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Facile electrochemical synthesis of Ni-Co-B film on Cu sheet for dual-electrocatalysis of hydrogen and oxygen evolution reactions

A. Jokar^a, A. Toghraei^a, M. Maleki^a, Gh. Barati Darband^{b,*}

^a Department of Materials Engineering, Faculty of Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran
^b Materials and Metallurgical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad 91775-1111, Iran

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ABSTRACT

Fabricating efficient and affordable electrocatalysts is essential to make electrochemical water splitting more feasible. However, to minimize the electrocatalysts' fabrication costs, developing bifunctional electrocatalysts has been proposed as a profitable strategy. Herein, the Ni-Co-B film was fabricated on a Cu sheet surface by a one-step and facile electrodeposition method. The optimized sample showed noticeable electrocatalytic activity for total water splitting. The required overpotential for hydrogen evolution reaction (HER) at -10 mA cm⁻² current density was recorded to be -145 mV, and in the case of oxygen evolution reaction (OER), this value was 276 mV at 10 mA cm⁻². The unique morphology of the optimized Ni-Co-B sample with a high number of spherical micro-nodules was proposed to be responsible for this high HER and OER catalytic activity. Moreover, the optimized value of the B, Ni, and Co in the coating was highly important in facilitating the electrochemical reactions. Density functional theory (DFT) calculations indicated that the better electrocatalytic activity of the Ni-Co-B electrode is due to the regulate the electronic structure and new active catalytic sites which are created by Co incorporation. Finally, the binder-free approach of fabricating the coating resulted in the long-time high stability of the fabricated Ni-Co-B/Cu electrode at high current densities.

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1. Introduction

The great need for energy in today's industrial world has led to the excessive usage of fossil fuels, which has caused concerns about their depletion. In addition, serious environmental problems caused by fossil fuel usage have attracted growing attention to renewable energies. Among renewable fuels, hydrogen is a suitable alternate source of energy, owing to its high energy density as well as its carbon-free feature [1-5]. However, it is crucial to produce hydrogen gas in a way that does not emit any greenhouse gases [6]. Compared to the other hydrogen production methods, electrocatalytic water splitting has been highlighted as a fruitful one [7,8]. Unlike the modification of hydrocarbons, water electrolysis is a clean method to generate hydrogen, and the hydrogen gas that is produced in this approach is very pure, which can be utilized directly in fuel cells [9,10]. Water electrolysis occurs in an aqueous environment by connecting anode and cathode to a power source [11]. In this electrochemical cell, OER and HER occur at the anode and cathode surfaces, respectively. These reactions require a high potential to conquer the kinetic and thermodynamic barriers,

* Corresponding author. E-mail address: baratidarband@um.ac.ir (Gh. Barati Darband). which is called overpotential. Using suitable electrocatalysts as the anode and cathode, the required overpotential can be effectively reduced [12,13].

Noble metal-based electrodes containing metals such as Pt, Pd, Ru, and Ir have represented a high HER/OER catalytic performance. Nevertheless, due to their high costs and scarcity, their usage in large-scale industrial applications has been limited [14]. A suitable alternative to the noble metal-based catalysts is transitional metal (TM)-based materials, which have been well accepted as efficient water splitting electrocatalysts. Compounding TMs such as Co, Fe, Mo, W, and Ni with certain non-metallic elements like B, P, S, and Se is a profitable strategy to improve the intrinsic activity of TMs [15–20]. Among the studied TM compounds, transition metal-based borides (TMBs) are presented as adequate electrocatalysts due to their noticeable activity, high conductivity, long-term stability, and abundant active sites [21]. Furthermore, the reverse electron transfer of boron leads to the richness of metal sites from electrons, facilitating the electrochemical reactions [22].

There have been numerous studies on the catalytic activity of TMBs. Different approaches have been utilized to synthesize TMBs. For instance, Ni₃B alloy was synthesized by a one-step sintering method [23], Ni-B_{0.54} electrocatalyst was fabricated by electroless deposition [24], and Co-B electrocatalyst was synthesized by the chemical reduction approach [25]. To be benefited from the syner-





gism effect of Ni, Co, and B, the fabrication of ternary alloys and their usage as water splitting electrocatalysts have been studied in recent years. Gupta et al. [22] synthesized Co-30Ni-B electrode by chemical reduction method and assessed the HER behavior of the alloy in neutral solution. The overpotential at -10 mA cm⁻² current density (η_{10}) was reported to be 170 mV, and the Tafel slope was determined to be 51 mV dec⁻¹. Sheng et al. [26] fabricated Co-50Ni-B on carbon cloth substrate by chemical reduction method, which exhibited high HER catalytic performance in 1 M KOH with η_{10} of 80 mV and a Tafel slope of 88.2 mV dec⁻¹. Fortunately, Ni-Co-B alloy is not only active through HER, and recent studies have shown its promising OER activity. Ni-Co-B nanosheets synthesized on graphene substrate possessed relatively high OER activity in 1 M KOH electrolyte ($\eta_{10} = 280 \text{ mV}$) [27]. In another study, the OER activity of nano-cotton like Ni-Co-B film on Ni foam substrate was examined where η_{10} was measured to be 300 mV.

As can be seen, TMBs have been synthesized by different methods. However, despite numerous advantages of the electrodeposition method, the synthesis of the Ni-Co-B electrode by electrodeposition method has not been reported as of yet. Electrodeposition is a fast, environmentally friendly, and cheap approach that can be done at room temperature [28]. Moreover, in this method, the catalyst loading adheres to the substrate without any binder. Polymeric binders that are usually used in many other synthesizing methods are known as a factor that deteriorates electrical conductivity, and they also decrease the long-term stability of catalysts [21,29,30]. So using the electrodeposition method to synthesize Ni-Co-B alloy makes it possible to decrease the fabrication costs and enhance the electrocatalytic performance, and eventually, make the industrial usage of this alloy more feasible.

Another approach to decrease the costs of the electrochemical water splitting process is to use a bifunctional electrocatalyst that can be used to catalyze both HER and OER. Using bifunctional electrocatalsyts, it is possible to reduce the production costs of electrocatalysts and to simplify the water-splitting cell [31]. For instance, Ye and colleagues [32] synthesized the Ni-Co catalyst for overall water splitting, which required only 1.56 V to reach a current density of 10 mA cm⁻². In other studies, Ni-P [33], Ni-Fe [34], and Ni-Fe-P [35] catalysts were synthesized, and at 10 mA cm⁻², their overall water splitting voltage was recorded to be 1.7, 1.83 V, and 1.508 V respectively.

As mentioned before, some studies showed the promising HER activity of Ni-Co-B, while some others have reported the acceptable OER activity of this alloy. Nonetheless, to the best of our knowledge, synthesizing a bifunctional HER/OER Ni-Co-B alloy has not been reported as of yet.

Herein, Ni-Co-B coating was electrodeposited on Cu substrate (Ni-Co-B/Cu), and its HER and OER performance was investigated in 1 M KOH electrolyte. The optimized sample exhibited high catalytic activity and durability through both the HER and OER. The remarkable electrocatalytic activity of the fabricated electrode can be assigned to the synergism effect of the constituting elements as well as the unique morphology of the coating. Numerous microscale hemispheres and bumps can be observed in the coating microstructure that can increase the active catalyst surface area effectively. It is the first report of synthesizing a bifunctional HER/OER Ni-Co-B electrocatalyst. The facile, one-step electrodeposition approach utilized to synthesize this alloy can make the fabricated Ni-Co-B electrode a promising candidate among the other TMBs.

2. Experimental section

2.1. Electrodeposition of Ni-B and Ni-Co-B coatings

All the reagents that were used to synthesize the coatings were of analytical grade and were provided by Merck Co. All the reagents were used as received, without any modification and purifying. Cu sheet with dimensions $(20 \times 10 \times 2 \text{ mm})$ was used as the substrate. Before the electrodeposition process, SiC papers were used to polish the Cu sheets down to 2000-grit size and then degreased in acetone for 15 min in an ultrasonic bath. Then, they were pickled in hydrochloric acid (20 wt%) for 20 s. Finally, the samples were washed with distilled water and dried in air.

To prepare the electrodeposition bath of the Ni-Co-B sample, the following reagents were dissolved in distilled water: 140 g L⁻¹ NiSO₄.6H₂O, 14 g L⁻¹ CoSO₄.6H₂O, 40 g L⁻¹ Na₂B₄O₇.10H₂O, 40 g L⁻¹ H₃BO₃ 30 g L⁻¹ NaCl, 1 g L⁻¹ C₆H₄SO₂NNaCO.2H₂O, and 70 g L^{-1} Na₃C₆H₅O_{7.}2H₂O. The electrodeposition bath utilized to synthesize Ni-B coating was obtained by dissolving the same chemicals, except that CoSO4.6H2O was absent. The pH of the solutions was adjusted to 4, using HCl and KOH. Electrodeposition was carried out at room temperature, using a galvanostatic approach. To deposit Ni-Co-B coating, constant current densities of 5, 10, 20, and 40 mA cm^{-2} were applied for 40, 20, 10, and 5 min, respectively. The electrodeposition times were determined in a way that the applied electrical charge density remained the same, and all the samples possessed a similar amount of catalyst loading. Ni-B coating was synthesized at 20 mA cm⁻² current density for 10 minutes. Cu sheet was selected as the cathode, and the nickel sheet was placed as the anode in the electrodeposition bath. The catalyst loadings on the Cu substrate was determined by weighing before and after electrodeposition process. That was measured to be 7 mg cm⁻².

2.2. Physicochemical characterization

A field emission scanning electron microscope (FESEM, TESCAN MIRA3) was utilized to study the morphology of samples. The FE-SEM instrument had an energy dispersive X-ray (EDS) which was used to obtain the elemental mapping of Ni and Co. To study the chemical composition of the synthesized catalysts, they were peeled off the substrate and measured by an inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian Vista Pro). X-ray diffraction (XRD, Philips Xpert MPD) was utilized to study the crystal structure of the fabricated coating. Finally, to identify the surface chemistry, X-ray photoelectron spectroscopy (XPS, Bes Tec Germany) was utilized.

2.3. Electrochemical measurements

To measure the electrochemical characteristics, an AUTOLAB 302N potentiostat/galvanostat was employed. The fabricated coating on Cu substrate was placed as the working electrode in the electrochemical cell, saturated calomel electrode (SCE) was placed as the reference electrode, and a platinum electrode was chosen as the counter electrode. Electrochemical tests were done at room temperature in 1 M KOH solution. In this study, all the potentials are reported versus the reversible hydrogen electrode (RHE) by using the formula $E_{RHE} = 0.242 + 0.059 \text{ pH} + E_{SCE}$ [36]. To evaluate the OER and HER activities, linear sweep voltammetry (LSV) tests were done (scanning rate = 1 mV s⁻¹), and iR correction was done to modify the LSV plots. Each of the LSV tests was done three times, and the average value was reported. To calculate the electrochemical active surface area (ECSA) of the samples, their doublelayer capacitance (C_{dl}) was measured by performing cyclic voltammetry tests in the non-faradic potential range at scanning rates of 5, 10, 20, 40, 60, 80, and 100 mV s⁻¹. To obtain the C_{dl} value, the $\Delta j=j$ $_{anodic}$ - j $_{cathodic}$ of the samples at different CV scanning rates were plotted against the scanning rates, where their slope was determined as the C_{dl}. Finally, the ECSA value was obtained using the formula $ECSA = C_{dl}/C_s$, where Cs is the capacitance of a flat surface $(40 \ \mu F \ cm^{-2}).$



Fig. 1. Schematics explaining the synthesizing procedure of Ni-Co-B coating on Cu sheet

To evaluate the HER kinetics and the catalysts conductivity, electrochemical impedance spectroscopy (EIS) tests were done in the frequency ranging from 100 kHz to 0.1 Hz at the potentials of -100, -200, and -300 mV. To examine catalyst stability, chronopotentiometry (CP) tests were performed at current densities of -100 mA cm⁻² (to examine HER durability) and 100 mA cm⁻² (to examine OER durability) for 10 h. In addition, to evaluate the cyclic stability of catalysts, 1000 voltammetry cycles were performed at a scanning rate of 100 mV s⁻¹ in the cathodic range of 0 to -0.1 V vs. RHE (to measure the HER CV stability) and also 1000 CVs in the anodic range of 1 to 1.568 V vs. RHE (to measure the OER CV stability). The overall water splitting test was investigated by a two-electrode system, where both the cathode and the anode were identical samples of optimized Ni-Co-B/Cu.

2.4. DFT calculation details

The density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package. Generalized gradient approximation (GGA) with Perdew-Burke-

Ernzerhof functional was employed for the DFT exchange correlation energy. The plane wave cutoff was set to 450 eV. The selfconsistent field (SCF) tolerance was 1×10^{-5} eV in energy and 0.01 eV Å⁻¹ in force. A $4 \times 4 \times 1$ and $11 \times 11 \times 1$ k-point grids were adopted for the structure relaxation and the density of state (DOS), respectively. During structural optimization, three layers of samples were fixed and the other layers were allowed to be relaxed. The Gibbs free energy of the adsorbed hydrogen was calculated as [37]:

$\Delta G_{H} * = \Delta E_{H} * + \Delta E_{ZPE} - T\Delta S$

Where ΔE_{H^*} is the hydrogen-binding energy and ΔE_{ZPE} and ΔS referred to the differences in zero point energy and the entropy between the adsorbed H and H₂ (g).

3. Results and discussion

3.1. Microstructure and composition

The Ni-Co-B film was electrodeposited on a Cu sheet by the galvanostatic approach, which is shown in the schematic of Fig. 1. The microstructures of the Ni-Co-B and Ni-B coatings that were electrodeposited at 20 mA cm⁻² current density are depicted in Fig. 2a and 2b. As can be seen in the FESEM images, although these coatings were electrodeposited in an identical condition, their morphology is quite different. In the microstructure of the Ni-Co-B (Fig. 2a) coating, numerous micro-scale spherical nodules can be seen. These nodules can enhance the electrode's active surface area. However, in the case of Ni-B coating (Fig. 2b), the nodules are absent, whereas some parallel, shallow crevices can be seen on



Fig. 2. FE-SEM images of a) Ni-Co-B/Cu, b) Ni-B/Cu electrodeposited at 20 mA cm⁻² current density, and c) The EDS elemental mapping images of the Ni-Co-B/Cu sample for Ni and Co.

the surface. Observing the elemental EDS mapping of the Ni-Co-B coating (Fig. 2c), it can be noticed that the Ni and Co elements are distributed evenly all around the coating surface. Due to the inaccuracy of EDS analysis to examine B content, the elemental mapping of B could not be provided [38].

To compare the effect of the electrodeposition current density on the morphology of the synthesized Ni-Co-B coatings, the FE-SEM images of the Ni-Co-B coatings that were electrodeposited at different current densities of 5, 10, 20, and 40 mA cm⁻² are represented in Fig. 3. As depicted in Fig. 3a and 3b, the coating's morphology is relatively flat at low current densities. By raising the electrodeposition current density to 20 mA cm⁻², the evolution of hydrogen bubbles on the cathode surface (Cu substrate) intensifies, which results in the appearance of the spherical nodules on the surface (Fig. 3c). However, as seen in Fig. 3d, further raising the electrodeposition current density to 40 mA cm⁻² results in a decrease in the number of nodules. This could be due to the change in the composition of the coating that can affect the internal stresses.

Considering the significant impact of the coating composition on the intrinsic activity of catalysts, the ICP results of different Ni-Co-B samples synthesized at various current densities were compared with each other. The diagram of the changes of the elements' content with the electrodeposition current density is displayed in Fig. S1. It can be noticed that by increasing the electrodeposition current, the B content in the coating decreased from 6.44% (for the sample deposited at 5 mA cm⁻²) to 2.14% (for the sample synthesized at 40 mA cm⁻²). By increasing the electrodeposition current density from 5 to 40 mA cm⁻², the Co content was changed from 25.14% to 33.95%. In the case of Ni, it was decreased from 68.42% to 63.91%. As other studies have shown, the B/TM ratio affects the morphology and electrocatalytic performance of the coating [24,39]. The effect of the coating composition on the catalytic activity is discussed in the electrochemical section.

The XRD test results of Ni-B/Cu and Ni-Co-B/Cu catalysts are shown in Fig. S2. In the Ni-B spectrum, the Ni and Cu peaks can be detected. The presence of Cu peaks can be a to the substrate



Fig. 3. FE-SEM images of Ni-Co-B/Cu, synthesized at current densities of a) 5, b) 10, c) 20, and d) 40 mA cm⁻².

as a result of the thin film thickness. The observed peaks of the nickel element at angles of 44.5 and 51.9 degrees correspond to the planes (111) and (200), indicating that the nickel crystals have a fcc structure. The same peaks were observed in Ni-Co-B, except that the nickel-sharp peak was less intense and the peaks slightly shift to the right. This shift can be ascribed to the existence of Co atoms and the formation of Ni-Co solid solution [36]. However, no peak could be detected for B which can be attributed to the low volume fraction of Ni-B species in the coating [40].

To study the chemical state of different elements in the optimized Ni-Co-B coating, XPS analyses were utilized (Fig. 4). The XPS survey spectrum (Fig. 4a) denotes the existence of the Ni, Co, and B elements as well as C and O. The oxygen peak may be a result of the surface oxidation due to the exposure of the sample to air [41,42]. Also, surface contamination of the sample can lead to the appearance of the carbon peaks in the XPS spectrum. Fig. 4b shows the high-resolution Ni 2p spectrum. The signals observed at 856.47 and 873.8 eV binding energies correspond to Ni



Fig. 4. XPS spectra of Ni-Co-B/Cu a) XPS survey, b) Ni 2p spectra, c) Co 2p spectra, and d) B 1s spectra.

 $2p_{3/2}$ and Ni $2p_{1/2}$, respectively, which can be attributed to the Ni²⁺ and was also reported in some other nickel boride coatings [38,43]. In this respect, it has been reported that the amorphous metal borides are immediately oxidized when exposed to air [38]. The peaks observed at 862.76 and 881.0 eV are the shake-up satellite peaks [44]. These shake-up satellite peaks have been caused by sudden changes in the colonic potential due to the passage of separated electrons through the capacitance bands [45].

Fig. 4c exhibits the XPS spectrum of Co 2p, which has two signals at 782.4 and 791.2 eV that can be related to $2p_{3/2}$ and $2p_{1/2}$ of Co³⁺, respectively. The two other signals, which are the shake-up satellite peaks, are seen at 787.6 and 797.4 eV, respectively [46]. Finally, the XPS spectrum of B 1s can be seen in Fig. 4d. The peaks at 186.8 and 190.5 eV are attributed to B 1s and boron-oxo, respectively [27]. The measured B 1s binding energy of 186.8 eV is 0.2 eV less than that of pure B 1s binding energy of 187 eV [25,27]. This difference of binding energy shows the partial electron donation of nickel to boron and indicates the partial negative charge of B atoms. The other signal is related to boron-oxo denotes the presence of boron oxide on the surface of the sample due to surface oxidation. Overall, the results of the XPS test, which showed the existence of all three coating elements, denotes the successful synthesis of Ni-Co-B coating.

3.2. HER electrochemical performance

To investigate the electrocatalytic behavior of the fabricated electrodes, LSV tests were performed in 1 M KOH. For comparing the samples' electrocatalytic activity, the required overpotential - 10, -20, and -100 mA cm⁻² current densities were compared with each other, which is shown by η_{10} , η_{20} and η_{100} symbols, respectively. First, the electrocatalytic behavior of the Cu sheet, the optimized Ni-Co-B/Cu electrode, and Ni-B/Cu were studied. The optimized Ni-Co-B and Ni-B coatings were both electrodeposited at the 20 mA cm⁻² current density. The polarization curves of these samples and the corresponding η_{10} , η_{20} , and η_{100} values are shown in Fig. 5a and 5b. Considering the polarization curve of Cu sheer,



Fig. 5. HER catalytic activity of samples in 1 M KOH a) LSV curves of optimized Ni-Co-B/Cu sample, Ni-B/Cu, and Cu sheet, b) Required overpotentials (in mV) at -10, -20, and -100 mA cm⁻² current densities, c) LSV curves of Ni-Co-B samples electrodeposited at 5, 10, 20, and 40 mA cm⁻² current densities, and d) Tafel plots of different samples.

one can notice that there is a need for a very high overpotential value of -490 mV to reach the -10 mA cm⁻² current density. This indicates the poor HER electrocatalytic activity of the Cu sheet. By coating Ni-B on the copper surface, the required overpotential at various current densities was significantly reduced. The recorded overpotentials at different current densities are as follow: $\eta_{10} = -229$, $\eta_{20} = -276$ and $\eta_{100} = -405$ mV. Finally, by adding Co to the structure and the formation of Ni-Co-B coating, the required overpotential was further reduced, and the η_{10} , η_{20} , and η_{100} of the optimized sample electrodeposited at 20 mA cm⁻² were measured to be -145, -197, and -331 mV, respectively.

The higher HER catalytic activity of the optimized Ni-Co-B coating compared to the Ni-B can be attributed to the role of Co in adjusting the binding energy of the hydrogen atoms to the catalyst surface, which facilitates the adsorption of hydrogen atoms on the catalyst surface and eases the desorption of produced H₂ bubbles. Rather than the role of Co in enhancing the intrinsic catalytic activity, it also changes the morphology. In comparison with the relatively flat surface of Ni-B coating (Fig. 2b), Ni-Co-B morphology (Fig. 2a) consists of several spherical micro-nodules that can provide a larger accessible catalyst surface for HER. The ECSA value of the samples was calculated using the double-layer capacitance (C_{d1}) of each sample (Fig. S3). Interestingly, the optimized Ni-Co-B/Cu sample showed a very high ECSA value of 255 cm² which is about 2.4 times higher than that of the Ni-B/Cu (107.5 cm²).

To understand the effect of changing the electrodeposition current density on the morphology and chemical composition of Ni-Co-B coating, which in turn changes the catalytic activity, the LSV curves of the Ni-Co-B coating formed at the current densities of 5, 10, 20, and 40 mA cm⁻² are presented in Fig 5c. The sample formed at 20 mA cm⁻² current density possesses the lowest value of overpotential among the others. Comparing the overpotential of samples (Fig. 5b), it can be noted that raising the electrodeposition current density to 20 mA cm⁻² results in an improvement in the HER electrocatalytic activity of Ni-Co-B/Cu. However, a further increase of deposition current to 40 mA cm⁻² leads to a drop in electrocatalytic activity. The standard deviation of the η_{10} , η_{20} , and η_{100} values are mentioned in Table S1.

To find out why the sample deposited at 20 mA cm^{-2} has the highest activity among the others, two parameters should be considered: The ECSA value of catalyst which determines the accessibility of the electrolyte to the active sites, and the intrinsic cat-

alytic activity which relies on the composition of the coating [47]. Regarding the calculated ECSA value of each of the samples, it can be seen that there is a direct relationship between the catalytic activity of samples and their ECSA value. The ECSA value for the Ni-Co-B/Cu samples electrodeposited at 5, 10, 20, and 40 mA cm⁻² were calculated to be 42.5, 57.5, 255, and 117.5 cm², respectively. Benefiting from much higher ECSA value, the sample deposited at 20 mA cm⁻² can facilitate mass transfer, which can be a big help for electrochemical reactions, especially at high current densities were the reaction in controlled by mass transfer [48]. However, it can be seen that even at low current densities, the sample deposited at 20 mA cm⁻² has lower overpotentials than the other ones (Fig. 5a). This emphasizes its superior intrinsic activity and can be explained considering the effect of each element in the intrinsic activity of samples.

The XPS results can be a help to do so. In the XPS spectra of B (Fig 4d), it can be seen that this element has a small negative charge that may be due to the higher electronegativity of B atoms than Ni and Co. This makes the B atoms preferable places for the adsorption of hydrogen atoms, facilitating the onset of hydrogen production reactions. However, the optimized value of Co and Ni is also important to modify the electronic structure and to provide more suitable sites for the adsorption of hydrogen atoms. As also reported in other studies, the presence of Ni and Co can increase the catalytic performance of TMBs by a synergistic effect [21,49,50].

Considering the trend of changing Co and B composition by increasing the current density (Fig. S1), it can be seen that in the case of the coating deposited at 5 mA cm⁻², the B and Co content is about 6.44 at% and 25.14 at%, respectively. By increasing the electrodeposition current to 20 mA cm^{-2} (the optimized sample), the B content is decreased slightly to 4.37 at% but Co is increased to 31.08 at%. This sharp increase of Co may be the reason why the intrinsic catalytic activity of this sample is higher than the samples deposited at lower current densities, despite the slight decline in B content. So it should be noted that both the alloying elements of B and Co are playing a role in regulating the electronic structure, determining the intrinsic activity. The sample deposited at 40 mA cm⁻² can further support this hypothesis. While it has the highest amount of Co among the others (33.95 at%), the B content (2.14 at%) is about one half of the sample deposited at 20 mA cm⁻². So as can be seen in Fig. 5a, the sample deposited at 20 mA cm⁻², which is benefited from both relatively high B and Co content has the highest catalytic activity.

By comparing the HER activity of the optimized Ni-Co-B/Cu sample with the reported catalytic activity of other TMBs, it can be seen that the fabricated electrode has higher HER activity than many other TMBs (Table S2).

To investigate the kinetics and probable mechanism of HER, the Tafel slopes and exchange current densities of the samples were calculated using their polarization curves. The Tafel plots indicate the relationship between the changes in HER current density and overpotential changes. To obtain the Tafel plots, the linear area of the LSV curves was fitted in the equation $\eta = a + b \times \log j$. In this equation, η is the overpotential, b is the Tafel slope, and a is the equation intercept, which is linked to the exchange current density (j₀). The Tafel slope is an indicator of the kinetics of hydrogen production. The lower Tafel slope indicates greater current density changes with a small change of overpotential, suggesting faster kinetics of hydrogen production on the electrocatalyst surface [51]. As shown in Fig. 5d, the Ni-Co-B/Cu sample deposited at -20 mA cm⁻² current density with a Tafel slope of -125 mV dec⁻¹ has the lowest Tafel slope among the other Ni-Co-B/samples. This optimized Ni-Co-B/Cu sample has also much faster HER kinetics than the Ni-B/Cu sample (Tafel slope = $164 \text{ mV } \text{dec}^{-1}$) and Cu sheet (Tafel slope = 273 mV dec^{-1}).

In addition, the exchange current densities of samples were obtained using the parameter "a" in the Tafel equation. The exchange current density can be considered as a parameter for estimating the intrinsic activity of electrocatalysts in equilibrium conditions. The value of j_0 is obtained at the overpotential of zero, which is directly related to the activation energy of the electrocatalyst surface [52,53]. This parameter can be calculated by extrapolating the linear part of the Tafel plots. Low Tafel slope (b) and high exchange current density (j_0) indicate a desirable electrocatalyst [51]. As shown in (Table S3), the Ni-Co-B/Cu sample deposited at 20 mA cm⁻² with an exchange current density of 0.734 mA cm⁻² has the highest exchange current density among the other samples, which indicates its high electrocatalytic activity.

The faster HER kinetics of the Ni-Co-B/Cu electrode among the other electrodes indicate the role of the optimized amount of Ni, Co, and B elements in regulating the binding of the intermediate HER components to the surface catalyst atoms. This, in turn, results in the facile adsorption of hydrogen atoms, rapid electrochemical reactions, and the ease of hydrogen bubbles release from the catalyst surface.

The Tafel slope was also used as an indicator to determine the HER pathways. The suggested electrochemical reaction paths for hydrogen production are the Volmer, Heyrovsky, and Tafel reactions, which have a Tafel slope of 120, 40, and 30 mV dec⁻¹, respectively. In alkaline solutions, these reactions are specified in the Eqs. (1), (2), and (3), respectively:

$$H_2O + Cat + e^- \rightarrow Cat - H_* + OH^-$$
(1)

$$H_2O + e^- + Cat - H_* \rightarrow H_2 + OH^- + Cat$$
(2)

$$Cat - H * + Cat - H * \rightarrow H_2 + 2Cat$$
(3)

The symbol Cat. in these electrochemical reactions indicates the surface of the electrocatalyst, and H^{*} indicates the hydrogen atom adsorbed on the surface of the electrode [51,54]. Since all the Tafel slopes of the synthesized samples are higher than 120 mV dec⁻¹, The Volmer reaction is rate determining step (RDS) in HER process. According to the Volmer reaction (Eq. (1)), first, the O-H bond of the water molecules is broken, and then atomic hydrogen is adsorbed on the catalyst surface. Afterward, the adsorbed H atoms react with each other, forming hydrogen molecules, which can be released as a bubble.

In order to investigate the rate of hydrogen production on the surface of catalysts more accurately, the electrochemical impedance spectroscopy (EIS) test can be used. This test was taken at overpotentials of -100, -200, and -300 mV vs. RHE for all the samples. The Nyquist plots of the samples and the electrical equivalent circuit (EES) that used to fit the Nyquist curves can be seen in Fig. S4. The model with one time constant for fitting Nyquist curves was selected as the best equivalent circuit. In the mentioned equivalent circuit, R_S is the solution resistance. R_{ct} is the resistance of electric current passage across the contact surface of the electrolyte and the electrode, which can be indicated by the diameter of the Nyquist semicircles. R_{ct} is an important parameter for electrical conductivity and the kinetics of hydrogen production. The C_{dl} of coating was substituted by the constant phase element (CPE) as a result of the non-ideal behavior of the capacitive elements [55,56].

The parameters obtained by fitting the Nyquist curves are shown in Table S4. According to the Nyquist curves and R_{ct} values of different samples in overpotentials of -100, -200 and -300 mV, it can be said that the larger the overpotential, the smaller the diameter of the Nyquist curves are, and so, the R_{ct} value was decreased. This decrease in R_{ct} and the shrinkage of Nyquist semicircles indicate a decrease in hydrogen reduction resistance and thus an in-

crease in hydrogen production kinetics at higher potentials. At the overpotential of -100 mV, the R_{ct} values of the Cu sheet, Ni-B/Cu, and Ni-Co-B/Cu catalysts electrodeposited at 20 mA cm⁻² current density were recorded to be 2609, 127.3, and 121.4 Ω cm², respectively. The small R_{ct} value of the Ni-Co-B/Cu electrode indicates its high hydrogen production kinetics compared to the other samples.

Also, to compare the kinetics of hydrogen production of Ni-Co-B/Cu samples that were electrodeposited at different current densities, their R_{ct} values can be compared (Table S4). One can see that at the overpotential of 100 mV, the samples produced at the current densities of 5, 10, 20, and 40 mA cm⁻² have an R_{ct} value of 370.31, 368.4, 121.4, and 138.6 Ω cm² respectively. Based on the R_{ct} values, the sample electrodeposited at 20 mA cm⁻² has the highest HER kinetics, which is in conformity with the Tafel slopes of the samples. The low amount of R_{ct} of the samples also indicates their high electrical conductivity, which can be due to the good bonding of the coating to the substrate that eliminates the need to use a binder. Various studies have shown that easier transfer of electrons to the catalyst surface can increase the electrocatalytic activity of the electrode [57,58].

3.3. OER electrochemical performance

To achieve a high rate of hydrogen production, both the H_2 evolution and O_2 evolution reactions should occur rapidly on the electrode surfaces. Therefore, the OER electrocatalytic behavior of the Ni-Co-B/Cu samples was also examined in 1 M KOH.

Generally, the intermediate oxygen evolution electrochemical reactions in alkaline electrolytes are suggested as follows [59].

$$M + OH^- \rightarrow MOH + e^-$$
 (4)

$$MOH + OH^{-} \rightarrow MO + H_2O + e^{-}$$
(5)

$$MO + OH^- \rightarrow MOOH + e^-$$
 (6)

$$MOOH + OH^{-} \rightarrow M + O_2 + H_2O + e^{-}$$
(7)

As shown above, OER consists of four intermediate electrochemical reactions that make the overall reaction more complex and sluggish than HER. Firstly, OH^- ions are adsorbed to the active catalyst sites (reaction (4)). Afterward, the adsorbed OH^- ions produce MO according to the reaction (5). The generated MO reacts again with OH^- to produce MOOH (reaction (6)), and eventually, the O_2 molecule is produced as seen in reaction (7).

The LSV curves of the Ni-Co-B/Cu sample synthesized at 20 mA cm⁻², Ni-B sample, and Cu sheet can be seen in Fig. 6a. Regarding the LSV curves and as can be seen in Fig. 6b, the measured overpotentials of Cu sheet at 10 and 20 mA cm⁻² current densities were 558.8 and 623.22 mV, respectively. The weak OER catalytic activity of the Cu sheet was improved significantly by the deposition of Ni-B coating. The values of 340, 366, and 447 mV were recorded for η_{10} , η_{20} , and η_{100} , respectively. Furthermore, by the addition of Co and the fabrication of the Ni-Co-B coating, the OER activity was increased further. The Ni-Co-B/Cu sample fabricated at 20 mA $\rm cm^{-2}$ current shows the best OER activity with η_{10} =276, η_{20} =305, and η_{100} =393 mV. The LSV curves of the Ni-Co-B/Cu samples fabricated at different current densities can also be seen in Fig. 6c, which show that the samples have relatively similar OER activity. The standard deviation of the samples was shown in Table S5.

To investigate the OER kinetics, similar to the HER, the Tafel slope and exchange current densities of the samples were calculated using their polarization curves. Fig. 6d shows that the highest value of the Tafel slope is $235 \text{ mV} \text{ dec}^{-1}$, which is related to



Fig. 6. OER catalytic activity of samples in 1 M KOH a) LSV curves of optimized Ni-Co-B/Cu sample, Ni-B/Cu, and Cu sheet, b) Required overpotentials (in mV) at 10, 20, and 100 mA cm⁻² current densities, c) LSV curves of Ni-Co-B samples electrodeposited at 5, 10, 20, and 40 mA cm⁻² current densities, and d) Tafel plots of different samples.

the Cu sheet and suggests its slow OER kinetic. After coating Ni-B on the Cu sheet, the OER kinetics increased, and the Tafel slope decreased to 137 mV dec⁻¹. All the Ni-Co-B/Cu samples show a higher OER activity than Ni-B/Cu electrode, where the optimum Ni-Co-B/Cu catalyst, synthesized at 20 mA cm⁻², reached the lowest Tafel slope among all the other samples, which was determined to be 88 mV dec⁻¹. The exchange current densities of the samples is also given in Table S6. The reason behind the superior OER activity of this sample can be again found in its unique morphology with the high number of spherical nodules, resulting in a high ECSA value. Moreover, this sample has a high amount of B and Co elements, which is suggested to reduce the OER activation energy [60]. Table S7 also demonstrates that the optimal Ni-Co-B/Cu sample has better OER electrocatalytic activity than many other TMBs fabricated in other studies.

Surface oxidation of the Ni-Co-B electrode during the OER process results in the formation of borates and boron oxides, which can significantly improve the electrocatalytic activity of the OER [61,62]. In addition, the synergistic effect of the simultaneous presence of nickel, cobalt and boron leads to improved electrocatalytic activity for OER [46]. Also, it is generally believed that the presence of metal species with the formation of metal oxyhydroxide /oxyhydrogen are as active sites for adsorption and reaction with OH⁻ ions [27].

3.4. Electrochemical durability

Rather than catalytic activity, electrochemical durability is the other important factor of electrocatalysts. The industrial application of an electrocatalyst is only possible if the catalyst shows high stability in long-time electrolysis. Electrochemical stability of catalysts can be achieved by methods such as measuring voltage changes in constant current density over long periods of time, which is known as chronopotentiometry (CP). The HER electrochemical stability of the optimized Ni-Co-B/Cu electrode was examined by CP test at the current density of -100 mA cm⁻². According to the CP curve (Fig. 7a), the potential changes during 10 h of electrolysis in the 1 M KOH electrolyte is insignificant, and the curve can be said to be constant. This indicates the high HER stability of the sample at high current densities. In addition, the 10 h CP test was also done to evaluate the OER electrocatalytic stability of Ni-Co-B/Cu catalyst at the current intensity of 100 mA cm⁻² for 10 h. As can be seen in Fig. 7b, the overpotential is almost constant



Fig. 7. Chronopotentiometry curves of the optimized Ni-Co-B/Cu sample electrolyzed for 10 hours at the current density of a) -100 mA cm⁻², and b) 100 mA cm⁻². The LSV curves before and after 1000 voltammetry cycles for c) HER and d) OER.



Fig. 8. The LSV curve of the optimized Ni-Co-B/Cu sample when used as both the anode and cathode in 1 M KOH solution.

during the electrolysis, indicating the OER electrocatalytic stability of the sample.

Another way to evaluate the stability of catalysts is to apply 1000 cycles in a specified potential range and compare the polarization curve before and after the application of voltammetric cycles. As can be seen in Fig. 7c and 7d, the polarization curve of the Ni-Co-B catalyst, after performing 1000 CV cycles, has moved only slightly to more negative potentials for HER and only slightly to more positive potentials for OER, which indicates the high stability of this electrocatalyst in the cyclic applications of hydrogen and oxygen production in alkaline environments.

3.5. Overall water splitting

As noted in the previous sections, the Ni-Co-B electrode synthesized in the current density of 20 mA cm⁻² was demonstrated good activity and durability for HER and OER. Therefore, in this part, the catalyst was used as a bifunctional electrode to evaluate its overall water splitting activity in 1 M KOH solution. Fig. 8 shows the polarization curve of the Ni-Co-B/Cu catalyst, which was used as both the anode and cathode. The cell potential was measured to be 1.65 V at the current density of 10 mA cm⁻². This shows the superior catalytic performance of the fabricated Ni-Co-B/Cu



Fig. 9. a) PDOS of the d bands of the Ni-Co-B and Ni-B systems. The Fermi level is set at 0 eV b) Calculated DOS for each element in Ni-Co-B. The Fermi level is set at 0 eV and c) DFT-calculated HER free energy for different sites.

electrode than other similar electrocatalysts such as $Co_2B/CoSe_2$ (1.73 V) [63], Ni-Co-Fe-B (1.81 V) [64], and Co-Fe-B-P (1.68 V) [65].

3.6. First principle calculations

To explore the effects of cobalt alloying on the improvement of the electrocatalytic property of the Ni-B electrode, the density functional theory (DFT) calculations were carried out. For the adsorption energy calculations, the (111) surfaces of Ni-Co-B and Ni-B were modeled with vacuum widths of 15 Å. The d-bands of the Ni-Co-B and Ni-B was compared (Fig. 9a). Results show that incorporating of the Co atoms into the Ni-B system leads to the downshift of the d-band center from -1.661 eV to -1.789 eV. In general, the downshift movement of the d-band center results in low antibonding state energy. Thus, improvement in adsorption of intermediates and consequently higher catalytic activity can be achieved [66]. Fig. 9b shows the DOS of each element in Ni-Co-B. In this catalyst system, the Ni d-orbit and Co d-orbit overlapped which indicates a covalent interaction between Ni atoms and Co atoms. Moreover, a covalent interaction between B, Ni, and Co in the metallic state was indicated by the continuity of the p-orbit of B.

To further understand the enhanced electrocatalytic activity of the Ni-Co-B as compared with Ni-B, the H adsorption on different sites and compare their ΔG_{H^*} values were done. It is well-known that the chemisorption energy of atomic hydrogen to the electrocatalyst surface (ΔG_{H^*}) is determine the HER activity [53]. The ΔG_{H^*} value should be neither too positive (weak hydrogen adsorption), nor too negative (strong hydrogen adsorption), and the optimum value should be close to 0 [67]. As illustrated in Fig. 9c, the value of free energy of hydrogen adsorption uptake for the cobalt site is close to zero ($\Delta G_{H^*} = 0.026$ eV) and it is quite obvious that with the addition of cobalt atoms, not only new active catalytic sites (Co sites) have been added to the system, but also the activity of nickel and boron sites has been increased (based on the lower absolute values of ΔG_{H^*}).

So, in conclusion, the better electrocatalytic activity of the Ni-Co-B electrode is due to the downshift movement of the d-band center and the new active catalytic sites of nickel and cobalt with high electron density, which lead to improved electron donor behavior and thus improve electrocatalytic behavior for HER. The presence of cobalt leads to the enrichment of boron on the electrode surface, which in turn leads to the provision of a large number of electrons on the surface and thus further improves the electrocatalytic activity. Therefore, the presence of cobalt is the most important reason for the better electrocatalytic activity of Ni-Co-B electrode than Ni-B [22,68]. So, the active sites on the surface of the electrode are Ni, Co, and B centers.

4. Conclusion

In a nutshell, the Ni-Co-B coatings were synthesized on a Cu sheet at different electrodeposition current densities. The HER and OER electrocatalytic activity of the synthesized samples were evaluated in 1 M KOH solution. The needed overpotential at -10 mA cm⁻² current density was measured to be -145 mV, showing its high HER activity. Moreover, the catalyst showed high OER activity with a η_{10} of 276 mV. The electrochemical durability of the catalyst was also verified by 10 h electrolysis at high current densities of ± 100 mA cm⁻². The unique microstructure of the optimized Ni-Co-B coating with several spherical micro-nodules was suggested to play a significant role in enhancing the accessible active surface area and, therefore, the catalytic activity. Moreover, the accelerated HER and OER kinetics can be attributed to the existence of an optimized amount of B, Ni, and Co that can facilitate the intermediate reactions. This first report of the bifunctional HER/OER activity of Ni-Co-B alloy that has been synthesized by a facile electrodeposition method can hopefully introduce this catalyst as an affordable candidate for industrial electrolysis.

Credit author statement

A. Jokar: Methodology, Investigation, Resources, Formal analysis, Writing.

A. Toghraei: Methodology, Investigation, Resources, Formal analysis, Writing.

M. Maleki: Methodology, Formal analysis, Writing.

Gh. Barati Darband: Conceptualization, Formal analysis, Writing - Review & Editing, Project administration.

Declaration of Competing Interest

The submitted work described in this article has not been published previously in any form of an abstract or as part of an academic thesis. And it is not under consideration for publication elsewhere. All authors have approved tacitly or explicitly of the submission and the work has been carried out with approval of all authors. We confirm that the submission if accepted, it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the Publisher.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2021.138691.

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