure 4h). After 1 h, the current density of the AuNPs-NiFe catalyst was ca. 52 mA cm^{−2}, followed by

decay characteristic of diffusion limited systems. Furthermore, the decay in current may be related to poisoning of the catalyst surface by adsorption of BOR intermediates (e.g., BH_3OH^- , $\text{B}(\text{OH})_3$). According to the CA measurements, the stability of the AuNPs-NiFe catalyst is insufficient and must be improved. The catalyst surface can be recovered from poisoning by sodium borohydride oxidation products using post-treatment cleaning (e.g., with NaBH_4) or electrochemical potential-step cleaning [44]. Furthermore, enhancing the long-term stability of the AuNPs-NiFe catalyst can be achieved by incorporating dopants or optimizing the electrode design.

Figure 4i presents the chronopotentiometric response of the AuNPs-NiFe catalyst at a constant current density of 10 mA cm^{-2} . The difference between the steady-state operating anode potential after 10 h and the open-circuit potential was very small, indicating good electroactivity. Table 2 shows a comparison of the peak current densities during the oxidation of NaBH_4 on the NiFe/Cu/PI and AuNPs-NiFe/Cu/PI catalysts, as well as on other catalytic materials reported in the literature. AuNPs-NiFe/Cu/PI exhibits higher electrocatalytic activity for the oxidation of NaBH_4 than the other catalytic materials, such as leached Ni/Zn-Ni (125.8 mA cm^{-2}) [36], nanoporous gold wire array (73.6 mA cm^{-2}) [45], $\text{Au}_2\text{Ni}_1\text{Cu}_1/\text{C}$ (61.4 mA cm^{-2}) [46], and Ni deposited carbon fiber (56 mA cm^{-2}) and is promising DBFC anode material.

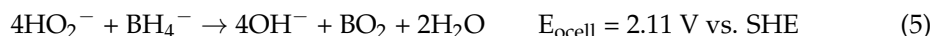
Table 2. Comparison of the peak current density during NaBH_4 oxidation on NiFe/Cu/PI and AuNPs-NiFe/Cu/PI catalysts and different catalytic materials.

Sample	Electrolyte	Scan Rate, mV s^{-1}	Peak Current Density, mA cm^{-2}	Ref.
NiFe/Cu/PI	0.05 M NaBH_4 + 1 M NaOH	10	6.3	This study
AuNPs-NiFe/Cu/PI	0.05 M NaBH_4 + 1 M NaOH	10	133.9	This study
Ni deposited carbon fiber	0.8 M NaBH_4 + 2 M NaOH	50	56.0	[38]
Ni/C	0.2 M NaBH_4 + 2 M NaOH	50	18.0	[28]
Leached Ni/Zn-Ni	0.02 M NaBH_4 + 1 M NaOH	10	125.8	[36]
Nanoporous gold wire array	0.02 M NaBH_4 + 1 M NaOH	10	73.6	[45]
$\text{Ni}_1\text{@Au}_1/\text{C}$	0.03 M NaBH_4 + 1 M NaOH	50	26.0	[16]
$\text{Au}_2\text{Ni}_1\text{Cu}_1/\text{C}$	0.1 M NaBH_4 + 2 M NaOH	50	61.4	[46]
Au-Y	0.03 M NaBH_4 + 2 M NaOH	50	34.0	[47]
$\text{Au}_{50}\text{Fe}_{50}/\text{C}$	0.1 M NaBH_4 + 3 M NaOH	20	33.8	[48]

The NiFe/Cu/PI and AuNPs-NiFe/Cu/PI catalysts have been investigated for use as anode catalysts in sodium borohydride–hydrogen peroxide fuel cells (DBHPFCs, $\text{NaBH}_4\text{-H}_2\text{O}_2$). DBHPFCs operate through the oxidation of BH_4^- at the anode (Equation (1)) and the reduction of hydrogen peroxide at the cathode (Equation (4)):



The overall reaction is as follows:



The performance of the DBHPFC was evaluated by recording the cell polarization and obtaining the corresponding power density curves at different temperatures. Figure 5 presents the cell polarization and peak power density curves recorded at different temperatures on NiFe (a) and NiFe modified with AuNPs (b) for $\text{NaBH}_4\text{-H}_2\text{O}_2$ fuel cell. A Pt sheet was used as the cathode. The fuel cells displayed an open circuit voltage of ca. 1.9 V when the NiFe and AuNPs-NiFe catalysts were employed as the anodes (see Figure 5). The summarized data are given in Table 3. The NiFe catalyst exhibited peak power density values of ca. $73.1\text{--}93.6 \text{ mW cm}^{-2}$ at temperatures of $25\text{--}55^\circ\text{C}$, whereas the AuNPs-NiFe

catalyst with a Au loading of $16.5 \mu\text{g}_{\text{Au}} \text{cm}^{-2}$ achieved greater peak power density values of ca. 89.7–126.3 at temperatures of 25–55 °C.

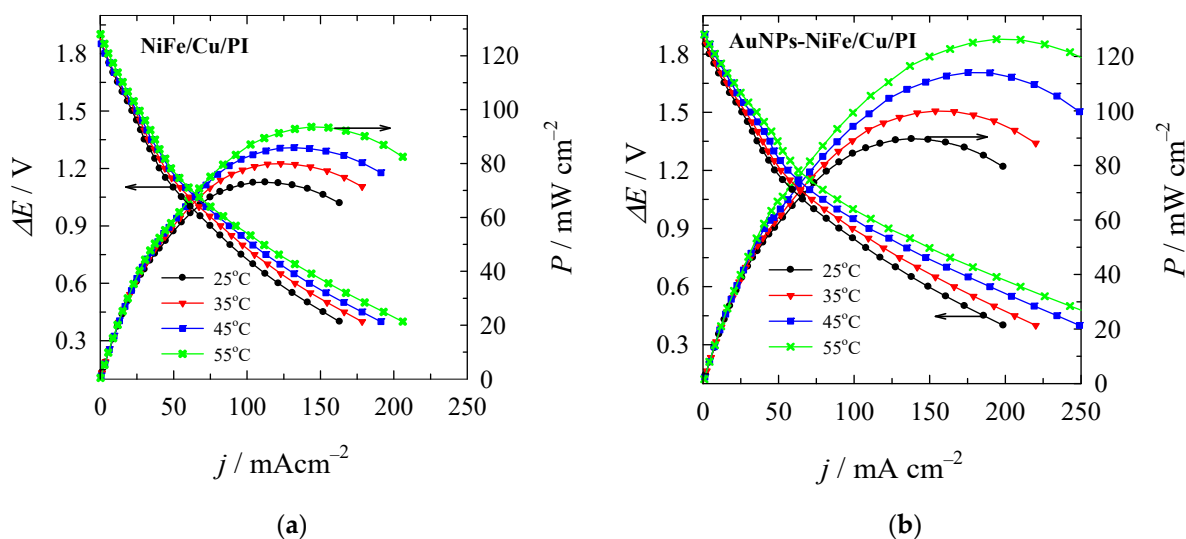


Figure 5. Cell polarization and power density curves for the direct $\text{NaBH}_4\text{-H}_2\text{O}_2$ fuel cell using NiFe/Cu/PI (a) and AuNPs-NiFe/Cu/PI (b) catalysts as the anodes/cathodes using the anolyte consisting of 1 M NaBH_4 and 4 M NaOH and the catholyte consisting of 5 M H_2O_2 and 1.5 M HCl at different temperatures.

Table 3. Fuel cell parameters of $\text{NaBH}_4\text{-H}_2\text{O}_2$ employing NiFe/Cu/PI and AuNPs-NiFe/Cu/PI anode catalysts.

Sample	$T, ^\circ\text{C}$	Peak Power Density, mW cm^{-2}	Peak Power Density, $\text{mW } \mu\text{g}_{\text{Au}}^{-1}$	Current Density at Peak Power Density, mA cm^{-2}	Cell Voltage at Peak Power Density, V
NiFe/Cu/PI	25	73.1	4.4	112.3	0.65
	35	80.0	4.8	122.9	0.65
	45	85.9	5.2	132.0	0.65
	55	93.6	5.7	143.9	0.65
AuNPs-NiFe/Cu/PI	25	89.7	5.4	137.9	0.65
	35	100.0	6.1	153.7	0.65
	45	114.1	6.9	175.4	0.65
	55	126.3	7.6	194.2	0.65

The AuNPs-modified NiFe anode exhibited superior power density (89.7 mW cm^{-2}) at room temperature and operational stability under alkaline conditions, whereas the unmodified NiFe anode exhibited 73.1 mW cm^{-2} . Specific peak power density values in the range of $5.4\text{--}7.6 \text{ mW } \mu\text{g}_{\text{Au}}^{-1}$ at 25–55 °C were obtained using the AuNPs-modified NiFe catalyst (Table 3). The comparison of DBPFC performance using different anode electrocatalysts is shown in Table 4.

Table 4. The comparison of DBPFC performance using different anode electrocatalysts.

Anode	Cathode	Anolyte	Catholyte	$P_{\text{max}}, \text{mW cm}^{-2}$	$T, ^\circ\text{C}$	Ref.
NiFe/Cu/PI	Pt	0.05 M NaBH_4 + 1 M NaOH	5 M H_2O_2 + 1.5 M HCl	73.1 93.6	25 55	[This work]
AuNPs-NiFe/Cu/PI	Pt	0.05 M NaBH_4 + 1 M NaOH	5 M H_2O_2 + 1.5 M HCl	89.7 126.3	25 55	[This work]
$\text{Ni}_1\text{@Au}_2/\text{C}$	Pt mesh	2 M NaOH + 0.5 M NaBH_4	4.5 M H_2O_2 + 2 M HCl	74	20	[16]
$\text{Cu}_1\text{Pd}_1/\text{C}$	Pt mesh	0.5 M NaBH_4 + 2 M NaOH	4.5 M H_2O_2 + 2 M HCl	39.82	20	[29]

Table 4. Cont.

Anode	Cathode	Anolyte	Catholyte	$P_{\max}$, mW cm ⁻²	T, °C	Ref.
Au ₅₀ Fe ₅₀ /C	Au/C	0.1 M NaBH ₄ + 3 M NaOH	2 M H ₂ O ₂ + 0.5 M H ₂ SO ₄	34.9	25	[46]
Au ₅₈ Ni ₄₂ /C	Au/C	1 M NaBH ₄ + 3 M NaOH	2 M H ₂ O ₂ + 0.5 M H ₂ SO ₄	45.74	20	[49]
HNAu/C	SNAu/C	1 M NaBH ₄ + 3 M NaOH	2 M H ₂ O ₂ + 0.5 M H ₂ SO ₄	25.8	20	[50]
Au@Co-B	LaCoO ₃	0.8 M KBH ₄ + 6 M NaOH	Air	85	25	[51]
Au _{0.75} Cu ₂₅ /C	Au/C	3 M NaOH + 1 M NaBH ₄	2 M H ₂ O ₂ + 0.5 M H ₂ SO ₄	37.4	25	[52]
Au/C	Pt/C	25% NaBH ₄ + 6 M NaOH	1 M H ₂ O ₂ + 1 M HCl + 3 M NaCl	34	20	[53]
Au/C	Pt/C	1 M NaBH ₄ + 3 M NaOH	0.15 M H ₂ O ₂ + 1 M HCl	25	25	[54]
Au-NP@rGO foam	Pd/C	0.4 M NaBH ₄ + 2 M NaOH	0.8 M H ₂ O ₂ + 2 M H ₂ SO ₄	60	30	[55]
CoNi-NS/Ni foam	Pd/Ti	0.5 M NaBH ₄ + 4 M NaOH	0.8 M H ₂ O ₂ + 2 M H ₂ SO ₄	80.6 140	30 60	[56]
Co ₄ -Au ₁ /C	Pt mesh	0.1 M NaBH ₄ + 2 M NaOH	4.5 M H ₂ O ₂ + 2 M HCl	102.4	25	[57]
Ni-P@NF	Pt sheet	3 M NaOH + 1 M NaBH ₄	0.5 M H ₂ SO ₄ + 2 M H ₂ O ₂	52.5	25	[58]
AuPPy-C	Pt mesh	2 M NaOH + 0.03 M NaBH ₄	1.5 M HCl + 5 M H ₂ O ₂	74.6	25	[59]
Au/CNT-G	Pt/C	2 M NaBH ₄ + 6 M NaOH	2 M H ₂ O ₂ + 1 M HCl	125	50	[60]
Au/MWCNTs	Au/MWCNTs	5 wt% NaBH ₄ + 10 wt% NaOH + 85 wt% H ₂ O	20 wt% H ₂ O ₂ + 5 wt% H ₃ PO ₄ + 75 wt% H ₂ O	74	-	[61]

It was found that the DBHPFC using AuNPs-NiFe had a power density of 89.7 mW cm⁻² at 25 °C, which is significantly higher than that of Ni₁@Au₁/C (74.0 mW cm⁻²) [16], Au₅₀Fe₅₀/C (34.9 mW cm⁻² at 25 °C) [46], Au₅₈Ni₄₂/C (45.74 mW cm⁻² at 20 °C) [49], Au/C (25.8 mW cm⁻²) [50], Au@Co-B (85 mW cm⁻² at 25 °C) [51], Au-NP@rGO foam (60 mW cm⁻² at 30 °C) [55], AuPPy-C (74.6 mW cm⁻² at 25 °C) [59], and Au/MWCNTs C (74 mW cm⁻² at 25 °C) [61]. This enhanced performance is attributed to the synergistic interaction between the highly active AuNPs and the conductive NiFe matrix, which promotes efficient borohydride oxidation and electron transfer collectively. When integrated with NiFe, AuNPs introduce synergistic effects that can improve reaction kinetics, stability, and surface reactivity.

4. Conclusions

In this study, NiFe coatings were successfully synthesized via electroless deposition on a Cu/PI surface. The coatings were then modified with AuNPs through galvanic displacement to enhance their electrocatalytic performance in NaBH₄ electrooxidation. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and inductively coupled plasma optical emission spectroscopy (ICP-OES) were used to examine the structural and morphological characteristics of the coatings, confirming the formation of a NiFe alloy matrix and the presence of dispersed AuNPs. Electrochemical characterization, including cyclic voltammetry, demonstrated that the AuNPs-modified NiFe coatings exhibited significantly enhanced catalytic performance, characterized by higher current densities, lower onset potentials, and reduced charge transfer resistance, compared to the unmodified NiFe coating. Further evaluation in a DBHPFCs configuration revealed that the AuNPs-NiFe anode exhibited a superior power density of 89.7 mW cm⁻² at room temperature and demonstrated operational stability under alkaline conditions, whereas the NiFe anode exhibited a power density of 73.1 mW cm⁻². This enhanced performance is attributed to the synergistic interaction between the highly active AuNPs and the conductive NiFe matrix, which promotes efficient borohydride oxidation and electron transfer collectively. This work presents a novel, cost-effective, and highly active anode engineering strategy for DBHPFCs with a focus on NiFe-based materials modified with a noble metal for use in electrocatalytic NaBH₄ electrooxidation and other hydrogen-based energy systems.

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Abbreviations

The following abbreviations are used in this manuscript:

AuNPs	Gold nanoparticles
BOR	Sodium Borohydride Oxidation Reaction
CV	Cyclic Voltammetry
CA	Chronoamperometry
CP	Chronopotentiometry
Cu/PI	Copper-coated polyimide
DBFCs	Direct Borohydride Fuel Cells
EDX	Energy-Dispersive X-ray Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LSV	Linear Sweep Voltammetry
MB	Morpholine borane
NaBH ₄	Sodium Borohydride
NaBH ₄ -H ₂ O ₂	Sodium Borohydride–Hydrogen Peroxide Fuel Cell
PI	Polyimide
ORR	Oxygen Reduction Reaction
SEM	Scanning Electron Microscopy
SILAR	Successive Ionic Layer Adsorption and Reaction

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