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# Corrosion behaviour of the nickel based materials in an alkaline solution for hydrogen evolution

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Experimental investigations on the nickel based materials in the form of foam and solid plate have been performed. Their application as the electrodes material in an alkaline electrolyzer has been studied. Corrosion potential and Tafels parameters are defined using DC methods, and Ohmic resistance of the electrolyte using AC methods. Active surface area of the foam is defined using BET method. Obtained polarizations curves result in decrease in the resistance to charge-transfer during increasing of electrodes overvoltage. A 1500 times larger active surface of foam insured higher hydrogen evolution at the same overvoltage. As long as it is used high concentrated aqueous media of *wt* 25% potassium hydroxide solution, corrosion stability of used electrodes material is the first priority.

**Keywords:** Hydrogen, Nickel foam, Alkaline solution, Material stability, Electrolyzer

The ecological awareness and the development of the environmental friendly technologies aim to replacing fossil fuels rich in carbon (whose combustion leads to the toxic gasses) with smaller molecules containing more hydrogen. Hydrogen is proved to be the most suitable energy carrier and efficient energy storage. Hence, a transition to the Hydrogen Economy is unquestionably. Hydrogen is abundant on the Earth in water bounded in form with oxygen[1]. With its application in hydrogen fuel cells its combustion produces only heat and water as the by-products. Hydrogen as a fuel has a capacious potential to replace fossil fuels. It can be produced via numbers of different techniques[2] although water electrolysis process is the most suggested. In combination with renewable energy sources (RES) it is the only commercial technique with zero carbon dioxide ($CO_2$) emission[3,4]. An alkaline water electrolysis is the process of hydrogen production with energy efficiency of 60-90%. Its advantage lies on simplicity with open views on maintenance and costs reduction. Because of its performances, it is suitable for application both in households and industry. The purity of the produced hydrogen via alkaline water electrolysis is 99.98% which satisfies gas purity demand for fuel cells operation. Electrolyte concentration used for this process ranges from *wt* 25% to *wt* 35%. The most often used electrolytes are potassium hydroxide (KOH) alkaline solution and sodium hydroxide (NaOH) alkaline solution[5-9]. A recent progress of alkaline electrolyzer, increasing of the system efficiency is of a high priority[10,11]. On increasing its efficiency the largest impact is on the chosen material for the electrodes design. Different materials have already been investigated for application in electrolyzers and fuel cells[5,12-15]. Nickel (Ni) takes wide interest in hydrogen scientific community in all of its modification such as the solid plate, foam, mesh[5,6,14,16].

The investigation in this work is the continuation of the work[5] where both Ni foam and Ni solid plate electrodes were investigated from the aspect of the electrolyzers operating (UI) characteristic. Here performed experiments were related to the electrochemical measurements. The experimental setup used for the experiments was set as the three - electrode cell using *wt* 25% KOH alkaline solution as an electrolyte in all performed measurements. The goal was to investigate stability and performances of the electrodes materials based on Ni for hydrogen evolution reaction (HER) using (direct current) DC and (alternating current) AC electrochemical methods. Improved catalytic activity of three- dimensional (3D) Ni foam is attributed to the increased active surface.

There were defined parameter related to the Ohmic resistance of an electrolyte for both type of the material form, coefficients of the Tafel polarizations, and effect of the electrodes active surface area on hydrogen evolution. An active surface area of the Ni foam electrode was measured and calculated via Brunauer-Emmet-Teller (BET) method for porous surface.

## Experimental Section

To improve electrolyzer properties, each part of it should be investigated separately. The improvment was related to involving new material in the form of foam as the electrode material. Tested material was designed of Ni foam with diameter of *Φ*16 mm, porosity of 95 – 99%, and nominal pore diameters of 600 µm manufactured by Mitsubishi Materials Corporation. It was compared to the Ni solid plate of INCONEL 600 with chemical structure of 76.85% Ni, 15% Cr, 8% Fe, and 0.15% C with diameter of *Φ*16 mm. In Fig. 1(a), the geometry of the electrodes tested samples is given. In general, this definition of electrodes geometry was of greatest importance since the internal resistances depends on it.

As long as it is used porous material, there is a need to define an active surface area. In this work, active surface area was measured via BET methodusing device of Micromeritis, Asap 2000. A Ni foam for this measurement was prepared as samples of 5×5×2 mm with overall minimum weight of 1g. An analysis gas for obtained measurement was nitrogen (N). Measurements of DC Electrochemical Methods (DCEM) were conducted using a device of EG & G PAR 273 A Potentiostat/Galvanostat. The surface morphology of the electrodes material was defined via Scanning Electron Microscopy (SEM) where chemical structure was observed using Energy Dispersion Spectroscopy (EDS) both using a VEGA TESCAN TS 5130 MM SEM equipped with Oxford Instruments INCA energy dispersive system. The measurements via EIS analysis were performed using a device of EGG Instruments, Model 5210, Lock - in Amplifier. For these measurements of SEM, EDS, DCEM, and EIS, Ni foam and Ni solid platewere prepared as samples of 10×10×2 mm, i.e. 1 cm$^2$ of the projected geometrical area.

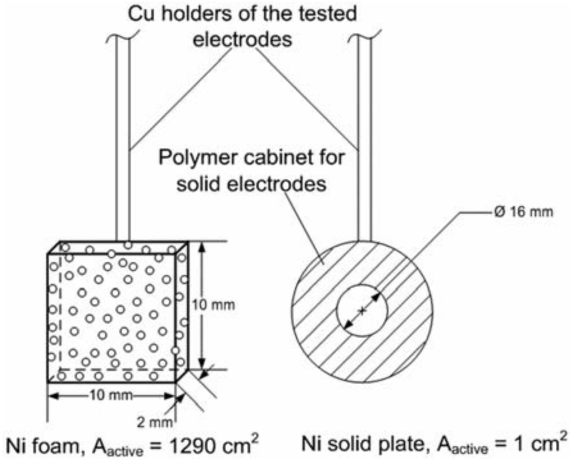

Fig. 1 — The geometry of the tested electrodes (Ni foam on the left and Ni solid plate on the right) in all performed measurements; The experimental set-up used in all experiments was three-elctrodes electrochemical cell

## Methodology

The BET theory was developed in 1938 named by the authors last names initials: Stephen Brunauer, Paul Hugh Emmet, and Edward Teller. It is the first method for specific surface measurement of finely divided and porous solids. Its application is based on adsorption of gas on a surface[17]. Since the one of the electrodes tested within this work was designed from porous material, the BET method was used for calculation of its active surface area. Then the surface morphologies and chemical structure of the Ni foam and Ni solid plate were studied. Electrochemical measurements were performed in accordance with the requirements of ASTM standards G 102 - 89[18]. In these tests a standard electrochemical cell was used. It was designed as the three-electrode system with graphite counter electrode, reference saturated calomel electrode of +0.2415 mV, and working electrode of Ni foam and Ni solid plate of a geometrical surface area of 1 cm$^2$. Experiments performed *via* DCEM were carried out in an electrolyte of 25% KOH alkaline solution with *p*H of 14 at the ambient temperature of 22 ± 2°C. The anodic and cathodic polarization methods were carried out by recording polarization curves in the potential range of ± 250 mV from the open circuit potential with rate of potential change of the 0.5 mV s$^{-1}$. Applying the method of Tafel extrapolation, corrosion current density ($i_{corr}$), the anodic slope of the Tafel curve ($b_a$), and the cathodic slope of the Tafel curve ($b_c$) were defined. The values of these parameters were obtained experimentally and calculated according to the Stern and Geary equation[19]:

$$i_{corr} = \frac{B\,\Delta i}{\Delta E} \quad \text{... (1)}$$

$$B = \frac{b_a\,b_c}{2.3\left(b_a + b_c\right)} \quad \text{... (2)}$$

The corrosion potential ($E_{corr}$) was monitored for 10 min and DC cathodic polarizations were performed at the 10 mV min$^{-1}$ scan rate ($\approx$ 0.17 mV s$^{-1}$).

## Results and Discussion

In the presented diagrams and tables a comparison of the investigated materials is given. An increase the electrodes over voltage decreases the resistance to the charge transfer both at the Ni foam and Ni solid plate electrode. This characterizes Ni based materials with a high stability in strong solutions. But progress is seen on using foam in an alkaline electrolyzer. The main contribution is related to the better performances of electrolysis when using porous material as the electrode. The use of DCEM proved that linear region of the hydrogen evolution using Ni foam is much wider in comparison to the Ni solid plate at the same conditions what implies higher hydrogen evolution using foam. EIS characterization resulted with lower resistances related to the electrolyte of 25% KOH alkaline solution using foam. With given results, a final selection of the material for electrodes in electrolyzer design was made. In comparison to the other materials, Ni proved itself as the stabile both as electrodes material and good catalysts whether the electrolyzer or fuel cell. The results obtained via BET method needed for surface calculation are given in the Table 1.

Comparison of the active surface area of Ni foam and Ni solid plate is given in the Table 2. In the case when Ni foam and Ni solid plate were used, the active surface area of the foam was approximately 1500 times larger at the same projected geometrical surface areas. This fact is related to the porous material of increased active area that allows 3D flow of electrolyte.

Table 1 — Summary report of BET method measurements for Ni foam definition

| 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 |

Table 2 — The comparison of Ni foam and Ni solid plate active surface area

| Electrodes material | Electrodes dimension, cm | Active surface area, cm$^2$ |
|---|---|---|
| Ni foam | 1 ×1 × 2 | 1509.5 |
| Ni solid | 1 ×1×2 | 1.0 |

To define electrodes morphology and chemical structure, SEM and EDS analysis was carried out for identification of the 3D layout structure of the foam and intermediate connections between bones. By this analysis the space inside the bones withfull filled bones was specified. This fact of full filled bones allows electrolysis process without capture of produced bubbles of hydrogen inside the bones. In Fig. 2(a) analysed point in which measurement was taken for definition of the Ni foam chemical structure observed via EDS analysis is given. Results of the chemical structure analysis show foam of the 100% of chemical element of nickel.

The surface morphology of the Ni solid plate obtained via SEM analysis used for the experiments is given in the Fig. 2(b). Which shows qualitative chemical structure of the Ni solid plate with a view of analysed point obtained via EDS analysis. Kinetic parameters for the HER on Ni metal foam and Ni solid plate were obtained from polarization curves and electrochemical impedance spectroscopy measurements. The corrosion potential was measured via DCEM. It showed very stabile Ni based materials to the corrosion both of foam and solid plate.

Tafel polarization curves are given in the Fig. 3. This plot represents rate of Ni corrosion and its electroplating. It applies to the hydrogen generation and oxygen reduction.

It was defined linear region of the hydrogen evolution. The given results show that it is much wider for the Ni foam in the comparison of the Ni solid plate at the same conditions. In the Table 3 are summarized electrochemical parameters: anodic and cathodic Tafel slopes ($b_a$ and $b_c$), corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and Stern-Geary constant ($B$), calculated from the polarization curves shown in the Fig. 3.

Current densities that characterize the rate of the HER on Ni foam and Ni solid plate electrode were calculated using the geometric area ofeach investigated electrode. A higher exchange current densities and lower overvoltage calculated in the Ni metal foam showed that this catalyst is the more active for the HER then Ni solid plate. Investigations were performed to define Ohmic resistance of the electrolyte. EIS spectra was modeled according to the simple electric equivalent circuit shown within Fig. 4. A double layer capacitance values were calculated from the elements of electric equivalent circuit using the relation (3):

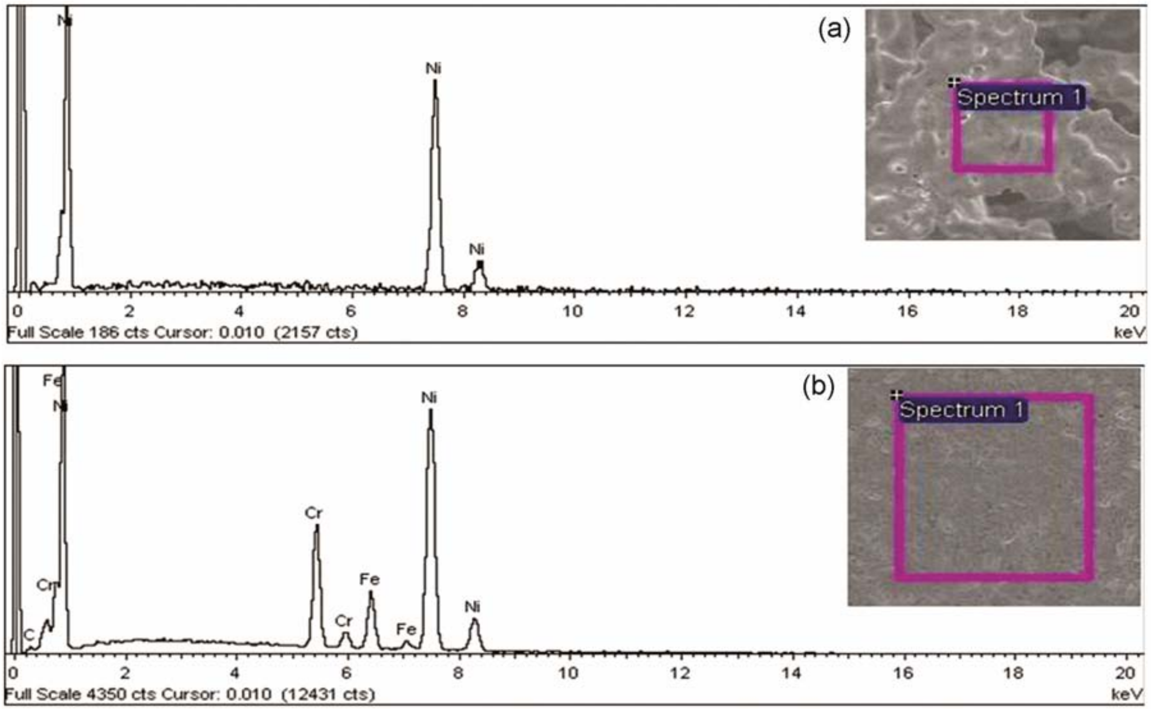

Fig. 2 — An EDS analysis of the Ni foam electrode: Analysed point of it and chemical structure (up right corner) (a) and An EDS analysis of the Ni solid plate electrode: An analysed point and chemical structure (up right corner) (b)

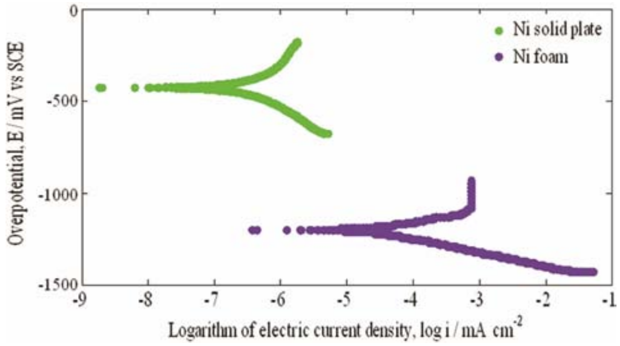

Fig. 3 — Diagram of the corrosion potential during the time of the 10 min with Ni foam and Ni solid plate electrodes in electrolyte of the 25% of KOH alakline solution

$$C_{DL} = \frac{1}{|Z|} \quad \text{... (3)}$$

EIS showed that an increasing of the electrodes overvoltage decreases the resistance to the charge-transfer both at the Ni foam and Ni solid plate but according to the calculation of the active surface area, hydrogen evolution is much higher using Ni foam at the same overvoltage. Electrochemical impedance spectra results are presented in the form of Nyquist diagram shown in the Fig. 4(a) and 4(b).

These diagrams showed progress of processes in the case when foam was used. Table 4 gives

Table 3 — Electrochemical parameters

| Type of electrode | $b_a$/V decade$^{-1}$ | $b_c$/V decade$^{-1}$ | $E_{corr}$/V vs SCE | $I_{corr}$/A cm$^{-2}$ |
|---|---|---|---|---|
| Ni foam | 65.81e-3 | 76.01e-3 | -1.16 | 24.42e-6 |
| Ni solid | 720e-3 | 397.3e-3 | -0.472 | 904.8e-9 |

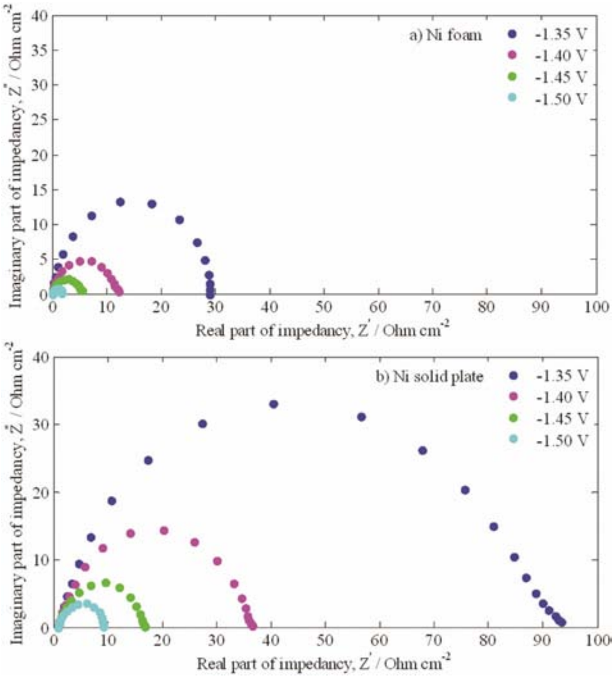

Fig. 4 — Anodic and Chatodic (Tafel) curves of the Ni foam and Ni solid plate electrodes in electrolyte of 25% KOH alkaline solution

Table 4 — The comparison of Ni foam and Ni solid plate active surface area

| Type of electrode | $R_{EL}$/Ohm | $R_{CT}$/Ohm | $C_{DL}$/F |
|---|---|---|---|
| Ni foam | 0.104 | 1.586 | 1.4143e-6 |
| Ni solid | 0.891 | 8.319 | 0.2165e-6 |

parameters values of the equivalent circuit needed for impedance spectra measurements at the chosen potential of the -1.5 V.

The inherent micro porosity of the Ni foam electrode with average pore diameter of 600 µm allows natural or forced electrolyte flow through the electrodes to be compared. Results of comparison of natural and forced flow of electrolyte are given in the reference[19].

Nevertheless, in the electrolyzers chosen electrodes material is from the great importance. It is highly important to choose a proper material with high stability and resistance in specific media and as good electrode and catalysts in the same time.

## Conclusion

The aim of this work was to investigate Ni based materials in form of the foam and solid plate. Their application was predicted to be in the alkaline electrolyzers and fuel cells. Given results brought conclusions in the favour of the foam in all points of investigations. First, the improvement was reffered to the active surface area of the porous electrode calculated via BET method that in this case was approximately 1500 times larger regarding to the solid plate. A linear region of the hydrogen evolution was defined via DCEM. Obtained results showed wider range of hydrogen generation using Ni foam. Furthermore, via EIS was shown that an increasing of the electrodes overvoltage decreases the resistance to the charge-transfer both at the Ni foam and Ni solid plate but according to the increased active surface area, hydrogen evolution is much higher using Ni foam at the same overvoltage. Additionally, the kinetic parameters were defined using the electrochemical methods, indicative for the HER activity, showed improved catalytic activity of Ni foam. All of those indicate that further development of electrolyzer is meaningful. From the economical aspect this research contributes to the reducing of the costs in the system design using foam that allows 3D flows of an electrolyte. The previous investigations of the author proved Ni foam as the most suitable and cheapest material for the electrolysis.

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