Pd surface functionalization of 3D electroformed Ni and Ni-Mo alloy metallic nanofoams for hydrogen production

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Abstract. The paper presents some experimental results regarding the functionalization of 3D electroformed Ni and Ni-Mo alloy nanofoams with Pd nanoclusters, as potential cathodic materials suitable for HER during seawater electrolysis. The electrodeposition from aqueous electrolytes containing NiCl₂ and NH₄Cl has been applied to prepare the 3D Ni nanofoams. Ni-Mo alloys have been electrodeposited involving aqueous ammonium citrate type electrolytes. Pd surface functionalization has been performed using both electroless and electrochemical procedures. Pd content varied in the range of 0.5 – 8 wt.%, depending on the applied procedure and the operation conditions. The use of a porous structure associated with alloying element (i.e. Mo) and Pd surface functionalization facilitated enhanced performances from HER viewpoint in seawater electrolyte (lower Tafel slopes). The determined Tafel slope values ranged from 123 to 105 mV.dec⁻¹, suggesting the Volmer step as rate determining step. The improvement of the HER catalytic activity may be ascribed to a synergistic effect between the high real active area of the 3D electroformed metallic substrate, Ni alloying with a left transition metal and surface modification using Pd noble metal.

1. Introduction
The hydrogen production through electrochemical water splitting under the assistance of electrocatalysts attracted an increased interest as one of the most promising routes among the existing processes. Moreover water represents an abundant resource, about 75% of the globe surface being covered by water, however mostly found as seawater. To use the abundant seawater instead of fresh water for hydrogen production through electrolysis may be a significant advantage, especially if the required electrical energy should be obtained involving sea waves generated power [1,2,3].

Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) represent the two significant electrochemical processes occurring during water electrolysis and Pt species are the most
preferred electrocatalysts. Although Pt electrode exhibits the highest efficiency and long-term stability, its high cost and limited occurrence restricts the commercial applications. Cheaper but high electrochemically active electrodes are needed in order to optimize the efficiency of hydrogen evolution reaction (HER) and the overall efficiency of electrolysis [4 and included references]. Nickel and nickel-based alloys obtained as coating layers involving electrochemical deposition process have been attracted an increased interest due to the low cost and promising electrocatalytic activity for HER. In addition, the use of electrodes possessing high surface area, including metallic nanofoams, may contribute to an improvement of the catalytic activity [5,6].

Among the electrodeposited Ni alloys, Ni-Mo electrocatalysts have been intensively investigated due to their excellent corrosion resistance and long-term stability, besides the high HER activity [4,7,8]. Wang et al. [8] reported the electrodeposition of 3D porous Ni-Mo alloy layers under super gravity field which presented enhanced electrocatalytic activity toward HER in 10% NaOH solution and good long-term stability. The extremely high real active area of the deposits facilitated the high catalytic activity. Gonzalez-Buch et al. [9] reported the electrodeposition of 3D macroporous NiMo cathodes for alkaline water electrolysis on a stainless steel AISI 304 substrate involving a double-template electrochemical process. 3D electroformed Cu foam served as a template for the Ni-Mo co-deposition. According to the obtained Tafel results the authors concluded that the NiMo electrodes exhibit higher intrinsic catalytic activity for HER than the pure Ni electrode as a consequence of alloying hypo–hyper-d-electronic transition metals.

The electrocatalytic HER characteristics of nickel and nickel based alloys may be improved through surface functionalization using noble metals (i.e. Pd, Ru, Rh or Pt) involving electrodeposition, spontaneous deposition or chemical reduction processes [10,11,12]. In addition, the research interest is focused on developing more active and stable Pd-based electrocatalysts in order to partially or completely replaces costly Pt [13].

Only few studies can be found related to the development of cathode materials aimed to catalyse HER process during seawater electrolysis. Jiang et al. [2] investigated the HER activity of the electrodeposited Ni–Fe–C films onto A3 steel substrate during simulated seawater (3.5 wt% NaCl) electrolysis. They found a non-linear correlation between the average coating grain sizes in the range of 4.3 – 6.4 nm and the hydrogen evolution overpotential. Moreover, the optimum hydrogen overpotential of Ni-Fe-C cathode was about 65 mV in 3.5% NaCl at 90°C and pH 12. Zheng [14] studied the synthesis of PtNi x electrocatalysts exhibiting high efficiency hydrogen evolution during seawater splitting. PtNi5 was found to provide the best catalytic behavior, with the Tafel slope of 119 mV dec⁻¹. The synthesized alloy electrodes showed a remarkable stability at -1.2V over 12 h. Binary platinum alloy electrodes, PtM (M = Fe, Co, Ni, Pd) electrodeposited on Ti foil involving a cycle voltammetry strategy have been also very recently reported as promising cathodic materials for HER during seawater electrolysis [15]. The author showed that by tuning M species, the Ti supported PtPd alloy electrode displayed a maximal efficiency, yielding an onset potential of −52 mV in HER. The long-term stability has also been increased by alloying Pt with M.

Therefore, the aim of this work was the preparation and characterization of Pd-modified 3D electroformed Ni and Ni-Mo alloy nanofoams using both electrochemical and electroless procedures, as potential cathodic materials suitable for HER during natural seawater electrolysis.

2. Experimental

2.1. Chemicals and materials

All used chemical reagents were of analytical grade and supplied by Sigma Aldrich and Fluka. They were used as received without any further purification. The seawater was taken from Black Sea – Constanta location (Romania) and filtrated to remove any suspended species.
2.2. Electrodeposition of 3D Ni and Ni-Mo alloy coatings
The Ni and Ni-Mo alloy coatings have been electrodeposited onto Cu metallic substrates under galvanostatic conditions using a DC power supply and a two-electrode cell configuration. The used Cu metallic substrates (70x35x0.2 mm) have been initially subjected to a mechanical polishing using 1000 and 2000 abrasive paper, followed by chemical pickling in 1:1 HNO₃: H₂O solution at 25°C for 20–30 s, then rinsed with running water and distilled water and air dried.

The Ni foams have been electrodeposited on Cu using the dynamic hydrogen bubble template [16, 17] from an aqueous electrolyte based on NiCl₂·7H₂O and NH₄Cl at 25°C against a Ni plate as anode. The Ni-Mo alloy coatings have been electrochemically deposited onto electroformed Ni foams as metallic substrates, against platinized titanium as anode involving aqueous citrate-ammonium type electrolytes. Table 1 summarizes the bath compositions and the experimental conditions used in the synthesis of the above mentioned coatings.

| Coating type     | Electrolyte composition                  | Operating conditions               |
|------------------|------------------------------------------|-----------------------------------|
| Ni foam (Ni)     | 0.1M NiCl₂·7H₂O                           | pH = 4-4.5                        |
|                  | 2M NH₄Cl                                 | T = 25°C                          |
|                  |                                          | i = 0.2-2 A/cm²                    |
|                  |                                          | time= 1-5 min.                    |
| Ni-Mo alloy (NiMo) | 0.4M NiSO₄·6H₂O                        | pH =6-6.5                         |
|                  | 0.025-0.064M Na₂MoO₄·2H₂O               | T = 50-60°C                       |
|                  | 0.2M Na₃C₆H₅O₇                          | i = 1-5 A/dm²                     |
|                  | 0.5M H₃BO₃                               | time = 10-20 min.                 |
|                  | 1-3 g/L saccharine                       |                                   |
|                  | 0.2 g/L tensioactive agent               |                                   |

2.3. Pd surface functionalization
To modify the 3D Ni and Ni-Mo alloy coatings using Pd, several procedures have been applied, involving either electrochemical or chemical sequences.

Therefore Ni-Pd alloy foams have been electrochemically synthesized through addition of 5-10 mM PdCl₂ to the NiCl₂-NH₄Cl electrolyte used to obtain Ni foams. Ni-Pd alloy coatings have been also applied involving a classical Ni based electrolyte with 5-10 mM PdCl₂ additions.

The chemical Pd deposition has been performed by dipping the pre-deposited Ni and Ni-Mo alloy foam electrodes in tetraammine palladium (II) chloride based solution for 1-10 min. at 50°C. The composition and the operation conditions applied during Pd surface functionalization are presented in Table 2.

The surface morphology and composition of the prepared coatings has been examined using scanning electron microscopy (SEM) associated with energy dispersive X-ray spectroscopy (EDX) (SU8230, HITACHI High-Technologies Corporation, Japan). The phase composition and structure were determined using X-ray diffractometry (XRD) involving a Rigaku Ultima IV equipment with graphite diffracted beam monochromator for CuKα radiation, at a speed of 2 s/step (1step = 0.05°).

| Coating type     | Solution composition                  | Operating conditions |
|------------------|--------------------------------------|----------------------|
|------------------|--------------------------------------|----------------------|

Table 1. Electrolytes composition and operating conditions for 3D Ni and Ni-Mo alloy coatings electrodeposition

Table 2. Solution composition and operating conditions for Pd surface functionalization
Ni-Pd alloy foam

| Ni-Pd alloy | foam | 0.1M NiCl₂, 7H₂O | T = 25°C |
|-------------|------|-----------------|----------|
| NiPd₄       | 2M NH₄Cl | 5-10 mM PdCl₂ | i = 0.2-2 A/cm² |
| Pd chemical deposition | 5.4 g/L [Pd(NH₃)₄]Cl₂, 2H₂O | T = 50°C |
| Pdₜₙ₃       | 67.2 g/L Na₂EDTA | immersion time= 1-10 min. |
|             | 650 mL/L NH₃ (28%) |
|             | 0.5 mL/L N₂H₄·H₂O |

2.4. Electrochemical measurements

All the investigations related to the assessment of the catalytic activity for HER on the prepared electrodes acting as working electrode (with a constant geometrical surface of 0.63 cm²) have been performed in a three-electrode configuration cell using natural seawater as electrolyte at room temperature. A platinum mesh was auxiliary electrode and the reference electrode was the Ag/AgCl electrode. The cell was connected to PARSTAT 4000 potentiostat controlled with VersaStudio software. HER polarization curves were recorded at a scan rate of 1 mV s⁻¹, from -1.7 V vs Ag/AgCl up to the equilibrium potential. Tafel slopes were determined from HER polarization curves. Before the tests, the working electrode was held at -1.70 V vs Ag/AgCl for 1000 s in the same solution, in order to reduce the oxide film present on the porous surface electrode layer. EIS measurements were also recorded after obtaining the polarization curves in the same cell configuration with 10 mV ac voltage within 100 kHz–50 mHz frequency range. The fitting of the impedance data has been performed using ZView 2.4 software from Scribner Association Inc., Derek Johnson.

3. Results and Discussion

The Ni foams electrodeposited onto Cu substrate involving the experimental conditions as shown in Table 1 exhibit a porous structure characterized by the presence of pores having different diameters, depending on the applied current density and deposition time. Regardless the applied operating conditions, uniform, black layers have been formed. The hydrogen bubbling occurring simultaneously to the electrochemical reduction of nickel ions promotes the development of this type of morphology. The final coating possesses a high surface area, which may enhance the hydrogen evolution during water electrolysis [10,11]. In addition it is suitable for further deposition of other metals and alloys which will take the 3D shape of the porous substrate with a very high accuracy [17].

Figure 1 presents an example of the obtained morphology for Ni-Pd alloy foams (NiPd₄) electrodeposited on Cu using a Pd-modified Ni electrolyte (see Table 1) and the spatial distribution profiles for the main elemental components.

Figure 1. SEM micrographs of Ni-Pd alloy foam (1 wt. % Pd) electrodeposited at 25°C for 3 min. (c.d. = 1 A/cm²) and EDX maps showing the distribution profiles of elements within the deposited alloy

As shown in figure 1, the addition of PdCl₂ in the electroforming electrolyte facilitates the co-deposition of Pd, while keeping the porous morphology of genuine Ni foam. Pd element is quite uniformly distributed within the alloy deposit. Usually the Pd content was in the range of 0.3-3 wt.%
with higher values on the increase of Pd concentration in the electrolyte or of the applied current 
density.

Quite similar morphology with a uniform Pd distribution has been also noticed in the case of 
Pd chemical deposition on previously electrodeposited Ni foam, as exemplified in figure 2.

As expected, an increased Pd content has been noticed as the immersion time was longer, in the range 
of 3-7 wt.% for 1-10 min. deposition periods. The Ni based porous structures usually consisted in 
macropores of 20-40 µm and micropores of 3-5 µm, with a nodular growth, leading to a cauliflower-
like morphology. The XRD analysis (not shown here) evidenced the characteristic peaks of Ni0.82Pd0.12 
phase, besides those of Ni. Based on XRD and using Scherrer equation, average sizes of crystallites 
between 22-62 nm have been estimated.

Electrodeposition of Ni-Mo alloys represents a classical example of induced co-deposition 
[18], when the reduction reaction of nickel enhances the co-deposition of molybdenum. The use of 
NiMo electrolyte (see Table 1) allowed the obtaining of different values of Mo content in the alloy (in 
the range of 10 – 30 wt.% Mo) by varying the applied operation conditions, mainly the current density 
and temperature. In addition the Ni-Mo alloy coatings possess promising protective characteristics in 
chloride aggressive environment as reported in [19,20]. Generally NiMo electrolyte facilitates the 
electrodeposition of uniform, bright-grey deposits, with an excellent adhesion to the Cu or Ni 
substrates. It is well-known that the electrochemical deposition is an atomic/molecular level process. 
Therefore a Ni-Mo deposited layer entirely takes the 3D shape of the Ni foam substrate with a very 
high accuracy and adhesion.

Figure 3 shows an example of the morphology and EDX maps for Ni-Mo alloy electrodeposited onto Ni-Pd foam.

The porous matrix of the NiPd is clearly observed in figure 3. The metallic elements are quite 
uniformly distributed within the deposit as EDX maps show.

A similar morphology and homogeneity has been also evidenced in the case of Pd chemical 
deposition onto Ni-Mo alloy/Ni substrate, as exemplified in figure 4.
Figure 4. EDX maps showing the distribution profiles of elements for Pd<sub>chem</sub> onto Ni-Mo alloy electrodeposited onto Ni<sub>f</sub> (6 wt. % Pd) at 60°C for 20 min. (c.d = 4 A/dm<sup>2</sup>)

The electrochemical activity of the electrodeposited electrodes towards HER has been investigated in natural seawater at room temperature. Figure 5 presents the recorded polarization curves of the different Pd-modified electroformed Ni and Ni-Mo alloy nanofoams. The cathodic Tafel slopes ($b$), exchange current densities ($i_0$), overpotentials at 1 and 10 mA.cm<sup>-2</sup> were determined from the corresponding cathodic current-potential curves and are listed in Table 3. The apparent exchange current densities were estimated by extrapolating the Tafel lines (not shown here) to the corresponding zero current potentials.

![Graphs showing polarization curves for different systems of Pd functionalized Ni and NiMo/Ni foams](image)

**Table 3.** Cathodic Tafel slopes, exchange current densities, overpotentials at 1 and 10 mA.cm<sup>-2</sup> for the prepared electrodes

| Working electrode type | $b$ / mV dec<sup>-1</sup> | $i_0$ / A cm<sup>-2</sup> | $\eta$/mV (i = 1 mA cm<sup>-2</sup>) | $\eta$/mV (i = 10 mA cm<sup>-2</sup>) |
|------------------------|---------------------------|--------------------------|-----------------------------------|-------------------------------------|
| Ni<sub>f</sub>         | 185                       | 6.64.10<sup>-5</sup>     | 289                               | 948                                 |
| NiPd<sub>f</sub>       | 123                       | 8.53.10<sup>-5</sup>     | 172                               | 851                                 |
| Pd<sub>chem</sub>/Ni<sub>f</sub> | 120               | 1.31.10<sup>-4</sup>     | 146                               | 827                                 |
| NiMo/Ni<sub>f</sub>    | 118                       | 1.57.10<sup>-4</sup>     | 108                               | 813                                 |
| NiMo/NiPd<sub>f</sub>  | 115                       | 1.35.10<sup>-4</sup>     | 113                               | 820                                 |
| Pd<sub>chem</sub>/NiMo/Ni<sub>f</sub> | 105          | 9.91.10<sup>-5</sup>     | 152                               | 903                                 |

It is clear from Table 3 and figure 5 that the HER activity of Ni<sub>f</sub> may be enhanced through Pd surface modification. The corresponding Tafel slopes for NiPd<sub>f</sub> and Pd<sub>chem</sub>/Ni<sub>f</sub> are of 123 and 120 mV.dec<sup>-1</sup>, respectively, suggesting that the HER process obeys Volmer reaction mechanism [7,14 and included references]. The higher value of Ni<sub>f</sub> may be related to the presence of oxides films on the surface [7]. The Pd functionalization of Ni-Mo alloy based systems determines only a slight improvement of the catalytic activity. The significant effect is mainly due to the presence of Mo as alloying element. The determined Tafel slope values ranged from 118 to 105 mV.dec<sup>-1</sup>, indicating the Volmer step as rate determining step.
Figure 6 shows examples of EIS spectra recorded on the developed Pd modified Ni and Ni-Mo alloy foams. As seen from figure 6a, a single semicircle was observed in the Nyquist plots of Pd modified Ni foams. This suggests that the HER is mainly controlled by a charge transfer process [7,21]. Therefore, one-time constant electric equivalent circuit model was used to fit the EIS experimental data as shown in the inset of figure 6a. During fitting, double layer capacitances were replaced by constant phase element (CPE). T (F s⁻¹ cm⁻²) was used as capacitive parameter. The recorded of EIS spectra on Pd modified Ni-Mo alloys foam present in the Bode plots (not shown here) a two-time constant response. A slightly modified equivalent circuit initially proposed by Armstrong and Henderson [22] has been used to fit the response of the HER, as shown in the inset of figure 6b.

The real surface area of the Pd modified Ni and Ni-Mo alloy foams was calculated through EIS results by means of the surface roughness factor (Rf) which was determined for each coating type by dividing Cdl by the double-layer capacitance of a smooth electrode, 20 µF·cm⁻² [7,8 and included references].

![EIS data recorded in seawater electrolyte at 25°C for Pd-modified Ni and Ni-Mo alloy foams as Nyquist plots (inset: the proposed equivalent circuit to fit the measured points)](image)

**Figure 6.** EIS data recorded in seawater electrolyte at 25°C for Pd-modified Ni and Ni-Mo alloy foams as Nyquist plots (inset: the proposed equivalent circuit to fit the measured points)

Table 4 presents the double layer capacitance, real surface area and corresponding surface roughness values for the investigated Pd modified foams calculated from the EIS data.

| Working electrode type | CPE_DL / mF | A_real/cm² | σ  |
|------------------------|-------------|------------|----|
| Ni_f                   | 2.47±0.2    | 123.6      | 196|
| Ni_Pd_f                | 3.09±0.2    | 151.5      | 240|
| Pd_clean/Ni_f         | 2.3±0.6     | 115.9      | 184|
| NiMo/Ni_f             | 4.9±0.9     | 248.5      | 395|
| Pd_clean/NiMo/Ni_f    | 4.5±0.9     | 224.5      | 356|

Obviously, the improvement of catalytic activity may be ascribed to the increase of real surface area. Current densities with respect to real surface area at a potential of -1.5V vs.Ag/AgCl were also calculated to compare the intrinsic catalytic activity of NiMo/Ni_f deposits. The values of i -1.5V/σ were 14.4 µA cm⁻² and 17.1 µA cm⁻² for NiMo/Ni_f and Pd_clean/NiMo/Ni_f respectively, suggesting a quite constant intrinsic catalytic activity. The improvement of catalytic activity may be however ascribed to the Pd surface functionalization. A more pronounced influence of Pd functionalization was observed in the case of Ni foam deposits. The determined values of the current densities with respect to real surface area at the same potential were 23.4, 26.6 and 32 µA cm⁻² for Ni_f, Ni_Pd_f and Pd_clean/Ni_f electrodes, thus suggesting an enhanced HER catalytic activity.
4. Conclusions
As a result of the performed investigations easy and effective methods to prepare Pd-modified 3D electroformed Ni and Ni-Mo alloy nanofoams have been developed involving both electrochemical and electroless procedures. Pd content varied in the range of 0.5 – 8 wt.%, depending on the applied procedure and the operation conditions.

The use of a porous structure associated with alloying element (i.e. Mo) and Pd surface functionalization facilitated enhanced performances from HER view point in seawater electrolyte (lower Tafel slopes). The determined Tafel slope values ranged from 123 to 105 mV.dec⁻¹, indicating the Volmer step as rate determining step.

The improvement of the HER catalytic activity may be ascribed to a synergistic effect between the high real active area of the 3D electroformed metallic substrate, Ni alloying with a left transition metal and surface modification using Pd noble metal.

These preliminary results showed that the Pd-modified 3D electroformed Ni and Ni-Mo alloy nanofoams may represent a promising technological approach to build cathodic materials suitable for seawater electrolysis. Moreover the investigations are considered to be a step forward toward real application of seawater for hydrogen production.

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