

Article

Advanced Alkaline Water Electrolysis Stack with Non-Noble Catalysts and Hybrid Electrical Connections of the Single Cells

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Abstract: In this research, a thin layer of multi-metallic non-precious catalyst is prepared by electroplating from an electrolyte bath containing Ni, Co, and Fe sulfates over pressed commercial nickel foam electrode. The composition of the deposited catalytic film and its morphology are characterized by scanning electron microscopy (SEM) with energy dispersion X-ray (EDX) techniques. The efficiency of the prepared binder-free electrodes for electrochemical water splitting is investigated in a self-designed short water electrolysis stack with zero-gap configuration of the integrated single cells and hybrid electrical connections. The separator used is a commercial Zirfon Perl 500 membrane, doped with 25% KOH. The performance of the catalyst, the single cells, and the developed electrolyzer stack are examined by steady state polarization curves and stationery galvanostatic stability tests in the temperature range 20 °C to 80 °C. The NiFeCoP multi-metallic alloy demonstrates superior catalytic efficiency compared to the pure nickel foam electrodes and reliable stability with time. The single cells in the stack show identical performance and the cumulative stack parameters strictly follow the theoretical considerations. The applied hybrid electrical connections enable scaling of both the stack voltage and the passing current, which in turn ensures flexibility with regard to the input power and the hydrogen production capacity.

Keywords: electrodeposited catalysts; hydrogen generation; water electrolysis; advanced stack design



Citation: Borisov, G.; Bachvarov, V.; Rashkov, R.; Slavcheva, E. Advanced Alkaline Water Electrolysis Stack with Non-Noble Catalysts and Hybrid Electrical Connections of the Single Cells. *Catalysts* **2024**, *14*, 179. <https://doi.org/10.3390/catal14030179>

Academic Editor: Yurii V. Geletii

Received: 16 February 2024

Revised: 1 March 2024

Accepted: 2 March 2024

Published: 4 March 2024



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1. Introduction

The hydrogen economy stands as a powerful instrument for reducing global carbon emissions and advancing sustainable energy solutions. The versatile applications of hydrogen across different sectors, including transportation, industry, and power generation, position hydrogen as a versatile and clean energy carrier. The inherent potential of hydrogen lies in its ability to store and transport energy efficiently, serving as a clean alternative to conventional fossil fuels. Moreover, the use of green hydrogen, produced through renewable energy sources, holds particular significance in mitigating environmental impact on the pathway to net-zero industry. The ongoing advancements in hydrogen production technologies, such as electrolysis powered by renewable energy, contribute to establishing a more resilient and sustainable energy infrastructure.

Electrochemical water splitting is the cleanest method for production of hydrogen for the needs of a hydrogen economy, which compared to natural gas conversion offers advantages such as high purity (>99.999%) of the produced hydrogen, lack of harmful emissions, simplicity, and compact size, as well as low maintenance of the system [1–4]. Water electrolysis, together with batteries and pumped hydroelectric power stations, is considered as one of the key technologies for storage of renewable energy. Among the existing variations of the technology, alkaline water electrolysis is the most mature, robust, and cost-efficient as it uses cheap construction materials (stainless steel, nickel-plated steel) and non-noble electrocatalysts (Ni and Ni-based multicomponent alloys) [5–7]. The

electrolyte used is concentrated alkaline aqueous solution (25–32% of KOH or NaOH) in which water splitting proceeds according to the overall reaction (1):



On the cathode, the water is reduced to hydrogen and hydroxyl ions according to (2):



The obtained hydroxyl groups move through the electrolyte reaching the anode and are oxidized producing oxygen according to (3):



Generally, traditional alkaline electrolyzers exhibit elevated internal ohmic resistance, primarily due to restricted OH^- ionic transport from the cathode to the anode in the liquid electrolyte. To maintain efficiency, these electrolyzers are typically operated at low current densities, approximately $0.2 \text{ A}\cdot\text{cm}^{-2}$. Therefore, to achieve high hydrogen production capacity large and heavy systems are required [8,9]. To overcome this disadvantage, an improvement in the cell design known as a “zero gap” cell has been proposed [10–13]. It is presented schematically in Figure 1.

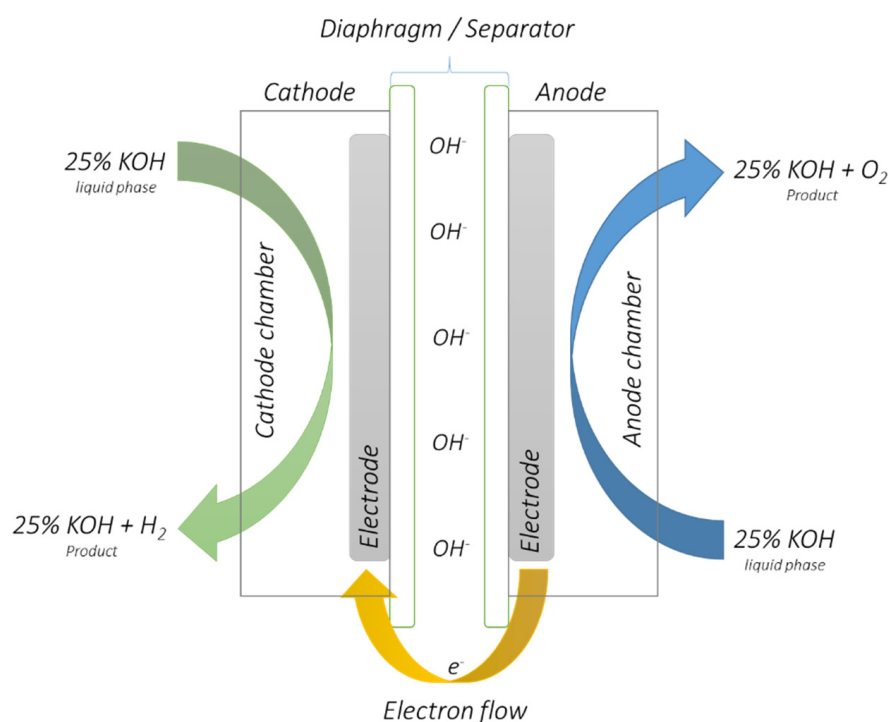


Figure 1. Principle scheme of the advanced “zero gap” cell configuration for alkaline water electrolysis.

The anode and cathode in the single “zero gap” cell are highly porous electrodes (usually foam Ni or Ni-plated stainless-steel foam) pressed on both sides of a hydroxide ion-conducting membrane which serves as a gas separator. The membrane is doped with concentrated alkaline electrolyte (20–30 wt.% KOH). The gap between the electrodes is equal to the thickness of the membrane (usually less than 0.5 mm compared to 2 mm or more that is the typical gap size in classical alkaline electrolysis). The gap reduction significantly reduces the ohmic resistance of the electrolyte. The optimal performance of the advanced “zero gap” cell is achieved at a low differential pressure between the cathode and anode compartments, elevated operating temperature in the range 60–80 °C, and constant circulation of the electrolyte in both the anode and cathode compartments to

prevent depletion of the reagent and drying of the membrane [14]. This type of advanced “zero gap” electrolyzers have faster response to the input power compared to the classical ones and are well compatible with renewable energy sources. However, at too high current densities the energy efficiency of the system may decrease since the produced gases (hydrogen and oxygen) in the flow field of the bipolar plates block part of the circulated electrolyte, thus impeding the rate of the partial electrode reactions and the efficiency of the electrolysis, which in turn increases the electrodes’ overpotential and could trigger degradation processes. Moreover, under these conditions the reagent is depleted very fast since the KOH in the doped membrane is in a limited volume. At high temperatures (above 80 °C depending on the type of the separator used), the balance is much more complicated because the electrolyte evaporation occurs gradually. Another construction problem is the uneven temperature distribution. The cells located in the middle of the electrolyzer stack overheat during long term operation which leads to corrosion phenomena and decreased performance. Therefore, further improvements of the system components including the type of catalyst, electrode architecture, and design and construction of the electrolysis stack are still required in order to increase the efficiency, the hydrogen production capacity, as well as the flexibility of the system with respect to intermittent renewable power.

The cell voltage is the driving force of the electrolysis and a key factor affecting the electrodes’ stability and durability, while the current density depends on the kinetics of the partial electrode reactions and determines the hydrogen production rate. In the case of zero-gap generators, in similarity to the alkaline water electrolyzers the typical operating cell voltage falls within the range of 1.8 V to 2.6 V. Usually, the single cells are connected in series based on their bipolarity. In such a case, the stack voltage increases with the increased number of the integrated cells. Figure 2 shows the electric scheme of two single “zero gap” cells connected in series.

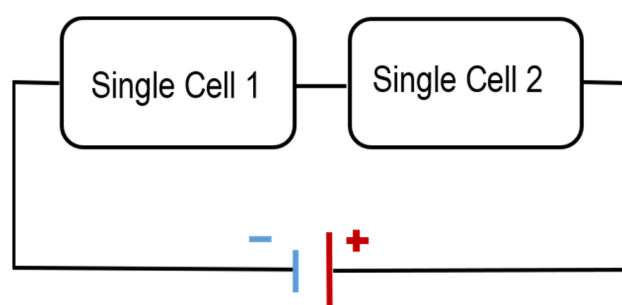


Figure 2. Electric scheme of two single cells (SC) connected in series.

The resulting voltage, current, and power of that short stack are expressed as follows:

$$U_{\text{stack}} = U_{\text{SC1}} + U_{\text{SC2}} \quad (4a)$$

$$I_{\text{stack}} = I_{\text{SC1}} = I_{\text{SC2}} \quad (4b)$$

$$P_{\text{stack}} = U_{\text{stack}} \times I_{\text{stack}} \quad (4c)$$

In the case of parallel connection schematically presented in Figure 3, the current density of the short stack is scaled twice, while the cell voltage keeps constant:

$$U_{\text{stack}} = U_{\text{SC1}} = U_{\text{SC2}} \quad (5a)$$

$$I_{\text{stack}} = I_{\text{SC1}} + I_{\text{SC2}} \quad (5b)$$

$$P_{\text{stack}} = U_{\text{stack}} \times I_{\text{stack}} \quad (5c)$$

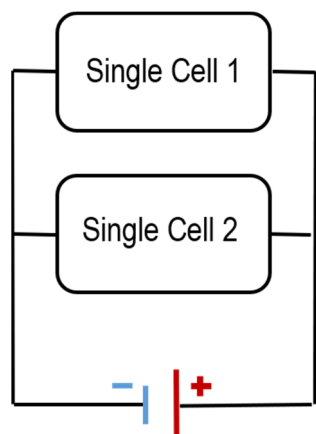


Figure 3. Electric scheme of two single cells (SC) connected in parallel (the combination is further called “Dual cell” (DC)).

The approach undertaken in this study is to use a hybrid electrical connection between the single cells in the stack, namely, to connect a defined number of pairs of single cells connected in parallel denoted as “Dual Cells” (DCs) in series. Figure 4 illustrates this type of hybrid circuit for the simplest case of an electrolysis stack with two Dual Cells, respectively, with four SCs. In this case the voltage, current, and power of the stack are expressed as follows:

$$U_{\text{stack}} = U_{\text{DC1}} + U_{\text{DC2}} \quad (6a)$$

$$I_{\text{stack}} = I_{\text{DC1}} = I_{\text{DC2}} \quad (6b)$$

$$P_{\text{stack}} = U_{\text{stack}} \times I_{\text{stack}} \quad (6c)$$

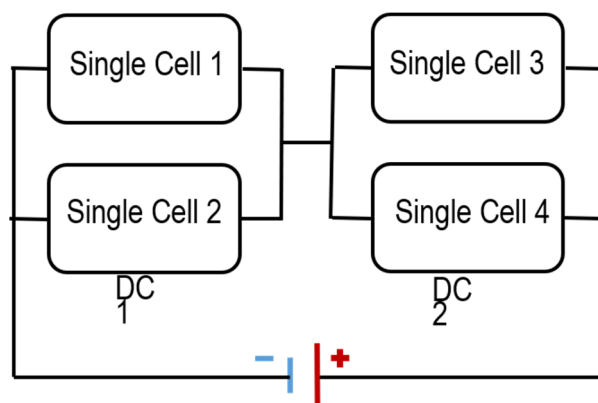


Figure 4. The “hybrid” electric scheme of two Dual Cells integrated in a short electrolysis stack.

The hybrid connection of the cells offers the possibility to increase the voltage of the stack and at the same time to duplicate the current density and the hydrogen production capacity, respectively, without detrimental effects on the electrodes’ durability due to increased overvoltage.

One of the most important issues for technically and economically efficient hydrogen production is the electrode material. The higher the catalytic activity of the electrode material, the lower the overpotential, consequently the lower the energy consumption of the electrolysis. Therefore, the availability of efficient nonprecious catalysts for the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) is essential in order to accelerate the sluggish electrochemical kinetics and achieve cost-effective production of green hydrogen via water electrolysis.

Precious metals such as Pt, Ir, Ru, their alloys, and/or mixed oxides are known to be the most efficient electrocatalysts. Many researchers have used alloying between these

expensive materials in order to decrease overpotential and increase the efficiency of the substrates. The detailed parameters of such types of catalyst are presented in [15,16]. However, they are also expensive and not abundant in nature and belong to the group of critical raw materials. In order not only to reduce the energy barrier of the electrochemical water splitting process but also to achieve a beneficial economical effect, more cost-efficient electrocatalysts are needed. Transition-metal-based catalysts such as Ni, Fe, Co, their alloys, oxides, sulphates, and nitrides are well known for their high electrocatalytic activity in terms of HER and OER in alkaline media [17–20]. They have been intensively studied for decades and are considered as the most promising alternative to noble metal catalysts. It has been demonstrated that due to their flexible composition and tunable electronic structures catalytic efficiency can be essentially boosted by applying various design-optimizing strategies. Different more or less sophisticated optimization approaches have been invented and applied. Generally, there are two basic strategies used to design superior electrocatalysts. One way is to improve the intrinsic activity, while the other is to enhance the number of accessible active sites through increased loading or tuned catalyst nanostructure. Other strategies such as surface modification, defect and strain engineering, and controlling nanoparticle segregation have been also successfully used and reported [21]. An important issue is also the reliability and reproducibility of the method used for preparation of the catalysts and for their integration in the structure of the electrodes so as to enable a highly developed active surface and long-lasting mechanical stability. Depending on the methodology of synthesis and operational parameters, the morphologies and particle sizes of the catalysts can be easily controlled. Electroplating is among the variety of well-established methods for catalyst preparation such as sol-gel, hydrothermal, pyrolysis, etc. It is a simple, convenient, and effective approach to prepare self-supported and easily scalable catalysts with precisely controlled composition, thickness, morphology, and robust structure. The electrodeposited layer follows completely the texture of the substrate and the catalytic loading can be controlled just by varying the current density and the deposition time.

Although significant progress has been made on the development of various combinations of multicomponent transition metal catalysts, the requirements of their large-scale applications in hydrogen production, such as low over-potentials, structural stability, long-term performance, etc., have not been met yet and further improvements are still required.

Based on all these considerations, in this study a multicomponent NiFeCoP thin film is electroplated on pressed Ni foam electrodes and investigated as a water splitting catalyst (both in HER and in OER) initially in a single “zero gap” electrolysis cell and afterwards in a short stack with a hybrid electric circuit. The goal is to verify the feasibility of the developed stack design and assess the efficiency and sustainability of electrolysis at varying operational regimes.

2. Results and Discussion

The electrochemical properties of the electroplated NiFeCoP alloy, its stability, and corrosion resistance are studied in detail and reported in previously published papers [22,23], where its catalytic efficiency has been unambiguously proven. Herein, the performance of this catalytic layer deposited on Ni foam is investigated in a laboratory electrolysis cell with “zero gap” configuration and in a short electrolyzer stack with the above-described hybrid electrical connections.

The results of SEM and EDX analysis of the electrochemically deposited NiFeCoP alloy on pressed nickel and copper foams are presented in Figure 5. The image in Figure 5a shows the characteristic globular morphology of the NiFeCoP coating. It is seen that the morphology of the electrodeposited layer strictly follows the texture of the substrate, penetrating in depth its volume, and thus increasing the active surface available for the partial electrode reactions of the electrolysis. The catalyst is tightly anchored on the Ni foam substrate (serving also as a current collector) which is a prerequisite for structural stability and durability of performance.

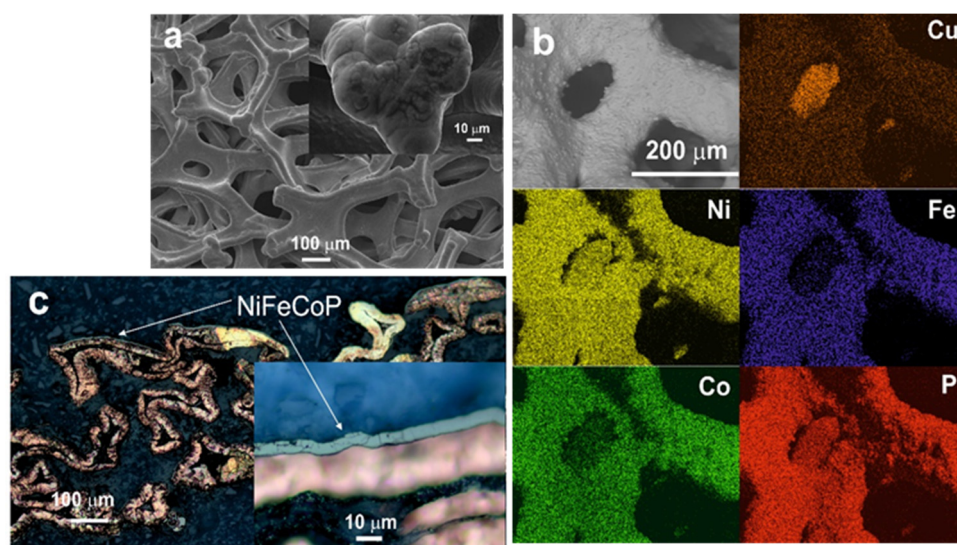


Figure 5. (a) SEM image of NiFeCoP on Ni foam; (b) elemental EDX mapping of Ni, Fe, Co, P of the NiFeCoP alloy on Cu foam; (c) cross-section of NiFeCoP film on Cu foam.

In order to examine the alloy composition and distribution of different elements in the alloy, eliminating the influence of nickel from the substrate, a sample of alloy deposited on Cu foam substrate is also investigated by Energy Dispersive X-ray analysis (Figure 5b). The determined alloy composition in weight percentages is as follows: Ni—66 wt.%, Fe—6 wt.%, Co—13 wt.%, and P—15 wt.%. The elemental EDX mapping of the NiFeCoP coating shows uniform distribution of the components on the film. Moreover, the alloy is deposited not only on the substrate surface—it penetrates inside its volume as is illustrated in the cross-section of the electroplated coating on a pressed Cu foam (Figure 5c). The thickness of the film varies between 2 μm inside the volume of the foam to 4 μm on the surface of the substrate.

In Figure 6 are compared the voltampere characteristics of two single electrolysis cells—one with pure Ni foam electrodes (both anode and cathode) and another with NiFeCoP electrodes (both anode and cathode). Both U/j curves show linearity in a wide experimental voltage range. The electrochemical water splitting in the cell with the bare Ni foam electrodes starts at a cell voltage of 1.65 V and the process gradually intensifies. The current density reaches a value of $0.2 \text{ A} \cdot \text{cm}^{-2}$ at a cell voltage of 2 V. The electrodeposited alloy demonstrates much better catalytic efficiency than the bare Ni foam. The electrolysis starts much earlier, at 1.45 V, and the current density reaches $0.2 \text{ A} \cdot \text{cm}^{-2}$ already at 1.65 V, i.e., the overvoltage in the case of the electrodes with the self-supported electroplated catalyst is about 0.4 V lower. Since the morphology and the active area of both investigated electrodes (Ni foam and NiFeCoP deposited on Ni foam) is identical, the enhanced performance should be ascribed to the chemical nature of the multicomponent electroplated catalyst and the occurrence of interatomic and/or interelectronic interaction between its components. The electronic interactions between the components of the alloy may result for instance in optimal proton adsorption and M–H bond strength regulated by the negatively charged P. At the same time, the transition metals are readily oxidized forming oxide layers which function as catalytic sites for the OER with reduced energy barriers. As a consequence, bifunctional activity of the electroplated NiFeCoP alloy and enhanced water electrolysis performance can be achieved. In addition, the achieved high current density at relatively low voltages could be explained by the good electrical conductivity of the binder-free electroplated catalyst.

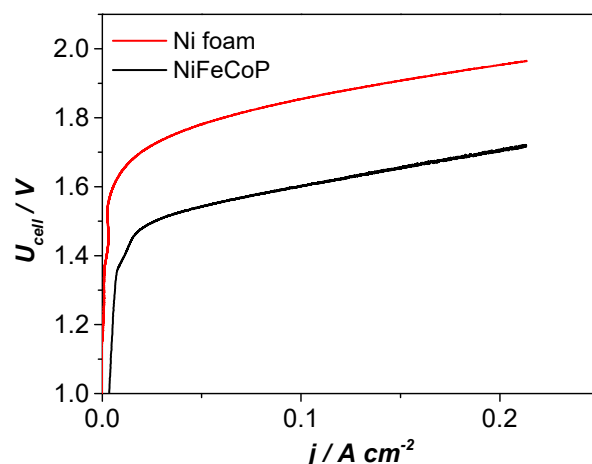


Figure 6. Performance of a single “zero gap” electrolysis cell with Ni foam electrodes and with electrodeposited NiFeCoP alloy in 25% KOH; potential scan rate 1 mV s^{-1} ; room temperature.

In a further experiment, two identical “zero gap” single cells with NiFeCoP electrodes, having a geometric area of 5 cm^2 and Zirfon Perl 500 separator, are connected in parallel, forming the so-called “Dual cell” (see Figure 3) to increase the hydrogen generation capacity. The results obtained are presented in Figure 7.

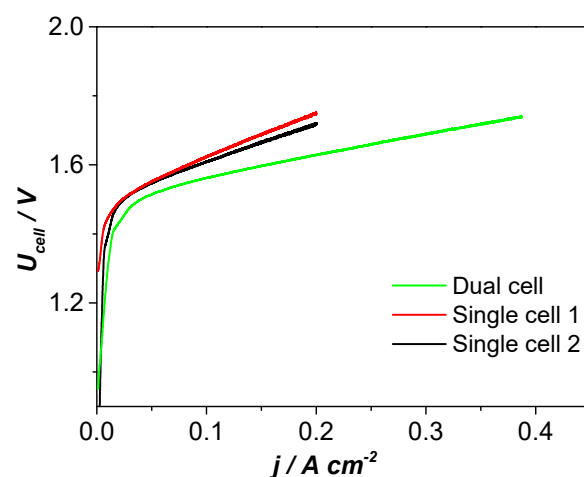


Figure 7. Performance of a laboratory “Dual Cell” with NiFeCoP electrodes (both anode and cathode) in 25% KOH; potential scan rate 1 mV s^{-1} ; room temperature.

Both single cells assembled in a “Dual cell” configuration show identical electrochemical performance with very similar voltampere characteristics. The results obtained are in accordance with the theoretical considerations described by Equations (5a)–(5c). The cumulative U/j curve of the Dual Cell results in twice as high a current density, which in turn should double the quantity of the hydrogen generated at constant cell voltage. The power of the electrolyzer is also doubled in accordance with Equation (5c). The electrochemical performance of each cell strongly depends on the ohmic losses, the MEA architecture, electrolyte distribution in the diaphragm/separator, and the amount of gas bubbles produced and accumulated on the electrode surface. These effects and their correlations to the performance of the electrolyzer are discussed in detail in the literature [11–14,24]. Herein, the focus of the research is put on the effect of hybrid electrical connection and the so-called “Dual Cell” approach.

In order to increase the voltage of the short stack, a second “Dual cell” is connected in series to the first one and the performance of the thus designed short electrolyzer stack is evaluated under identical experimental conditions. The results obtained are presented in

Figure 8. It can be seen that the U/j characteristics of both DCs coincide demonstrating the ideal reproducibility of the applied electrode preparation procedure and the single-cell assembling. The construction of the short stack with two DCs enables an increase in the operating voltage (the stack voltage is twice as high as the cell voltage of each DC in accordance with Equation (4a) and at the same time the current density is doubled following Equation (5b). By further multiplication of the number of DCs integrated in the stack, it is possible to adjust the stack parameters on demand, e.g., to enlarge the stack in accordance with the available renewable power and the desired hydrogen production capacity.

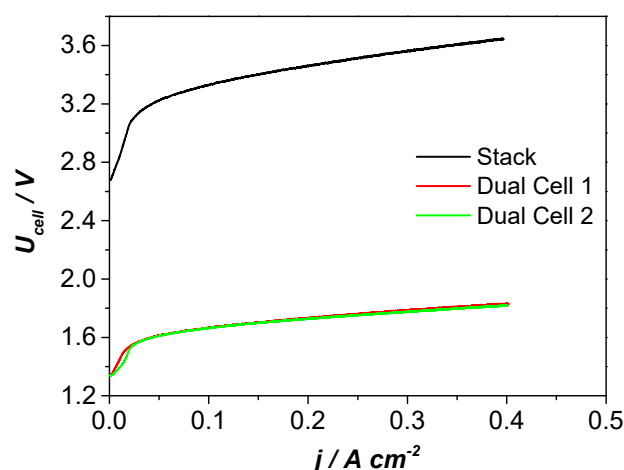


Figure 8. Performance of laboratory electrolyzer stack with two DCs connected in series; NiFeCoP electrodes; 25% KOH; potential scan rate 1 mV s^{-1} ; room temperature.

The operation of the stack at elevated temperatures generally leads to a decrease in the activation energy and facilitates the kinetics of electrochemical water splitting. At the same time, the increase in temperature results in a decrease in electricity consumption keeping the hydrogen production more efficient [25,26]. In this study, the performance of the developed “zero gap” Dual Cell short electrolysis stack at elevated temperature is also studied. The temperature control is realized by circulating heated electrolyte through each single cell of the stack using an auxiliary peristaltic pump. The results obtained are shown in Figure 9. As expected, the increase in the operating temperature leads to an increase in the current density, and thus to higher hydrogen production capacity. The slope of the U/j curves decreases with temperature which indicates the decrease in the ohmic resistance and activation energy of the water splitting process.

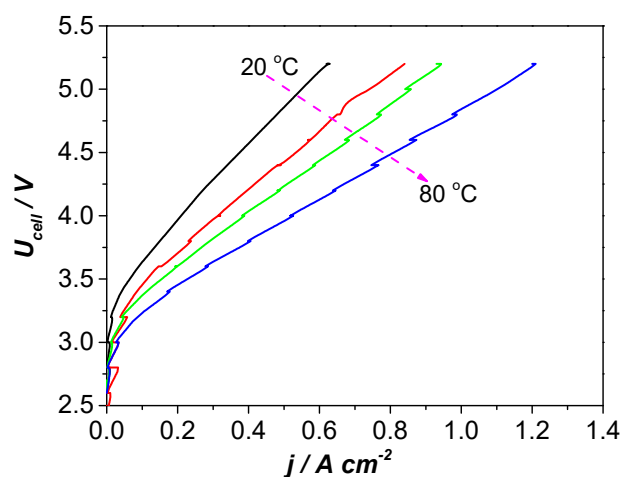


Figure 9. Performance of the developed short electrolysis stack in 25% KOH at elevated temperatures; potential scan rate 1 mV s^{-1} .

Finally, the performance of the stack over time is investigated by applying dynamic stress tests using an NI6008 DAQ recorder (Farnell, Bulgaria). The procedure includes a stepwise increase in current density with step of $100 \text{ mA}\cdot\text{cm}^{-2}$ as at each step the current is held constant for a period of 180 s. The measurements are carried out at 80°C . The results obtained are presented in Figure 10. They show a stable response of the stack cells' voltage with increasing current in the whole range tested (starting from $100 \text{ mA}\cdot\text{cm}^{-2}$ up to $600 \text{ mA}\cdot\text{cm}^{-2}$) and identical performance of both Dual Cells. No initiation of any degradation phenomena was detected; however, it should be noted that this is a short-term experiment and further much longer tests are required to make substantiated conclusions.

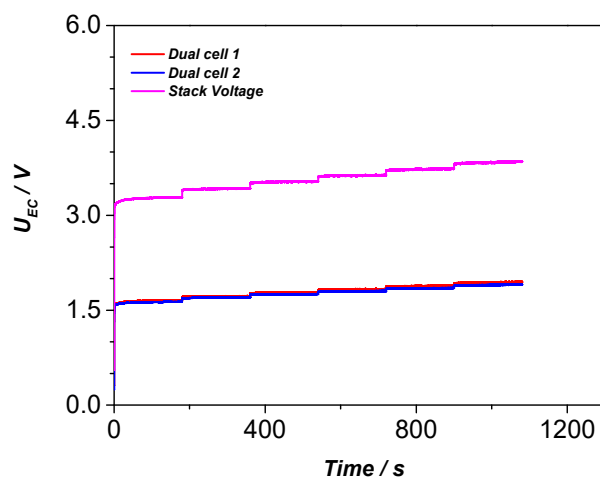


Figure 10. Stack performance in 25% KOH at 80°C under dynamic galvanostatic stress test conditions.

In general, at this stage the research performed proved that the proposed stack design ensures homogenous distribution of reagents, temperature, and current flows over the electrode surface of all integrated single cells. No local increase in the operation temperature was observed, nor a sharp deterioration in the volt-ampere characteristics of any of the four single cells integrated in the stack (two DCs), which is a prerequisite for their sustainable simultaneous operation. The stack design offers reliable performance and flexibility with respect to intermittent renewable energy. Further research is in progress focused on the scaling up of the electrode surface as well as on the number of integrated DCs in the device to achieve practically reasonable values of stack voltage and hydrogen generation capacity.

3. Materials and Methods

The NiFeCoP alloy is electrochemically deposited under galvanostatic conditions ($10 \text{ A}\cdot\text{cm}^{-2}$; duration 5 min). Pressed nickel and copper foams are used as catalyst substrates. Before deposition, the Ni and Cu foams are etched in 20% H_2SO_4 and HCl 1:1, respectively, to remove surface oxides, and then washed with distilled water. The electroplating bath contains Ni, Co, and Fe sulfates as well as complexing agents. Detailed information about the conditions of the electrodeposition process and electrochemical properties of the film is reported elsewhere [27]. Herein, the morphology of the obtained multi-metallic alloy, the distribution of the elements, and the thickness of the coating are examined by scanning electron microscopy (SEM) with energy dispersion X-ray (EDX) by means of JEOL JSM 6390 with INCA Oxford software (1.4 version) and optical microscopy (Acvahim, Bulgaria, Sofia, official representer of ZEISS Microscopy), respectively.

Although numerous HER catalysts with excellent performance at high current density have been reported, there are few catalysts for water electrolysis that can truly perform well as bifunctional catalysts. In this study, identical electrodes with self-supported binder-free electroplated NiFeCoP alloy on pressed nickel foam with a geometric surface area of 5 cm^2 are used both as anode and cathode. The electrodes are integrated in a single electrolysis cell with “zero gap” configuration and in a short four-cell electrolysis stack with

hybrid electrical connections as shown in Figure 4. The diaphragm/separator between the anode and cathode departments of each single cell is a commercial membrane Zirfon Perl UTP 500 with average thickness of 0.5 mm doped with 25%KOH having approximately zero cross-over under no differential pressure conditions [22]. The electrodes and the separator are integrated in the cells applying an optimized mechanical strength of 12 Nm on the current collectors and the end-plates of the stack. The applied compression leads to 25% deformation of the Zirfon Perl 500 which does not deteriorate the electrochemical performance. The electrolyte used is a 25% KOH which circulates in the cells by means of an auxiliary peristaltic pump with 10 mL/min in volume for each cell up to 25 mL. The evolved hydrogen and oxygen are taken out of the cell with the circulating electrolyte. Two reservoirs are used for each gas outlet. The temperature control of the entire installation is ensured by the circulation of heated water in the housing of the stack.

The cell and stack performances during electrochemical water splitting are investigated by recording a quasi-steady state polarization curve with potential scan rate of 1 mV s^{-1} . The experiments are carried out in a self-designed cell and in a short lab-scale stack (Utility model, 41466U1/03062021) in operating temperature range $20\text{--}80^\circ\text{C}$ and constant flow of 25%KOH electrolyte in each single cell of the stack. The picture of the developed prototype is presented in Figure 11. All electrochemical measurements are performed using POS 2 Bank Elektroniks Potentiostat/Galvanostat and a Voltcraft PPS 1600 power supply equipped with a National Instruments data logger NI6008.

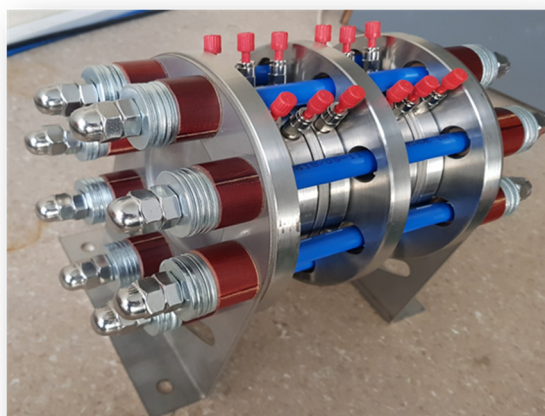


Figure 11. Picture of the advanced alkaline water electrolyzer, Utility model 41466U1/03062021.

4. Conclusions

In this research, an advanced short “zero gap” electrolyzer stack with four single cells and hybrid electrical connection is developed. The proposed “Dual Cell” design is facile and scalable and enables flexibility of the stack size by multiplying the number of integrated DCs aiming at better adjustment to the intermittent energy from renewable sources. It contributes to the development of lower-cost, highly efficient, and stable non-noble metal electrocatalysts prepared by means of the easily handled and highly reproducible electroplating method. The multi-metallic NiFeCoP alloy under study with homogenous element distribution is successfully electrodeposited from an electroplating bath based on Ni, Co, and Fe sulfates over commercial Ni foam electrodes. The catalyst demonstrates enhanced catalytic efficiency for alkaline water electrolysis compared to the pure Ni foam electrodes, excellent reproducibility, and sustainable efficiency both at room and elevated temperatures. The achieved high performance of the developed electrolyzer stack with NiFeCoP catalyst integrated both on the cathode and the anode, namely a current density of 0.6 A.cm^{-2} at cell voltage of less than 2.0 V at 80°C , is very promising and gives credence to consider this electroplated alloy as a potentially favorable bifunctional electrocatalyst for electrochemical water splitting and production of green hydrogen.

Author Contributions: Conceptualization: E.S. and G.B.; methodology: G.B. and V.B.; validation: G.B., R.R. and V.B.; writing—original draft preparation: G.B. and R.R.; writing—G.B. and E.S.; visualization: G.B. and V.B.; supervision: E.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Bulgarian Ministry of Education and Science under the National Research Program “Low Carbon Energy for the Transport and Households” (E+), grant agreement D01-214/2018. Part of the experiments were performed using the equipment of Research Infrastructure “Energy Storage and Hydrogen Energetics” (ESHER), granted by the Bulgarian Ministry of Education and Science, grant agreement № Д01-161/28.07.2022.

Data Availability Statement: The data pertaining to the results presented in this article are considered of significant proprietary interest. Unfortunately, we are unable to provide direct access to these results as they fall under the purview of financial support programs. Permission to disseminate or share these results can only be granted by the respective financial organization responsible for the funding.

Conflicts of Interest: The authors declare no conflicts of interest.

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