A significant improvement in material of foam

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ABSTRACT

In investigation of different materials for electrodes used in electrolysers for hydrogen production, nickel foam shows wide interests in hydrogen scientific community. This paper brings novel results of performed experiments on pure nickel foam and nickel foam silver coated. The electrochemical behavior of chosen material in high concentrated alkaline media was studied using potentiostatic and potentiodynamic DC and AC electrochemical methods: linear polarization, electrochemical impedance spectroscopy. It was shown that using silver coatings enable higher hydrogen generation. There is defined linear region of the hydrogen production with evidence that an increasing of the electrodes overvoltage decreases the resistance to the charge transfer.

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1. Introduction

Investigations focused on hydrogen as the fuel are mostly oriented on possibilities of the system efficiency improvement [1–4]. As long as there does not exist hydrogen as a free element on the earth, it has to be produced. Energy needed for the process of hydrogen production can be used from the renewable energy sources (RESs), i.e. direct conversion of solar energy into electrical energy using photovoltaic modules [3,5–10]. The oldest process for hydrogen production is the process of water electrolysis where the most important component of the system is the type of a chosen material for the electrodes design. Nickel (Ni) is a frequently used material in hydrogen generation process because of its good properties both as the catalyst and the electrode [11–15]. It is founding in forms of a bulk, the foam, a raney, a mesh and different alloys. The investigations for comparison of the bulk and pure foam have been already done where obtained results gave improved process using pure foam [13]. As the progressive continuation of that author's work, in this investigation experiments, both on the pure Ni foam and Ni foam silver (Ag) coated, were performed. It was chosen Ag because of its highest electrical conductivity in the comparison to the other elements in a high concentrated alkaline media. Experimental setup used for the experiments of hydrogen evolution reaction (HER) was designed as the three electrodes system with electrolyte of 25% KOH alkaline solution in all performed measurements. An improved catalytic activity of a three dimensional (3D) Ni foam is attributed to the increased active surface area. This work is realized to achieve the wanted goal of system efficiency increasing. In accordance with that wanted goal the measurements were carried out to define electrodes parameter related to the electrolysers operation. A behavior of the investigated material was studied using potentiostatic and potentiodynamic Direct current (DC) and Alternating Current (AC) electrochemical methods. The applied methods were Brunauer–Emmet–Teller (BET) method, Direct Current Electrochemical Methods (DCEMs), Electrochemical Impedance Spectroscopy (EIS), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) [16–20].

2. Methodology

The used methodology was chosen after preliminary definition of the needed parameters to investigate the effect of the coated foam. According to the wanted goals, DC and AC methods were defined. An active surface area of the foam needed to be defined using combination of measurement and calculation. A BET theory was developed in 1938 named by the author's last names initials: Stephen Brunauer, Paul Hugh Emmet and Edward Teller. It is the first method for specific surface measurements of finely divided and porous solids. Its application is based on adsorption of gas on the surface [21]. An analysis gas for described measurement was nitrogen (N_2). These measurements were carried out using device of Micromeritis, Asap 2000. The surface morphology and chemical composition of the foam were determined using a VEGA TESCAN TS 5136 MM Scanning Electron Microscope equipped with Oxford Instruments INCA energy dispersive spectroscopy. Electrochemical measurements were carried out in accordance with the requirements of ASTM standard of G 102-89 [22]. The preferred characterizations of the foam both pure and Ag coated were performed out using a device of EG&G PAR 273A Potentiostat/Galvanostat. A standard electrochemical reactor was consisted of the graphite counter electrode, reference saturated calomel electrode (+0.2415 mV) and working electrode of

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Table 1
Silver deposition solution.

Component	Concentration (M)	Total time (min)
AgNO₃	0.1	
Ammonia	1.83	
Acetic acid	0.73	10
Hydrazine-hydrate	0.1	
Additives	<0.01	

Table 2
Summary report of BET method measurements.

Type	Active surface area ($m^2\,g^{-1}$)
BET	1.9710
Single point at P/Po 0.2002	0.8095
BJH cumulative adsorption of pores between 17 and 300.000 nm diameter	1.1083
BJH cumulative desorption of pores between 1.7 and 300.000 nm	1.1488

active surface area of 1 cm². The experiments were carried out using an electrolyte of 25% KOH alkaline solution of 14pH at the ambient temperature of 22 ± 2 °C. The Tafel curves were recorded in the potential range of ±250 mV from the open circuit potential with a rate of potential change of the 0.5 m V s⁻¹. Applying a method of Tafel extrapolation, values of wanted parameters were calculated according to the Stern–Geary equation written below [23].

$$I_{corr} = (B \times \Delta i)/\Delta E \tag{1}$$

$$B = (b_a \times b_c)/[2.3 \times (b_a + b_c)] \tag{2}$$

where i_{corr} (mA cm⁻²) is corrosion current density; B (V) is Stern–Geary constant; Δi (mA cm⁻²) is corrosion current density change; ΔE (V) is potential change; b_a (mV decade⁻¹) is anodic slope of Tafel curve; b_c (mV decade⁻¹) is cathodic slope of the Tafel curve.

The corrosion potential was recorded for 500 s. During this time DC polarizations have been carried out at 10 mV min⁻¹ scan rate (≈0.17 mV s⁻¹). The measurements were performed using a device of EGG Instruments, Model 5210, Lock-in Amplifier.

3. Experiments

The previous investigations of the author have proven Ni foam as the material the most suitable for the process of water electrolysis in all levels of the experiments. Because of its porosity, the amount of produced hydrogen is higher in the comparison to the produced hydrogen using Ni solid electrodes at the same conditions. According to that, in this work were performed experiments on the foam with same characteristics but improved with Ag coating on its surface. These measurements were carried out as the continuation of the previous work to define parameters which directly take effects on the electrolyser operation [13]. The electrodes material used for the experiments was pure Ni foam (active surface area: 1510 cm²; density: 0.681 g cm⁻³ with porosity of 95–99% and nominal pore diameters of 600 μm, manufactured by Mitsubishi Materials Corporation, Japan) and Ni foam Ag coated (active surface area: 1531 cm²; density: 0.6905 g cm⁻³). The Ag layers were coated from AgNO₃ based solution via electroless deposition method. Ammonia and acetic were used as a buffer to adjust the pH in the range from 10 to 10.6. In this solution metal ions of Ag were directly reduced into pure Ni foam by the involving of reducing agent of hydrazine-hydrate. A detailed bath composition is specified in Table 1.

As long as it is used porous material, there is a need to define and calculate an active surface area. In this work, active surface area was measured and calculated via BET method. The foam was prepared as the samples of 5 × 5 × 2 mm with overall minimum weight of 1 g. The surface morphology of the foam was characterized and defined via SEM as well as chemical structure observed via EDS. For these measurements of SEM, EDS, DCEM and EIS the foam was prepared as sample of 10 × 10 × 2 mm what matches to the 1 cm² of geometrical surface area.

4. Results and discussion

All given results are in the accordance with wanted goals of the system efficiency increasing by using materials of improved performances. The important role in an increasing of electrolysers efficiency plays the active surface area which is proportional related to the hydrogen production. According to that, involving of the porous materials gives much larger active surface area in comparison with nonporous materials at the same geometrical surface area.
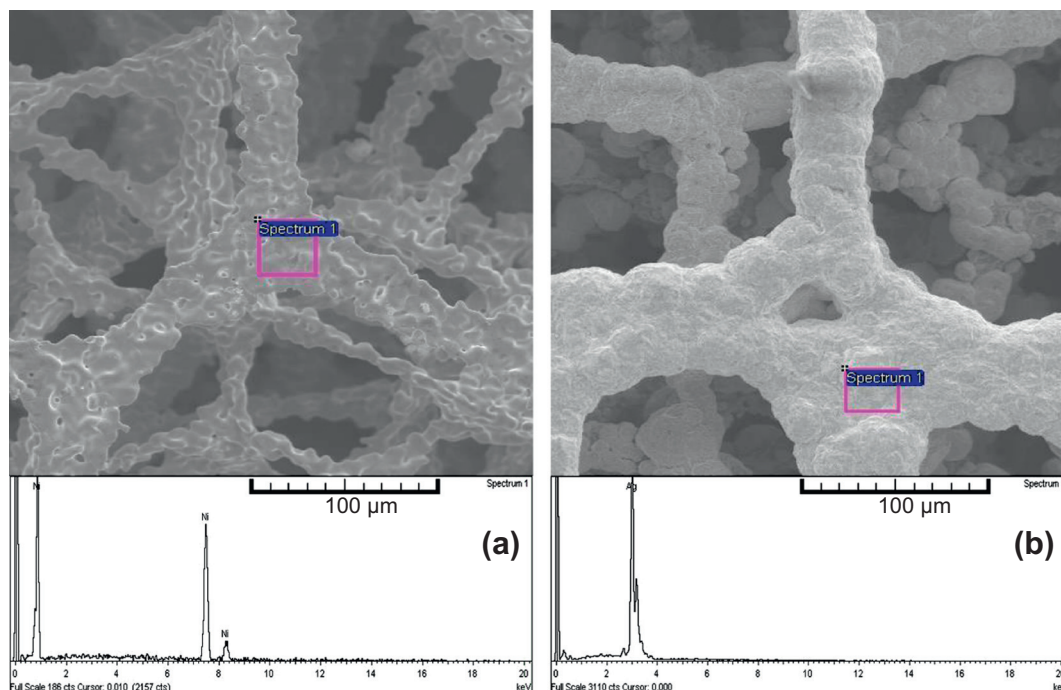
Fig. 1. SEM analysis of the pure Ni foam: 3D layout structure (zoom of 200×) and EDS analysis of chemical composition of the Ni foam with an analyzed point in the right up corner (a); SEM analysis: Ni foam Ag coated: 3D layout structure (zoom of 200×) and EDS analysis of chemical composition of the Ni foam Ag coated with an analyzed point in the right up corner (b).
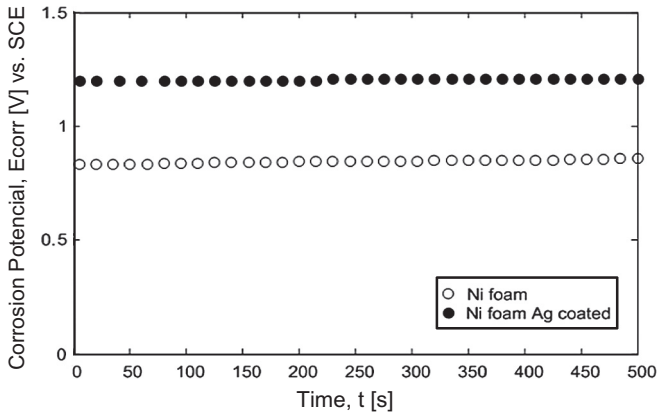
Fig. 2. Diagram of the corrosion potential (E_{corr}) during the time of the 10 min on the pure Ni foam and Ni foam Ag coated in an electrolyte of 25% KOH alkaline solution.
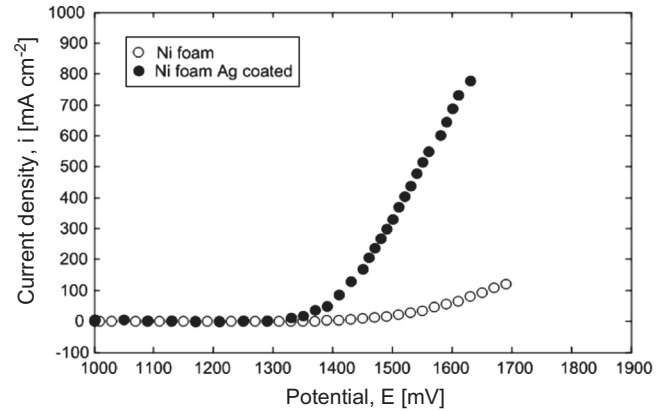

Fig. 4. Polarization curves of the pure Ni foam and Ni foam Ag coated in an electrolyte of 25% KOH alkaline solution.
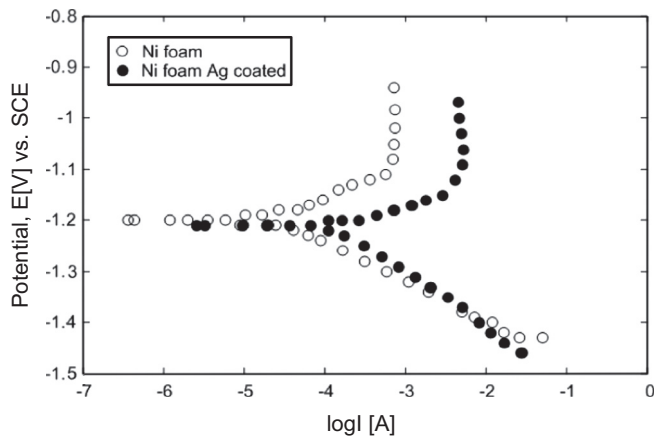

Fig. 3. Polarization curves, anodic and chatodic (Tafel) curves of pure Ni foam and Ni foam Ag coated in an electrolyte of 25% KOH alkaline solution.
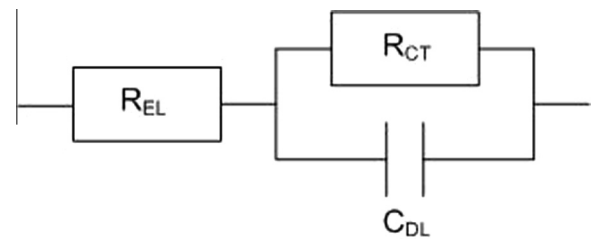

Fig. 6. An equivalent circuit of the pure Ni foam and Ni foam Ag coated electrodes for the EIS measurements where R_{EL} (Ω) is resistance of the electrolyte; R_{CT} (Ω cm^2) is the charge transfer resistance and C_{DL} (F) is the capacitance of the electrochemical double-layer.

Table 4
Values of parameters of the equivalent circuit pure Ni foam Ni foam Ag coated.

	Ni foam		Ni foam Ag coated	
E (V)	−1.45	−1.5	−1.45	−1.5
R_{EL} (Ω)	0.103	0.104	0.0831	0.0993
R_{CT} (Ω)	5.257	1.616	1.3669	0.5208
C_{DL} (F)	9.712	9.491	12.035	10.066

This property of porosity transforms two-dimensional electrolyte flow (2D) to the three-dimensional (3D) electrolyte flow. The results of BET method are given in Table 2.

A comparison of the geometrical surface area and an active surface area of the 3D electrodes gives approximately 1000 times lar-
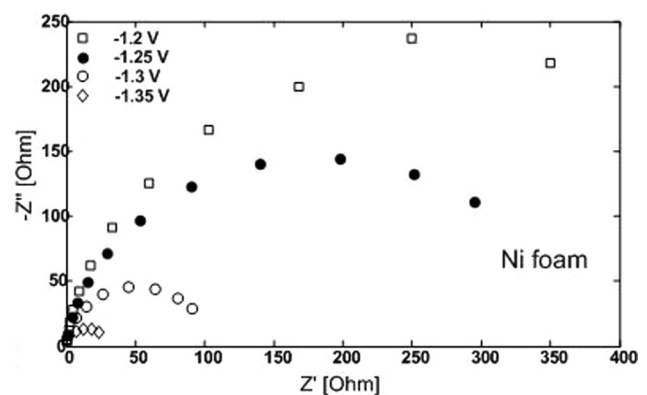
Table 3
Measured and calculated electrochemical parameters.

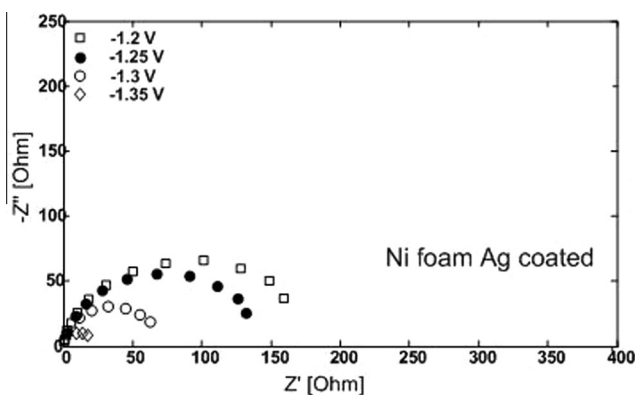|	b_a (V decade^{-1})	b_c (V decade^{-1})	E_{corr} (V) vs. SCE	i_{corr} (Acm^{-2})	B (V)
Pure Ni foam	5.81e−3	76.01e−3	−1.16	24.42e−6	0.015
Ni foam Ag coated	50.9e−3	110.7e−3	−1.22	157.6e−6	0.015

Fig. 5. Nyquist plots of the pure Ni foam and Ni foam Ag coated in an electrolyte of 25% of KOH alkaline solution in potential scale range from −1.2 V to −1.35 V with step size of −0.5 V.
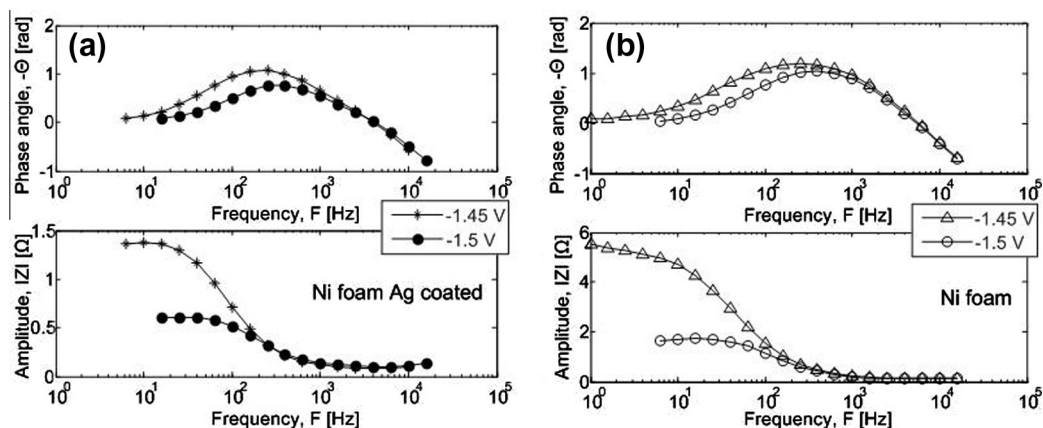
Fig. 7. Bode plots: Phase angle and amplitude of Ni foam Ag coated (a) and pure Ni foam (b) at the potentials of −1.45 V and −1.5 V.

ger active surface area. This data depend on the electrodes weight what takes impact to the costs reduction. The surface morphology of the electrodes material via SEM analysis both of the pure Ni foam and Ni foam Ag coated is given in Fig. 1. From the SEM analysis it is seen 3D layout structure of the pure Ni foam and a view of intermediate connections between bones with diagrams of the chemical composition observed via EDS analysis.

Fig. 1 shows Ni foam of the 100% of the Ni (a) and Ni foam Ag coated of 100% of the Ag intensity (b). For determination of the corrosion potential, Tafel slopes and polarization curves DCEM methods were used. In Fig. 2 it is given measurement of the corrosion potential. In recording time of 500 s the both analyzed samples of the foam shown stability needed for their application in a concentrated alkaline media.

The results of the measured corrosion potential gave Ag coating as more electropositive. During polarization within Tafel scanning it was seen a generation of protective passive film layers in regard to SCE at the potential of −1.1 V for both testing samples of electrodes. The results are shown in Fig. 3.

Using Tafel extrapolation corrosion velocities were determined which because of their low values are negligible. The numeric results of the Tafel extrapolation are obtained in Table 3.

The obtained results are electrochemical parameters of anodic and cathodic Tafel slopes (b_a and b_c), corrosion potential (E_{corr}), corrosion current density (i_{corr}) and Stern-Geary constant (B) which actually was calculated from the polarization curves. A given anodic Tafel slope with higher value insures higher hydrogen generation. Furthermore, wider anodic domain of Ag coating in Fig. 4 confirmed higher hydrogen generation using coated foam at the same voltage values.

A higher hydrogen evolution is enabled by the range of corrosion current density between 100 mA cm^{-2} and 800 mA cm^{-2}. The results of Fig. 4 are obtained using DC polarizations. Obtained results for evaluating electrochemical impedance data are presented in the format of Nyquist plots. The responses for cell voltages of 1.2 V, 1.25 V, 1.3 V and 1.35 V are given in Fig. 5.

This plot illustrates the expected responses of the simple circuit but reached the goal of this investigation. From the plotted results there is seen that using Ag coating are obtained apparent lower resistances of the electrolyte. Hence, significantly reduced resistance to the charge transfer was achieved. According to the equivalent circuit of the single electrochemical cell shown in the Fig. 6, the numerical values of the parameters were calculated for the potentials of −1.45 V and −1.5 V.

Calculations data are given in Table 4.

Graphical results are processed in the plotting format of Bode plot and shown in Fig. 7. It is graphically explained how impedance depends on the frequency.

The same as in the Nyquist plot, Bode plot also gave improved results obtained using Ag coating. At the highest value of frequency the impedance does not depend on it. It is defined by resistance of the electrolyte. For the same frequency values, pure Ni foam is defined with a greater resistance in comparison to the Ni foam Ag coated.

5. Conclusions

The investigations related to the electrodes material with application in an alkaline electrolyser for hydrogen production were carried out. Tested materials were pure nickel foam and nickel foam silver coated. A using of the porous material leads to the increasing of the electrolyser efficiency because of the increased active surface area of the porous material. Moreover, nickel as the good catalyst and electrode with an upgrading of the existing material by different chemical elements contributes to the improvement. The scientific contribution of this work is related to the active surface of 1500 times larger in comparison to the geometrical surface area. Recent progress in the electrodes design was involving of the silver coatings. From the aspect of polarization curves and impedance measurements, the obtained results shown wider range of the hydrogen generation using nickel foam silver coated. It provided an improved current collection compare to the pure nickel foam due to the reduction of the electrolyte resistance and charge transfer resistance. The increasing of the electrodes overvoltage decreases the resistance to the charge-transfer both at the nickel foam and nickel foam silver coated. According to the results of performed DC and AC methods, at the same voltages higher hydrogen generation using nickel foam silver coated was achieved. Mentioned improvements lead to the costs reduction in the electrolyser system related to the reduction of components size in the system in general. Future investigations will be based on durability time of the chosen material of electrodes in laboratory design electrolyser.

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