



# Article Influence of Substrate Preparation on the Catalytic Activity of Conical Ni Catalysts

Katarzyna Skibińska <sup>1,2,\*</sup>, Safya Elsharkawy <sup>1,3</sup>, Anna Kula <sup>1</sup>, Dawid Kutyła <sup>1</sup>, and Piotr Żabiński <sup>1</sup>

- <sup>1</sup> Faculty of Non-Ferrous-Metals, AGH University of Krakow, al. A. Mickiewicza 30, 30-059 Krakow, Poland; elsharka@agh.edu.pl (S.E.); kula@agh.edu.pl (A.K.); kutyla@agh.edu.pl (D.K.); zabinski@agh.edu.pl (P.Ż.)
- <sup>2</sup> CBRTP SA Research and Development Center of Technology for Industry, Ludwika Waryńskiego 3A, 00-645 Warszawa, Poland
- <sup>3</sup> Chemistry Department, Faculty of Science, Tanta University, Tanta 31527, Egypt
- \* Correspondence: kskib@agh.edu.pl

Abstract: The production of hydrogen using electrolysis contributes to the development of more important renewable energy sources. Nowadays, the synthesis of alloys, which can be successfully applied as catalysts instead of precious metals, is carefully investigated. One-step electrodeposition is a surface engineering method that allows for the control of the morphology of the deposit by changing deposition parameters. It is a simple and low-cost process based on electrochemical synthesis from electrolytes, usually non-toxic crystal modifiers. In this work, a conical Ni structure on Cu foil was produced using this technique. The effect of the copper substrate on the morphology of the developed nanocones was analyzed using a Scanning Electron Microscope (SEM). Then, the catalytic performance of the synthesized coatings was carefully analyzed based on the results of a linear sweep voltammetry experiment and the measurements of their wettability and electrochemical active surface area. The proposed method of Cu treatment, including polishing with sandpapers, influenced the growth of cones and, consequently, increased the catalytic activity and active surface area of the Ni coatings in comparison to the bulk Ni sample.



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** electrodeposition; nanocones; crystal modifier; substrate preparation; hydrogen evolution reaction

## 1. Introduction

Surface engineering defines all technologies that improve component performance in different science and engineering applications [1]. However, one of the first steps in this process is the preparation of a substrate relative to the used method [2]. In the case of metal surfaces for catalytic applications, surface engineering relies mainly on the behavior of materials to design the most promising catalysts [3]. Numerical simulations can be successfully applied to understand some phenomena [4,5]. The importance of surface preparation on catalytic activity has already been confirmed in [6,7].

Nickel and its alloys are commonly used catalysts in many reactions, such as watersplitting [8–10], ethanol oxidation [11,12], and  $CO_2$  reforming of methane [13,14]. They can be synthesized in several forms, e.g., bulk coatings [15,16], thin films [17,18], micropatterned electrodes [19,20], nanosheets [21,22], and sponges [23,24]. However, the substrate used is also essential in enhancing catalytic performance [25]. The one-step method is a chemical approach to surface engineering [26]. It is just a simple electrodeposition process performed in an electrolyte containing an addition of a crystal modifier. This chemical component is usually a non-toxic substance [27–29]. By blocking the horizontal direction of growth and promoting the vertical one, conical structures can be synthesized. The mechanism of their growth is still not well understood. However, it is believed to be based on the screw-dislocation-driven crystal growth theory [30,31]. Cl<sup>-</sup> ions are crucial to controlling the direction of growth, allowing for the fabrication of cones [32]. By means of the one-step method, the active surface area of the coating can be easily increased [33].

In this work, the influence of substrate preparation on the morphology and, above all, on the catalytic activity of Ni nanocones was carefully examined. The novelty of this paper relates to the detailed investigation of one of the parameters of surface engineering in an example of the one-step method. In our research, cones grew in all directions, and then the increase in the value of the active surface area of the conical samples was noticeable. The received results highlight the importance of the substrate preparation procedure in synthesizing catalysts.

#### 2. Materials and Methods

Copper foil, with a thickness of 0.3 mm, was chosen as a substrate for the deposition of Nickel coatings. The surface of the Cu plates was 2.8 cm<sup>2</sup>. Before the deposition, the procedure of copper preparation was investigated. Chemical etching was performed in a mixture of  $H_3PO_4$ ,  $HNO_3$ , and  $CH_3COOH$  concentrated acids in a 1:1:1 volume ratio at 80 °C. The chosen substrates were polished with 400-, 800-, and 1200-grit sandpapers. The procedure for their polishing was repeated always in the same way.

The deposition of Nickel samples was performed in a two-electrode cell with a Cu working electrode (WE) and Pt foil as a counter electrode (CE). The pH of the electrolyte containing the crystal modifier was 4. A bulk sample refers to a Nickel coating electrode-posited from the electrolyte without adding the crystal modifier. The parameters of the electrochemical deposition are listed in Table 1. The deposition was performed using an SP200 BioLogic potentiostat (Seyssinet-Pariset, France).

Table 1. Parameters of the bulk and structured Ni coatings.

Coating	Composition of Electrolyte [g/L]				m []	Current Density	Temperature
	NiSO <sub>4</sub> ·7H <sub>2</sub> O	NiCl <sub>2</sub> ·6H <sub>2</sub> O	H <sub>3</sub> BO <sub>3</sub>	NH <sub>4</sub> Cl	lime [min]	[mA/cm <sup>2</sup> ]	[°C]
Bulk	200	-	40	-	10		Room
Conically structured	-	200	100	20	5	10	60

The influence of the Cu substrate preparation was analyzed based on microstructure observations performed using the Optical Microscope Nikon Elipse LV150 (Nikon, Tokyo, Japan) at a magnification of  $\times 100$ .

Top-view images of the bulk coatings were taken using SEM JEOL-6000 Plus (Tokyo, Japan). The detailed morphology of the conical structures was investigated using a Hitachi SU-70 SEM (Hitachi, Tokyo, Japan) Scanning Electron Microscope (SEM). All the specimens were  $40^{\circ}$  tilted during SEM observation to visualize the deposited cones better. The chemical compositions of the conical Ni coatings were analyzed using SEM JEOL-6000 Plus equipped (JEOL, Tokyo, Japan) with an Energy Dispersive X-ray Spectrometer (EDS). The SEM images (top views and tilted) were analyzed using the Image J software to determine the number of cones per 1  $\mu$ m<sup>2</sup> and their height. The roughness of the polished substrates and conical samples was characterized using Atomic Force Microscopy (AFM) NTegra Aura NT MDT (Moscow, Russia) in a semicontact mode using an NSG03 tip. X-ray diffraction (XRD) of the Ni cones deposited on the etched Cu was performed with a Rigaku MiniFlex II apparatus (Tokyo, Japan).

All the electrochemical experiments, i.e., the CV scans and linear sweep voltammetry (LSV), were performed with an SP300 BioLogic potentiostat (Seyssinet-Pariset, France). The geometric surface of the samples was 0.79 cm<sup>2</sup>. The electrochemical active surface area (ECSA) measurements were based on performing CV at a very tight range of potentials, where no currents connected with the reaction on the electrodes would be registered, just the ones from the loading of the double-layer. The registered changes in the double-layer capacity (CDL) with the CV scan rate allowed for the determination of the ECSA.

measurements were performed in a 1 M NaOH solution. The catalytic activity was analyzed in a three-electrode cell with the Ni coating as a working electrode, a Pt foil as the anode, and a Saturated Calomel Electrode (SCE) as the reference electrode. The linear sweep voltammetry (LSV) measurements ranged from the Open Circuit Potential (OCP) value to 1.5 V vs. the SCE in the non-stirred 1 M NaOH solution. The scan rate was equal to 5 mV/s The onset potential ( $E_{ONSET}$ ) values, at which hydrogen evolution started were determined, were determined based on the obtained curves. The stability of the conical electrodes was analyzed with the chronoamperometry technique by applying 1.3 V for 120 min.

The wettability measurements were performed using a high-speed camera Model:9501 with the HiBestViewer 1.0.5.1 software. A 10  $\mu$ L droplet of deionized water was applied four times to the surface of each sample. The contact angle was determined through contour analysis utilizing the Image J software version 1.8.0. The measurements were performed on freshly deposited coatings.

#### 3. Results and Discussion

### 3.1. Procedure of Substrate Preparation

Copper has been successfully used as a substrate for the deposition of cones in [32,34]. However, the influence of its preparation on the conical structures was not investigated in these works.

#### 3.1.1. Chemical Etching

Chemical etching was performed from 0 to 60 s. This process allows for the removal from the substrate surface of oxides and impurities originating from the production and transport processes. Photos of the Cu substrates before and after chemical etching are shown in Figure 1.



**Figure 1.** Influence of the chemical etching time—(**a**) 0, (**b**) 5, (**c**) 10, (**d**) 20, (**e**) 30, and (**f**) 60 s—on the surface of the Cu substrates. The scale bar is 100  $\mu$ m.

Based on the photos taken, it can be assumed that 30 s of chemical etching smoothens the surface by removing scratches developed by the producer during the rolling process. Increasing the etching time results in hole formation, as is visible in the left-down corner in Figure 1f. The etching time was set to half a minute for the next step of the preparation procedure.

#### 3.1.2. Polishing

To increase the surface of a substrate and activate the growth on the boundaries, the Cu was polished using sandpaper with different grits. All the photos of the substrates are shown in Figure 2.



**Figure 2.** Copper substrates after (a-d) 30 s of chemical etching and polishing with (b) 400-, (c) 800-, and (d) 1200-grit sandpapers. The scale bar is 100  $\mu$ m.

As shown in Figure 2b–d, the applied polishing produced scratches on the surface compared to Figure 2a. They are deeper for the lower grit of the sandpaper. The bulk and structured Ni coatings were deposited on each substrate, as shown in Figure 2.

Additionally, the roughness of the polished substrates was investigated using the AFM method. 3D images are shown in Figure 3. The scanned area was 20  $\mu$ m  $\times$  20  $\mu$ m. The average surface roughness S<sub>a</sub> was determined. It is calculated as the arithmetic mean height difference of each point to the average height of the surface.

The images, as expected, show the scratches visible in Figure 2. The lower the grit of the sandpaper, the more scrapes are visible. The roughness values obtained for the polished substrates are the following: 195.4 nm, 235.8 nm, and 75.5 nm for the samples polished with 400-, 800-, and 1200-grit sandpaper, respectively. It means that the shallowest scratched lines were made with the 1200-grit sandpaper and the deepest with the 800-grit one. However, the difference between the scratches produced with 400 and 800 grits is about 40 nm. This variety is probably connected to the chosen area on the substrate and has an approximate character.



**Figure 3.** 3D images of the substrates, polished with (**a**) 400-, (**b**) 800-, and (**c**) 1200-grit sandpaper, acquired using the AFM.

## 3.2. Synthesis of Ni Cones

Nickel coatings were deposited as described in the Section 2. The difference in the morphology of the coatings was analyzed based on the SEM photos. The chemical composition of the samples had been measured and compared before using the EDS and XPS methods. The results are described in [35,36]. Both the bulk and conical coatings are composed of metallic Ni and its oxide on the surface. The presence of Ni/NiO on the surface is desirable to increase catalytic performance.

#### 3.2.1. Bulk Coatings

The Ni bulk coatings were first deposited on the etched Cu substrates, as shown in Figure 4.



**Figure 4.** Ni bulks deposited on (**a**,**b**) chemically etched Cu substrates.

As shown in Figure 4, the deposited bulk coatings are flat. The measured average roughness of this coating is about 64 nm [36].

## 3.2.2. Nickel Cones

Generally, the synthesis of cones is desirable to increase the active surface area and, consequently, enhance the catalytic properties of coatings. Ni cones are usually electrodeposited as a mix of smaller and bigger sharp-ended deposits [32]. Conical structures were deposited on the etched and polished substrates (Figure 2). The SEM observations of the Ni cones performed on tilted samples are shown in Figure 5. The chemical composition of the Ni cones synthesized on different substrates was analyzed using the EDS. The results are listed in the Supplementary Materials (Table S1). There is no influence of the applied procedure of substrate preparation on the content of Ni, O, and Cl. The chlorine content is within the margin of error. Moreover, an XRD analysis was performed (Figure S1). The obtained diffraction pattern confirmed the synthesis of cubic Ni.



Figure 5. Ni cones deposited on (a-h) etched and polished with (c,d) 400-, (e,f) 800-, and (g,h) 1200-grit sandpapers.

It can be noticed that, in the case of conical structures, 5 min of deposition is enough to cover the scratches made with the 1200-grit sandpaper (Figure 5g,h). However, the cones are better developed than the ones deposited on the just-etched substrate (Figure 5a,b). For the conical structures synthesized on the Cu substrates polished with 400-(Figure 5c,d) and 800 (Figure 5e,f)-grit sandpapers, the cones were growing in all directions which should significantly increase the active surface area. A few developed structures are especially visible in the left corner of Figure 5f. To compare the coatings' morphology, the number and height of the cones were determined based on the SEM photos, as shown in Figure 6. To count the structures, three squares of 2  $\mu$ m × 2  $\mu$ m were drawn in the top-view photo. Then, the number of tips in each figure was noted and divided by four, and the results are listed in Table 2. The tilted photo was chosen to measure the height of the 20 cones.





**Figure 6.** (a) Top view and (b) tilted photos of the structures deposited on the etched substrate. Examples of determination of (a) number and (b) height of the cones. (a) The green square corresponds to 2  $\mu$ m × 2  $\mu$ m area. (b) The numbering of the measured heights is indicated with white font on the black background.

Coating Deposited on Cu Substrate	Number of Cones per 1 $\mu m^2$	Height of Cones [nm]	
Etched	$11 \pm 1$	$463\pm126$	
Etched and polished (400 grit)	$12\pm 1$	$499\pm98$	
Etched and polished (800 grit)	$14\pm 2$	$510\pm85$	
Etched and polished (1200 grit)	$16 \pm 1$	$545\pm119$	

Table 2. Influence of the substrate preparation on the number of cones and their height.

Based on the obtained results, the higher the value of the paper grit, the higher the height of the cones. Moreover, the higher the grit of the sandpaper, the more cones were deposited. This suggests that the scratches act as areas of nucleation of the deposits. Compared to the results obtained in [32], the conditions applied in this work allowed for the deposition of more cones per 1  $\mu$ m<sup>2</sup> for most cases.

The roughness of the coatings was also measured for the Ni cones deposited on the polished substrates (Figure 7).





**Figure 7.** AFM images of Ni cones deposited on Cu substrates polished with (**a**) 400-, (**b**) 800-, and (**c**) 1200-grit sandpapers.

The values of  $S_a$  determined based on Figure 7a, b and c are 33.5 nm, 133.4 nm, and 90.9 nm, respectively. The lowest value was obtained for the substrate polished with the 400-grit sandpaper. On this substrate, the conical structures grew in all directions, as shown in Figure 5d. It means that, during the AFM scans, instead of analyzing a cone's tip, its sidewall was detected. In the case of the higher grit (800), the cones were also growing upwards. For these cones, the difference between the measured point and the average height of the surface was the largest. There were no visible scratches for the sample deposited on a substrate polished with 1200 grit, meaning that the measured roughness is related to the cones. However, many fine structures are visible (Figure 5h).

# 3.3. Catalytic Activity

# 3.3.1. Active Surface Area

One of the crucial factors determining the catalytic activity of catalysts is their active surface area. As mentioned, the aim of the synthesis of conical Ni structures is the development of this site. The electrochemical active surface area (ECSA) was determined using Helmholtz double-layer capacitance (DLC) measurements during the CV scans, as described in [37]. In this work, the CV scans were performed for a narrow range of scan rate values, from 0.02 to 0.2 V/s.

The ECSA can be calculated based on the following equation:

$$ECSA = C_{DL}/C$$
(1)

 $C_{DL}$  is the double layer's capacity, and C is the capacitance of a catalyst's ideal flat surface, commonly assumed to be 0.04 mF/cm<sup>2</sup> [35,37]. CV scans allow for the determination of the current values in the function of the scan rates (Figure 8). The slope of the obtained curve is equal to the value of the  $C_{DL}$ . The results for the coatings synthesized in this work are listed in Table 3.



**Figure 8.** Dependency between the charging currents and scan rates for the Ni cones synthesized on the etched Cu substrate. The linear trendline is marked with its slope in the graph.

Table 3. Results of the ECSA measurements.

Sample	Substrate Preparation	ECSA [cm <sup>2</sup> ]
Ni bulk	Etched	0.7
	Etched	2.1
N.T.	Etched and polished (400 grit)	2.2
N1 cones	Etched and polished (800 grit)	2.5
	Etched and polished (1200 grit)	5.1

The geometric surface of sample  $S_g$  was 0.79 cm<sup>2</sup>. As listed in Table 3, the synthesis of conical structures, especially on the Cu substrate etched and polished with 1200 grit, increased the active surface area of the coatings. The higher the grit, the higher the active surface area. This can be related to the increased number of cones (Table 2). The value for the Ni bulk is slightly smaller than the geometric one, probably because of the approximate character of this determination, i.e., C = 0.04 mF/cm<sup>2</sup>.

#### 3.3.2. Wettability

Wettability is an essential factor in a hydrogen evolution reaction. The decrease in the value of the contact angle results in the evolution of smaller bubbles [38]. The bulk coating showed a hydrophobic character with a contact angle equal to  $112^{\circ} \pm 3^{\circ}$ . The received result complies with previous research [39], where Ni coatings were deposited from three electrolytes and showed hydrophobic properties.

The same analyses were performed for the conical structures synthesized on just etched and polished surfaces (Figure 9).



Figure 9. Wettability of Ni cones.

As expected, the values of the determined contact angles for the Ni cones are higher than for the bulk coating [35]. There is no clear influence of the polishing process on this value. However, the lowest angle value with the lowest standard deviation was noted for the sample deposited on the Cu substrate polished with 1200-grit sandpaper. As shown in Figure 5g,h, there are no scratches visible anymore on the sample surface, and the cones are better developed than the ones synthesized on the etched Cu (Figure 5a,b). Furthermore, the contact angle is slightly higher for this coating. Moreover, the slightly higher wettability of the sample polished with the 800-grit sandpaper is in accordance with the roughness measurements.

#### 3.3.3. Hydrogen Evolution Reaction

Nickel and its alloys are well known for their catalytic activity in hydrogen evolution reaction (HER) [40–47]. In this work, the catalytic performance of the Cu substrate was not investigated. Before each LSV measurement, the ohmic drop determination technique was applied. This method allows for the IR determination and compensation by means of the impedance measurement technique (ZIR).

The LSV curves for all the synthesized coatings are shown in Figure 10. The geometric surface was considered for all the samples to determine the current density.

As expected, the synthesis of Ni in conical structures increased the coatings' catalytic performance. The best catalytic activity was shown in the sample deposited on the substrate etched and polished with the 400-grit sandpaper. However, there is no clear dependency between the preparation of the Cu substrate and the activity of the cones. During intensive evolution, hydrogen bubbles were probably trapped between the cones synthesized on the polished samples. This phenomenon can influence the results of the hydrogen evolution. Indeed, stuck bubbles can block the surface of the electrode and, therefore, its further

reaction. But, even if the catalytic performance was worsened due to the blocking of the active sites, the Ni catalyst, synthesized on the Cu etched and polished with 1200-grit sandpaper, showed a better activity than the bulk Ni electrode.



**Figure 10.** Determined curves with 85% IR-drop compensated. The curve for the Ni bulk is marked with the color black. The rest of the curves are related to the Ni cones.

The values of the ONSET potential, at which hydrogen evolution started, are listed in Table 4. To determine the values of this potential, two tangents were plotted on the curve of the potential dependence on the current density (Figure 10). The point of their intersection indicates the ONSET potential (Figure S2).

Table 4. Values of the determined E<sub>ONSET</sub>.

Sample	Substrate Preparation	E <sub>ONSET</sub> [V]
Ni bulk	Etched	-1.33
	Etched	-1.25
NT:	Etched and polished (400 grit)	-1.26
NI cones	Etched and polished (800 grit)	-1.26
	Etched and polished (1200 grit)	-1.29

The earliest evolution of hydrogen was observed on the Ni cones deposited on the etched substrates. This process began last for the bulk coating. Therefore, the etching of Cu is the best way to prepare the substrate for the deposition of a suitable conical Ni catalyst. Moreover, the stability of the Ni cones deposited on the etched Cu was investigated in

1 M NaOH. The obtained curve is shown in Figure 11. The result of the stability test confirms that conical Ni structures are a suitable material

The result of the stability test confirms that conical Ni structures are a suitable material for a catalyst in an HER.



**Figure 11.** Results of chronoamperometry measurements for the Ni cones deposited on the etched Cu substrate.

## 4. Conclusions

Nickel cones can be successfully produced on Cu substrate using the one-step method. However, the influence of substrate preparation on the quality of Ni cones has not been investigated before. After choosing the proper chemical etching time, Cu foil was also polished with sandpaper. SEM observations were performed to compare the morphology of the developed Ni deposits, as well as their size and number. Smaller and larger cones were produced, growing in all directions, on the scratches after polishing. The evolution of such morphology suggests an increase in active surface area. The double-layer capacitance measurements confirmed this observation, however, without the evident influence of the polishing process. The wettability of the samples was also determined. All the coatings showed hydrophobic properties. The results of hydrogen evolution confirm the enhancement of catalytic properties due to the conical shape of the deposits. However, they are not significantly influenced by substrate preparation. The main obstacle in the case of polishing the substrate seems to be the further blocking of nucleating hydrogen bubbles between the cones. Therefore, etching is a sufficient procedure for surface preparation. Generally, substrate preparation procedures can significantly influence the deposition of cones of other metals and alloys and should always be considered.

**Supplementary Materials:** The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/coatings13122067/s1: Table S1: Chemical compositions determined by the EDS technique. Figure S1: XRD diffraction pattern of the conical Ni coating deposited on the etched Cu substrate. Figure S2: Determination of the ONSET potential.

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