



Electrocrystallization of Ni nanocones from chloride-based bath using crystal modifier by electrochemical methods



Gh Barati Darband^a, M. Aliofkhazraei^{a,*}, A. Dolati^b, A. Sabour Rouhaghdam^a

^a Department of Materials Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran

^b Department of Materials Science and Engineering, Sharif University of Technology, Azadi Ave., P.O. Box 11155-9466, Tehran, Iran

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ABSTRACT

The early stages of nucleation and growth of nanostructures can control the shape and final size of the fabricated nanostructure. Therefore, the study of the nucleation and growth mechanism of nanostructures is of great importance. The purpose of this study is to investigate the nucleation and growth mechanism of nickel nanocones from a chloride-based bath containing ethylene ammonium dichloride as a crystal modifier. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry tests were employed to investigate the nucleation and growth mechanism and also the mechanism of crystal modifier performance on the growth of nanocones. Electrochemical studies revealed that the deposition of Ni nanocones occurs as nucleation and growth, and the growth of Ni nanocones can be considered as a competitive growth between two-dimensional and three-dimensional growth. By increasing the concentration of crystal modifier in the coating bath, the growth rate accelerates in the vertical direction, leading to enhance in three-dimensional growth. In general, according to the results of this study, the growth of nickel nanocones can be attributed to the synergistic effect between crystal modifiers and growth caused by screw dislocation.

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1. Introduction

Nanostructures with high aspect ratios such as nanowires, nanotubes, and nanocones have received a great deal of attention in recent years due to their unique properties. The important applications which these nanostructures can have include usage in interconnects [1,2] optoelectronics, nanosensors [3] and nanobiotechnology [4]. In general, the properties of these nanostructures are governed by their size, and through changing their size, new properties can be added or the existing ones can be altered. Metallic nanostructures such as nanowires and nanotube have been synthesized by various methods. However, in many cases, these nanostructures are randomly distributed which is the main obstacles to their usage in important applications.

One of the recent nanostructures that have attracted a lot of attention is the metallic nanocones. These nanocone materials can be used in numerous applications, including HER electrocatalyst [5–8], super-hydrophobic surfaces [9] and the use of their field

emission properties [10]. In recent years, a small number of metallic nanocone cases have been reported, most of which have fabricated based on a template-based method. Although these nanocones are regular and possess desirable properties, the use of the template to create them is one of the major barriers due to the dimensional limitations of the used templates [11,12]. In addition, the method for creating nanocones materials using template-based methods is often difficult and tedious. One of the single-step and important methods for making metallic nano-materials is the use of the electrochemical deposition method. In the electrochemical deposition method, the dimensions of the nanocones are also a function of treatment variables. Since the number and size of the initial nuclei can be successfully changed by changing the variables governing the electrochemical deposition method, such as the overpotential and the chemical composition of the bath, the electrochemical deposition method is regarded as a popular method for the formation of metallic nanocones.

Generally, the initial stages of nucleation and growth are essential when it comes to the method of electrochemical deposition [13–15]. Understanding the mechanism of nucleation and growth in electrocrystallization is an important step in controlling the shape and final size of nanostructures and consequently, their

* Corresponding author.

E-mail addresses: maliofkh@gmail.com, khazraei@modares.ac.ir (M. Aliofkhazraei).

application [16–18]. This first stage of electrochemical phase change can include one-dimensional, two-dimensional, and three-dimensional nucleation [19]. In general, a number of crystals modifier has been utilized for the creation of cones in an electrochemical deposition method, among which boric acid [20] and CaCl_2 [21] can be mentioned. But microscopic studies of the cones created by these crystal modifiers show that the use of these compounds does not lead to the formation of cones with nano dimensions. The most desirable crystal modifier that can be used to create nanocones materials is ethylenediammonium dichloride ($\text{C}_2\text{H}_{10}\text{Cl}_2\text{N}_2$). As stated, finding the mechanism of nucleation and growth is of great importance. So far, efforts have been made to find the nucleation and growth mechanism of the cones by various methods, but there is no comprehensive mechanism for the growth of the nanocones in a bath containing crystal modifiers. For example, Rahimi et al. [20,22] used the method of density functional theory (DFT), Monte Carlo and AFM to investigate the mechanism of the operation of boric acid in the formation of cones. To the best of our knowledge, the study of the nucleation and growth mechanism of nickel nanocones in the bath containing ethylenediammonium dichloride has not yet been carried out by electrochemical methods. Therefore, the purpose of this study is to investigate the nucleation and growth mechanism, of nanocones by electrochemical methods, and also to investigate the mechanism of ethylenediammonium dichloride performance as crystal modifier for the fabrication of metallic nanocones.

2. Experimental details

In this study, high purity test materials were acquired from Merck Company. The basic chemical composition of the bath used was $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (238 g/L) and boric acid (H_3BO_3) at 31 g/L. Different concentrations of ethylenediammonium dichloride (50, 100, 150, 200 g/L) were added to the coating bath to evaluate the mechanism of crystal modifier performance. The pH of the solution was adjusted to 4. To conduct the electrochemical experiments, a standard three-electrode cell was used, in which saturated calomel electrode (SCE), glassy carbon electrode (GCE) and a graphite rod served as a reference electrode, working electrode and an auxiliary electrode, respectively. The GCE was properly prepared prior to the start of the experimentations. GCE was first sanded to the degree of mirroring, and then polishing operations were performed. The GCE was then ultrasonically degreased in acetone for 15 min and washed with distilled water. All electrochemical experiments were performed by Potentiostat-Model SP300. The EIS test was performed at various potentials needed to generate 2, 5, and 10 mA/cm^2 in the range of 100 kHz to 100 mHz. In order to plot the chronoamperometry curves, the potentials were applied in two stages, where the potential of the first stage was a small value in which deposition did not occur, and then a second stage potential was applied where the deposition occurred. The first stage of potential was used to reduce the background current. Furthermore, field scanning electron microscope (FESEM) (MIRA3-TESCAN) was employed for microscopic examination.

3. Results and discussion

3.1. Cyclic voltammetry

The cyclic voltammetry curve of the GCE in a chloride-based solution containing 200 g/L ethylenediammonium dichloride is shown in Fig. 1a. According to the figure, with increasing the potential from 0 to -512 mV vs. SCE, the current is almost zero. With increasing potential in the negative direction, the cathodic current density is increased and a cathodic peak is observed. The formation

of a cathodic peak is due to the decrease of the concentration of nickel ions in the interface between the electrode and the electrolyte, which makes the system in diffusion control. Afterwards, with increasing potential, the cathodic current density increases linearly. An increase in current at -512 mV potentials range indicates crystallization. Moreover, the reason for increasing the cathodic current density at potentials greater than -630 mV vs. SCE is reaching water-splitting reaction, during which the hydrogen evolution reaction occurs. The presence of a cathodic peak in a cathodic scan indicates that the electrodeposition of Ni nanocones is in diffusion-controlled. The returning anodic scan reveals that the potential shift to the anodic values decreases the cathodic current density. Furthermore, the returning scan has two crossovers with the cathodic scan. A crossover at potential is more negative than the crystallization of the nickel ions, and another is in the zero current, which indicates the metal deposition on an external substrate. In anodic scanning at greater anodic potentials, there is an anodic peak, indicating the separation of the formed nanocones in the cathodic scan. The difference between the potential of anodic and cathodic peaks shows that the electrochemical deposition of nickel nanocones materials is irreversible [23,24]. Additionally, Fig. 1b represents the variations in the cathodic part of CV curves formed at different scanning rates (5–100 mV/s). It can be observed that with increasing scanning rate, the current density of the cathodic peak is also increases and that the cathodic peak position shifts to more negative values. From these curves, $E_p - E_{p/2}$ variations (in which E_p is the potential in the cathodic peak and $E_{p/2}$ is the potential in the half-cathodic current peak) were plotted in terms of the root of the scanning rate, as well as peak current changes based on the root rate of scanning, as shown in Fig. 1c and d, respectively. The linear variations of these curves indicate that the reduction of nickel ions in the presence of crystal modifiers is irreversible, and a process controlled by charge transfer [25]. The greater amount of current in the anodic scan indicates that the nickel deposition on the nickel surface is easier than the deposition of nickel on the GEC surface.

3.2. Electrochemical impedance spectroscopy

To further examine the mechanism of nickel deposition, and to find out more about the mechanism of nickel deposition in the presence of crystal modifiers in a coating bath, EIS studies were used at different cathodic potentials. The potentials used in this study were the potentials needed to generate the currents of 2, 5 and 10 mA/cm^2 . Nyquist curves for samples produced in baths with different concentrations of crystal modifiers, as well as in different potentials, are shown in Fig. 2. The electrical equivalent circuit (EEC) used to analyze the EIS data is also displayed in Fig. 3. In this equivalent circuit, R_s represents the solution resistance, CPE1 represents the constant phase element of the charge transfer reaction, R_1 is the charge transfer resistance, L_1 represents the induction, and R_2 represents the inductive resistance. Considering the equivalent circuit, it can be concluded that in the chloride-based baths containing crystal modifiers, charge transfer and induction behavior can be observed. Regarding the Nyquist curves, it has been observed that the curves include two semicircles at high and low frequencies ranges, respectively, which are referred to as capacitive and inductive loops. As shown in the curves and the equivalent circuit, the Nyquist curves at the high frequencies ranges include a semicircle indicating a charge transfer reaction in parallel with a double-layer capacitance, and at low frequencies range include a half inductive circle. Both the charge and induction resistance are subject to environmental conditions and potential functions. In general, the interpretation of data in the impedance spectrum at lower frequencies is more difficult than high frequencies, however,

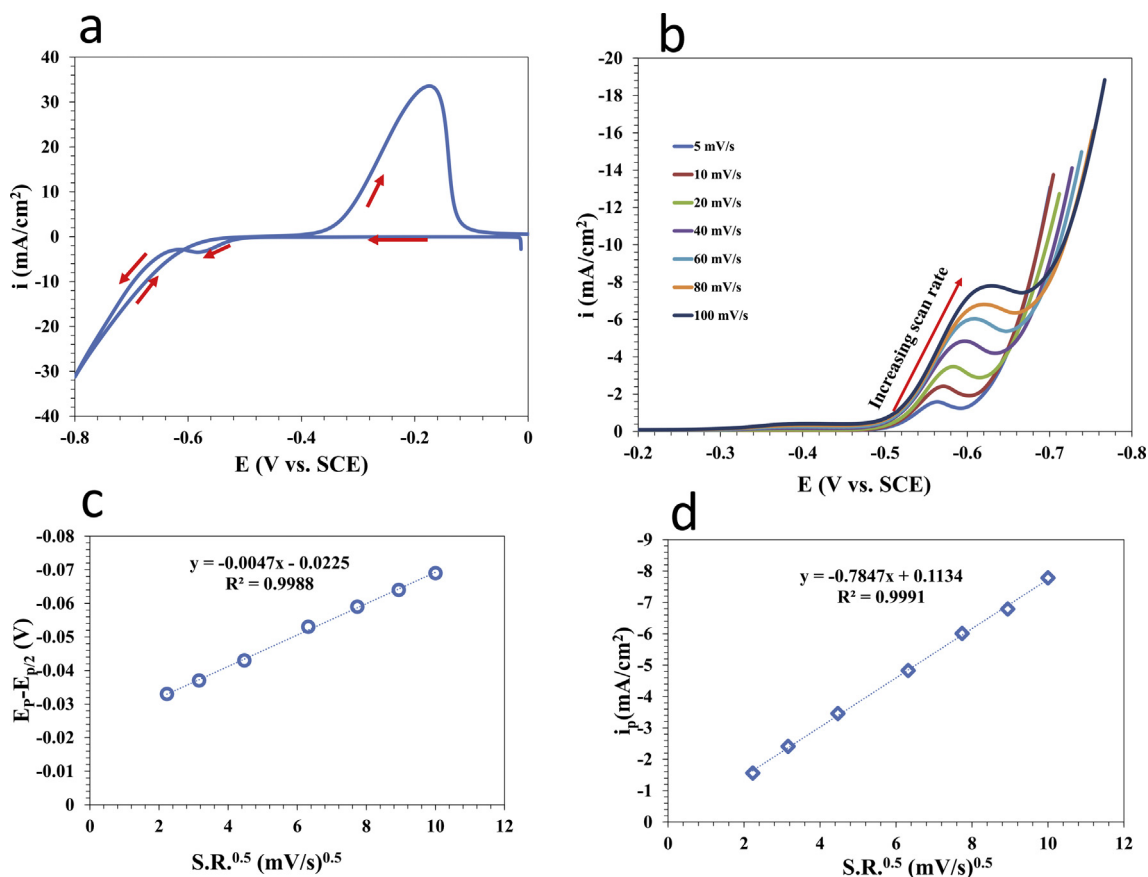


Fig. 1. a) CV curve of Ni deposition from bath containing crystal modifier with a scanning rate of 20 mV/s, b) CV curves of Ni deposition on the GCE at different scanning rates, c) variation of $E_p - E_{p/2}$ as a function of the root of the scanning rate and d) variation of cathodic current density peak as a function of root of the scanning rate.

the presence of an induction loop in the Nyquist curve indicates that adsorption occurs successfully [26]. Moreover, this behavior can be attributed due to the release of ions inside the solution [27]. According to Kabi et al. [28], the observed induction loop at low frequencies can be attributed to the influence of the active electrochemical species that participate in the electrochemical reaction. Furthermore, according to studies by Malpass et al. [29], the emergence of an induction loop in chloride solutions can be associated with the slow adsorption of anionic species, which in their studies, consisted of chloride-containing complexes. It is also observed that by increasing the cathodic potential, the charge transfer resistance is decreased. The reason for reducing the amount of charge transfer resistance in greater cathodic potentials is to increase the driving force energy of nickel deposition. Because in this situation, the number of electrons is higher and the amount of energy needed to reduction of nickel ions in the surface is lowered. Furthermore, according to Wang et al. [30], the decrease in the charge transfer resistance by increasing the cathodic potential can be a result of increased surface ion penetration. In general, the magnitude of the charge resistance is a sign of the simplicity of the reaction [31]. By studying the Nyquist curves of the nanocones formed at various concentrations of the crystal modifier, it can be concluded that at the more positive potentials of the Nyquist curve, there is a semicircle indicating the charge transfer resistance in parallel with a layer capacitance, another induction loop is also present in the curve. The difference between the impedance curves for baths with different concentrations of crystal modifiers is to reduce the charge resistance due to the increase in the crystal modifier concentration in the coating bath, which means decrease

of the energy needed for nucleation and growth by increasing the amount of crystal modifiers. This means that the addition of crystal modifiers simplifies nucleation and growth. It is generally known that charge transfer occurs in three stages. The first stage involves the transfer of ions from the double-layer to the terrace sites and adsorption onto them, the second step involves the surface penetration of the adsorbed ions onto the terrace sites, and the third step is the surface penetration of the adsorbed ions onto suitable active sites for subsequent reduction. Therefore, in general, it can be concluded that by increasing the number of surficial active sites for the reduction of nickel ions, the charge transfer resistance will be decreased. The addition of crystal modifiers to the coating bath will increase the surficial active surfaces for the reduction of nickel ions on the surface, thereby lowering the charge transfer resistance.

3.3. Chronoamperometry

Chronoamperometry test was used to study the electrocrystallization kinetics, and to obtain more information about the mechanisms of nucleation and growth. Since the nucleation and growth driving force can be changed by changing the overpotential in the electrochemical reactions, the current-time method can be used to study the nucleation and growth kinetics during electrocrystallization. In this study, in order to investigate the effect of ethylenediammonium dichloride concentrations on nucleation, growth, as well as kinetic growth of nickel nanocones, chronoamperometry curves at different application potentials and different concentrations of ethylenediammonium dichloride (50, 100, 150 and 200 g/L). chronoamperometry curves at different

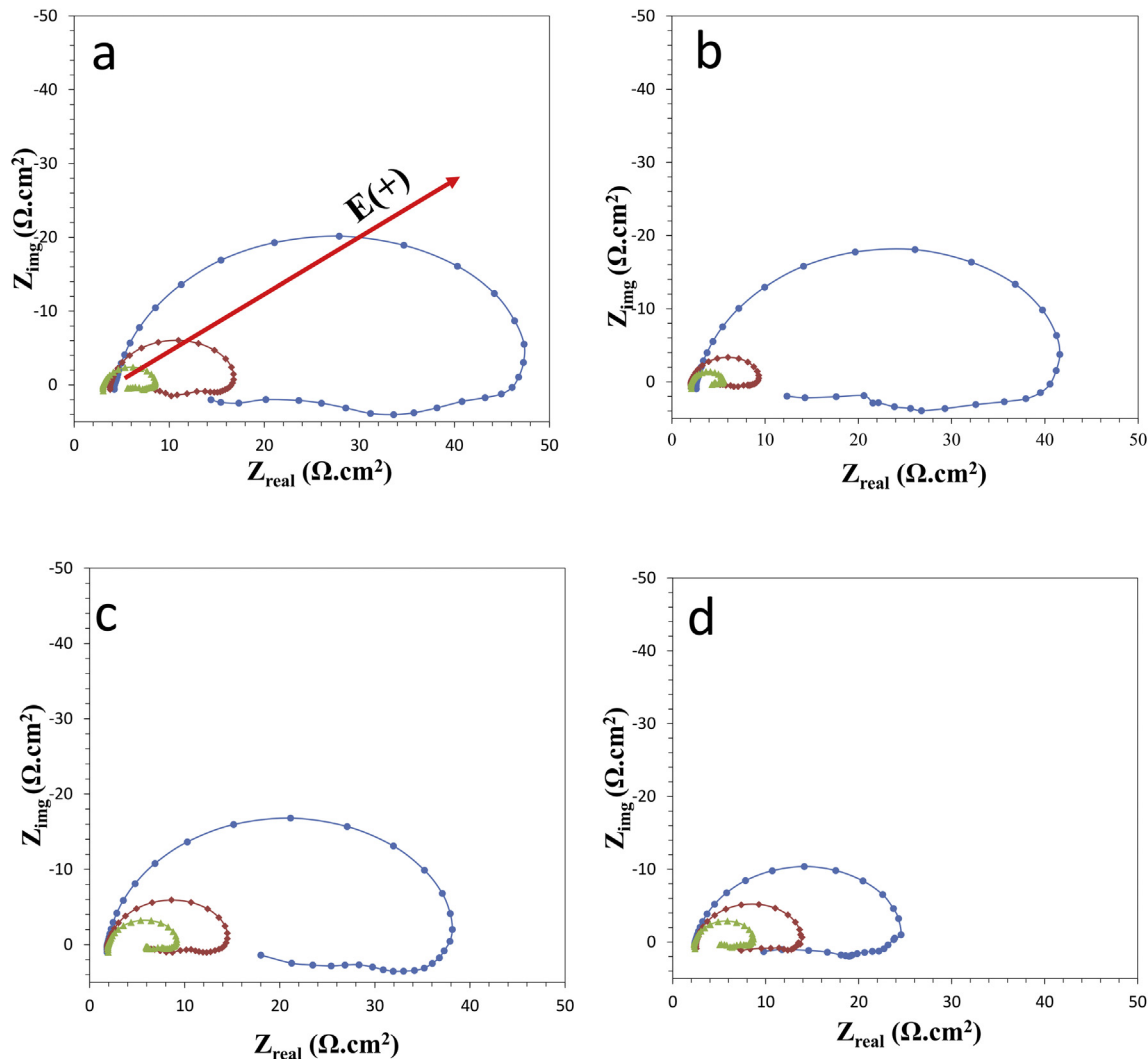


Fig. 2. Nyquist curves during electrodeposition of the Ni nanocones on the GCE in the chloride based-bath containing different amounts of crystal modifiers a) 50 g/L, b) 100 g/L, c) 150 g/L and d) 200 g/L.

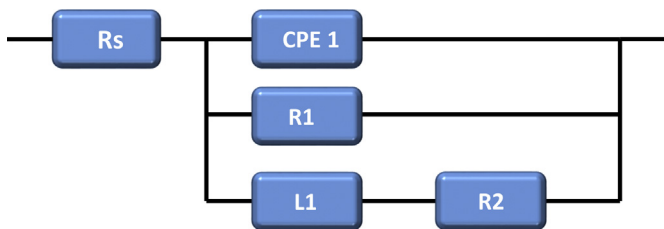


Fig. 3. Electrical equivalent circuit used for analyzing the EIS data.

crystal modifier concentrations and different applied potentials are shown in Fig. 4. By analyzing the shape of the curves, a nucleation and growth mechanism can be obtained. The shape of the curves in this study reveals that the nucleation and growth process occurs in the electrochemical deposition of the nickel nanocones, which is consistent with the nucleation loop observed in cyclic voltammetry curves. Generally, at the start of each curve, there will be a charging current that will decrease rapidly during the nucleation and growth of nanocones. Initially, there is a slight drop in current at the starting times. Such a decrease exists in current-time curves in electrochemical deposition systems, which can be attributed to

various processes such as adsorption [32,33], multi-stage charge-transfer reactions [34] and redox processes [35]. With respect to these curves, it is observed that after the initial decrease in current, it is later increased. Analysis of this section shows that increasing the current before a large peak in the current indicates that the nucleation stage had led to a new phase [36]. At this stage of nucleation and growth, a diffusion zone will be created around the nuclei. Over time, due to the linear influx of ions towards the electrode, the current should be reduced and directed towards the diffusion current. However, the nucleation and growth of a new layer on the surface of the previous layer prevent the current from decreasing. Therefore, after creating a peak in the curve, the current is increased and approaches a constant value. It is seen that in different potentials and different concentrations of ethylenediammonium dichloride, the overall shape of the curves is similar. However, the time required for reaching the potential at maximum current (t_{max}) is decreased and also the maximum current (i_{max}) is increased. Decrease of t_{max} by increasing the overpotential is caused by the decrease in the activation energy of nucleation and growth.

According to the shape of the curves observed in this study, a nucleation and growth mechanism can be obtained for nickel

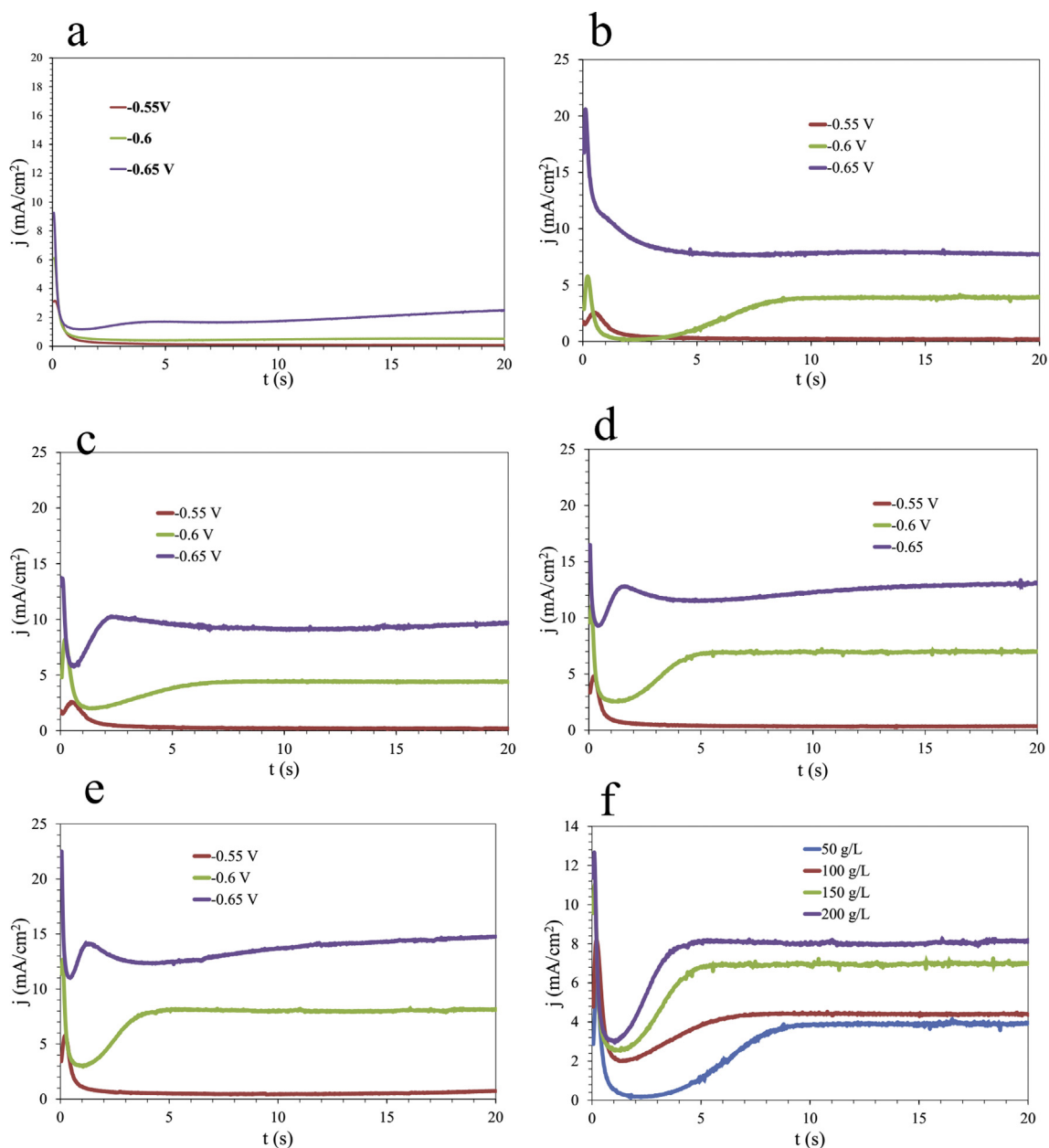


Fig. 4. Current–time transients of Ni nanocones in the bath at different concentration of crystal modifier a) 0, b) 50, c) 100, d) 150 and d) 200 g/L and under different applied potential and f) the current–time transients at different concentration of crystal modifier and applied potential of -0.6 V vs SCE.

nanocones. Considering the shape of the nanocones, it can be assumed that the growth of these nanocones is due to the competition between two-dimensional and three-dimensional growth. Therefore, the first stage is the growth of the nanocones via layer-by-layer deposition. This stage of growth can be expressed by the theory stated by Bewick et al. [37]. In this theory, a two-dimensional growth model is considered in which a nucleus is initially created, and then the growth rate is determined by the insertion of ad-atom into this growing nucleus. Moreover, in this theory, the overlap of these growing center is also considered. The theory suggests that there will be two types of nucleation including instantaneous and progressive. During instantaneous nucleation, all nuclei will be created in the beginning of growth, whereas throughout the progressive nucleation, nuclei will also be created during growth. Consequently, in instantaneous nucleation, all nuclei will grow together and the size of the nucleus will roughly be

the same. However, in the progressive model, the size of the growing nucleus will not be different. In this theory, the current generated by instantaneous and progressive nucleation will be as the following equations:

$$I_{2DI} = \frac{2nFMHN_0K^2t}{P} \exp\left[\frac{-nN_0M^2K^2t^2}{P^2}\right] \quad (1)$$

$$I_{2DP} = \frac{nFMHN_0K^2t^2}{P} \exp\left[\frac{-nAN_0M^2K^2t^3}{3P^2}\right] \quad (2)$$

By analyzing these currents, it can be concluded that each of these current includes a peak in which the i_{max} and t_{max} for instantaneous and progressive nucleation can be expressed as:

$$t_m = \left(\frac{p^2}{2.7 N_0 M^2 k} \right)^{0.5} \quad (3)$$

$$I_m = nFhk (2.7 N_0)^{0.5} \exp\left(-\frac{1}{2}\right) \quad (4)$$

$$t_m \left(\frac{2p^2}{.7 AN_0 M^2 k} \right)^{1/3} \quad (5)$$

$$I_m = nF \left(\frac{4.7 AN_0 k p}{M} \right)^{\frac{1}{3}} \text{hexp}\left(-\frac{2}{3}\right) \quad (6)$$

With respect to the currents, it can be seen that during high and low times, the current tends to be zero, however according to current-time curves, it was observed that the current initially is zero and that it was increased for an extended period following the initial peak of the current, and then goes to non-zero values. Therefore, it can be stated that the growth of nanocones is a competitive growth between two-dimensional and three-dimensional growth.

Electrocrystallization of a new phase on an external surface may involve the formation of a three-dimensional growth center at an early stage. After the creation of the layer which was expressed by Bewick theory, the second layer grows upon the first one and this growth continues in the three-dimensional mode. Three-dimensional growth can be expressed by Armstrong theory [38]. In this theory, it is assumed that the growth center can be represented by a growing cone. In this model, the growth occurs in two directions, which shows the growth constant in the horizontal direction with k_3 and growth in the vertical direction by k'_3 . The current generated by the Armstrong model for instantaneous and progressive nucleation can be expressed as follows:

$$I_{3DI} = nFK'_3 \left(1 - \exp\left(\frac{-.7M^2K_3^2 N_0 t^2}{p^2}\right) \right) \quad (7)$$

$$I_{3DP} = nFK'_3 \left(1 - \exp\left(\frac{-.7M^2K_3^2 A_3 t^3}{p^2}\right) \right) \quad (8)$$

The above equations can also be stated as the following equations in the initial times:

$$I_{3DI} = \frac{nFK'_3 .7 M^2 K_3^2 N_0}{p^2} t^2 \quad (9)$$

$$I_{3DP} = \frac{nFK'_3 .7 M^2 K_3^2 A_3}{p^2} t^3 \quad (10)$$

During extended times, the current of both nucleation mechanisms in the Armstrong theory can be expressed as the following:

$$I = nFk'_3 \quad (11)$$

It can be observed that in Armstrong's theory during initial times, the current is equal to zero, and at long current times, the current is close to a certain amount which is somewhat related to the growth rate in the vertical direction. Therefore, in current-time curves, the final current may indicate the growth rate constant in the vertical direction. Consequently, in general, the total current generated by the formation of nickel nanocones on the surface of GCE can be written as follows:

$$I = I_{DL} + I_{2DI} + I_{2DIP} + I_{3DI} + I_{3DP} \quad (12)$$

According to the points discussed, the role of increasing the concentration of ethylenediammonium dichloride in the formation of nanocones can now be expressed. As stated, in Armstrong theory, the current has a direct relation with the growth rate in the vertical direction. The current-time curves at a static potential (-0.6 V vs. SCE) in baths with different concentrations of ethylenediammonium dichloride are represented in Fig. 4f. Moreover, the current related to 3-D growth is also shown in Fig. 5a. With respect to these curves, it is seen that increasing the concentration of ethylenediammonium dichloride increases the amount of current related to 3-D growth. This means that by increasing the crystal modifier concentration in the coating bath, the growth rate is enhanced in the vertical direction, which leads to the formation of nanocones. Another important point that can be deduced from current-time curves is the required time to reach 3D growth. If the time needed to reach the 3-D growth is smaller, then more 3D growth nuclei will be created and the diameter of the nanocones will be decreased while their length will be increased. The variation curve of the three-dimensional growth time according to the concentration of ethylenediammonium dichloride is illustrated in Fig. 5b. It can be observed that with the increase in the concentration of the crystal modifiers in the coating bath, the required time to reach the three-dimensional growth is decreased, which results in the growth of three-dimensional growth nucleation centers, thereby reducing the diameter and increasing the length of the nanocones.

Based on the aforementioned results, a 2D-3D growth mechanism of Ni nanocones is schematically represented in current-time transient in Fig. 6. It is seen that firstly, a layer is formed and then a 3-D growth center is created and that the growth at the center will result in the formation of nanocones structure. Another factor that can be discussed is the nanometric stage created on the surface of the nanocones. The creation of nanometric stages on the surface of the nanocones can be ascribed to the presence of screw-dislocation edges on the surface of the growing center. Furthermore, these edges play an essential role in the electrochemical deposition of nickel nanocones. These edges provide the adsorption pathway with lower energy for the adsorption of nickel ions and nickel complexes, leading to the creation of nanosteps on the surface of the nanocones. Therefore, in general, the mechanism of creating nanocones with nanosteps on the surface could be the simultaneous effect of a crystal modifier which increases the growth rate in the vertical direction and the presence of the edges due to screw dislocations, which results in the screw dislocation-driven mechanism of growth.

3.4. Microscopic studies

In order to study the effect of ethylenediammonium dichloride concentration on nucleation and growth, and to confirm the results obtained from electrochemical methods, FESEM was employed to investigate the morphology of the nanocones created at various concentrations of crystal modifiers under different coatings time. FESEM images from a sample surface at a concentration of 200 g/L of ethylenediammonium dichloride under different times on the current-time curve are displayed in Fig. 7. It can be seen from the FESEM images that at first, the nucleus grows in two-dimensional shape, and at the stage of reaching the three-dimensional growth of the nanocones, growth is continue with the time, which confirms that these images are in accordance with the theory expressed in the current-time studies.

In addition, the effect of crystal modifiers concentration on the morphology of the nanocones was microscopically studied. FESEM

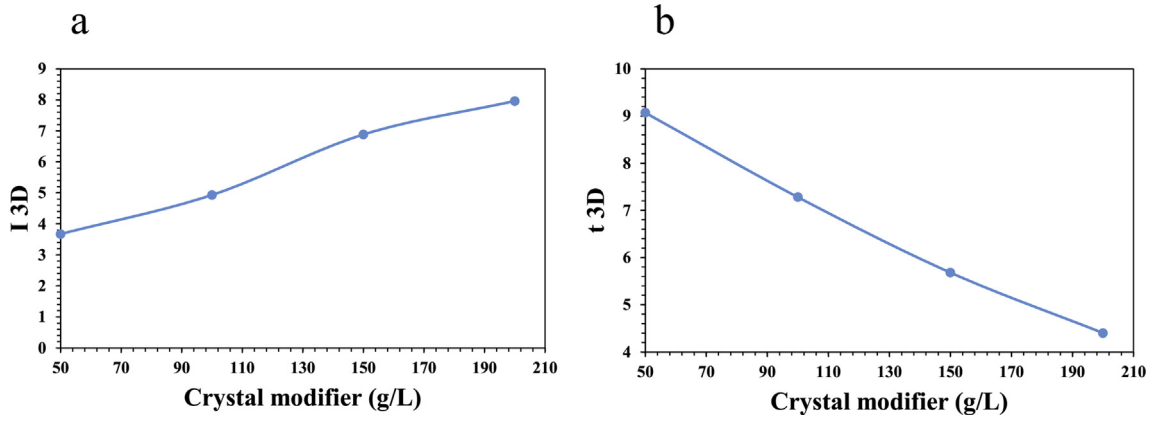


Fig. 5. a) the current related to 3-D growth (I_{3D}) as a function of crystal modifier concentration in the coating bath and b) the time at reaching 3-D growth as a function of crystal modifier concentration in the coating bath.

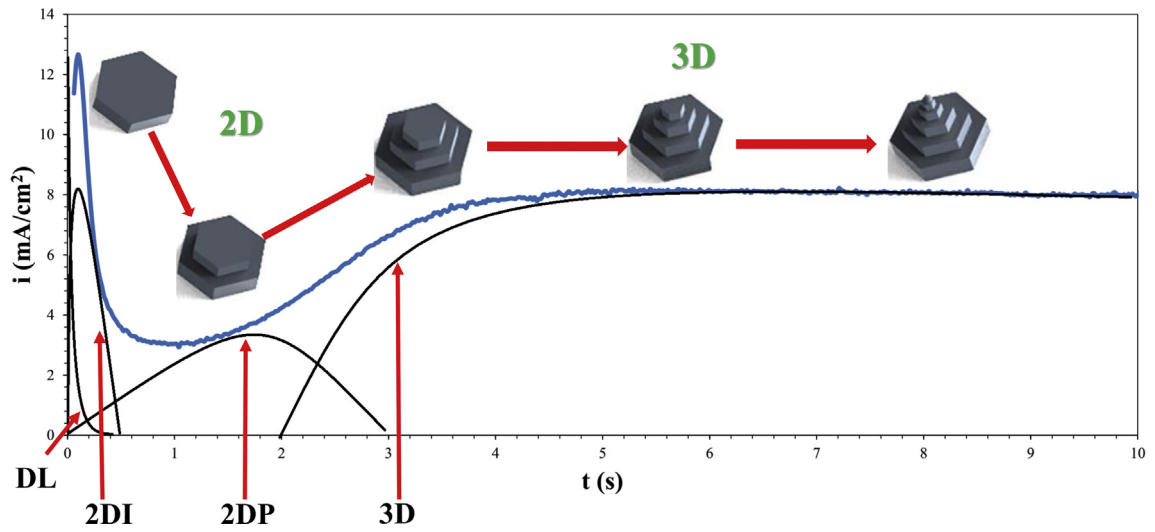


Fig. 6. Schematic showing 2D-3D nucleation and growth mechanism of nanocones structure.

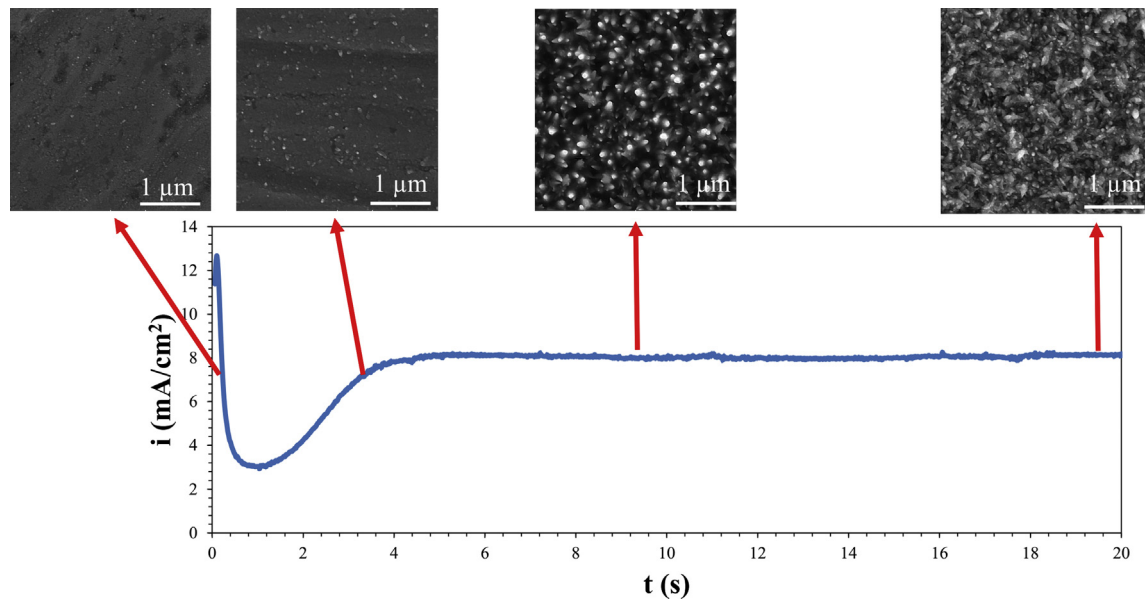


Fig. 7. FESEM images at an early stage of nucleation and growth on the current-time curve.

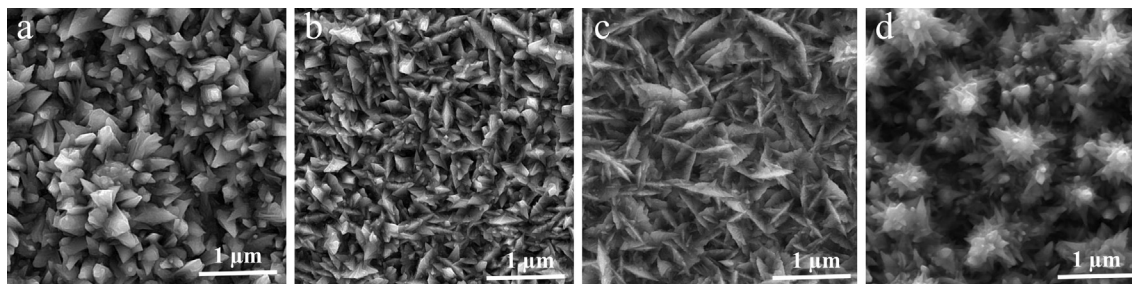


Fig. 8. FESEM images of nanocones fabricated in the baths with different concentrations of crystal modifiers.

images of nanocones surfaces formed at different concentrations of crystal modifier are shown in Fig. 8. With respect to the shapes, it can be observed that by increasing the concentration of crystal modifiers in the coating bath, the diameter of the cones is decreased and their lengths are increased. In other words, the growth contribution of the three-dimensional growth is enhanced and finally, at a concentration of 200 g/L of ethylenediammonium dichloride, the smallest diameter of the nanocones and the greatest contribution of the three-dimensional growth is observed. The results of microscopic studies are in accordance with the results obtained from the electrochemical evaluations.

4. Conclusion

In this study, the mechanisms of nucleation and growth for Ni nanocones were studied using electrochemical methods. The results proved that the electrochemical deposition of Ni nanocones is nucleation and growth under diffusion control. Moreover, electrochemical studies revealed that nucleation and growth of nanocones are a competitive mechanism between two-dimensional and three-dimensional growth, where the two-dimensional growth can be determined by Bewick's theory, and the three-dimensional growth can be expressed by Armstrong's theory. First, a two-dimensional layer is created on the surface, and then prior to the growth of the first two-dimensional layer, the three-dimensional growth takes place on the surface of the first layer. It was also observed that increasing the concentration of crystal modifiers resulted in increase of the contribution of three-dimensional growth, while also reduce the time required to reach three-dimensional growth. Microscopic studies were found to be in agreement with the results obtained from the electrochemical studies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] R. Langford, T.-X. Wang, M. Thornton, A. Heidelberg, J. Sheridan, W. Blau, R. Leahy, Comparison of different methods to contact to nanowires, *J. Vac. Sci. Technol. B: Microelect. Nanometer Struct. Proc. Meas. Phenom.* 24 (2006) 2306–2311.
- [2] R. Agarwal, C. Lieber, Semiconductor nanowires: optics and optoelectronics, *Appl. Phys. A* 85 (2006) 209.
- [3] B.J. Murray, E.C. Walter, R.M. Penner, Amine vapor sensing with silver mesowires, *Nano Lett.* 4 (2004) 665–670.
- [4] J.L. Elechiguerra, J.L. Burt, J.R. Morones, A. Camacho-Bragado, X. Gao, H.H. Lara, M.J. Yacaman, Interaction of silver nanoparticles with HIV-1, *J. Nanobiotechnol.* 3 (2005) 6.
- [5] G. Barati Darband, M. Aliofkhaezrai, A. Sabour Rouhaghdam, Three-dimensional porous Ni-CNT composite nanocones as high performance electrocatalysts for hydrogen evolution reaction, *J. Electroanal. Chem.* 829 (2018) 194–207.
- [6] G.B. Darband, M. Aliofkhaezrai, A.S. Rouhaghdam, Nickel nanocones as efficient and stable catalyst for electrochemical hydrogen evolution reaction, *Int. J. Hydrogen Energy* 42 (2017) 14560–14565.
- [7] G.B. Darband, M. Aliofkhaezrai, A.S. Rouhaghdam, M.A. Kiani, Three-dimensional Ni-Co alloy hierarchical nanostructure as efficient non-noble-metal electrocatalyst for hydrogen evolution reaction, *Appl. Surf. Sci.* 465 (2019) 846–862.
- [8] G.B. Darband, M. Aliofkhaezrai, A.S. Rouhaghdam, Facile electrodeposition of ternary Ni-Fe-Co alloy nanostructure as a binder free, cost-effective and durable electrocatalyst for high-performance overall water splitting, *J. Colloid Interface Sci.* 547 (2019) 407–420.
- [9] G. Barati Darband, M. Aliofkhaezrai, S. Khorsand, S. Sokhanvar, A. Kaboli, Science and engineering of superhydrophobic surfaces: review of corrosion resistance, chemical and mechanical stability, *Arab. J. Chem.* (2018), <https://doi.org/10.1016/j.arabjc.2018.01.013> (in press).
- [10] T. Hang, H. Ling, A. Hu, M. Li, Growth mechanism and field emission properties of nickel nanocones array fabricated by one-step electrodeposition, *J. Electrochem. Soc.* 157 (2010) D624–D627.
- [11] Z. Tang, N.A. Kotov, M. Giersig, Spontaneous organization of single CdTe nanoparticles into luminescent nanowires, *Science* 297 (2002) 237–240.
- [12] G. Heydon, S.R. Hoon, A. Farley, S. Tomlinson, M. Valera, K. Attenborough, W. Schwarzacher, Magnetic properties of electrodeposited nanowires, *J. Phys. D Appl. Phys.* 30 (1997) 1083.
- [13] M.d.C. Aguirre, Nucleation and growth mechanisms of palladium, nanoflower-shaped, and its performance as electrocatalyst in the reduction of Cr(VI), *J. Appl. Electrochem.* 49 (2019) 795–809.
- [14] M.H. Mamme, J. Deconinck, J. Ustarroz, Transition between kinetic and diffusion control during the initial stages of electrochemical growth using numerical modelling, *Electrochim. Acta* 258 (2017) 662–668.
- [15] M.H. Mamme, C. Köhn, J. Deconinck, J. Ustarroz, Numerical insights into the early stages of nanoscale electrodeposition: nanocluster surface diffusion and aggregative growth, *Nanoscale* 10 (2018) 7194–7209.
- [16] Y. Deng, H. Ling, X. Feng, T. Hang, M. Li, Electrodeposition and characterization of copper nanocone structures, *CrystEngComm* 17 (2015) 868–876.
- [17] W. Zhang, Z. Yu, Z. Chen, M. Li, Preparation of super-hydrophobic Cu/Ni coating with micro-nano hierarchical structure, *Mater. Lett.* 67 (2012) 327–330.
- [18] Z. Feng, L. Wang, D. Li, S. Gao, Q. Sun, P. Lu, P. Xing, M. An, Nucleation and growth mechanism of a nanosheet-structured NiCoSe₂ layer prepared by electrodeposition, *Nanotechnology* 30 (2019) 245602.
- [19] F. Barry, V. Cunnane, Synergistic effects of organic additives on the discharge, nucleation and growth mechanisms of tin at polycrystalline copper electrodes, *J. Electroanal. Chem.* 537 (2002) 151–163.
- [20] E. Rahimi, A. Rafsanjani-Abbasi, A. Imani, A.R.K. Rashid, S. Hosseinpour, A. Davoodi, Synergistic effect of a crystal modifier and screw dislocation step defects on the formation mechanism of nickel micro-nanocone, *Mater. Lett.* 245 (2019) 68–72.
- [21] J.M. Lee, K.K. Jung, S.H. Lee, J.S. Ko, One-step fabrication of nickel nanocones by electrodeposition using CaCl₂·2H₂O as capping reagent, *Appl. Surf. Sci.* 369 (2016) 163–169.
- [22] E. Rahimi, A. Davoodi, A.R. Kiani Rashid, Characterization of screw dislocation-driven growth in nickel micro-nanostructure electrodeposition process by AFM, *Mater. Lett.* 210 (2018) 341–344.
- [23] S. Fletcher, Some new formulae applicable to electrochemical nucleation/growth/collision, *Electrochim. Acta* 28 (1983) 917–923.
- [24] S. Fletcher, C. Halliday, D. Gates, M. Westcott, T. Lwin, G. Nelson, The response of some nucleation/growth processes to triangular scans of potential, *J. Electroanal. Chem. Interfacial Electrochem.* 159 (1983) 267–285.
- [25] A.J. Bard, L.R. Faulkner, Fundamentals and applications, *Electrochem. Meth.* 2 (2001) 482.
- [26] F. Giannopoulos, N. Chronopoulou, J. Bai, H. Zhao, D. Pantelis, E. Pavlatou, A. Karantonis, Nickel/MWCNT-Al₂O₃ electrochemical co-deposition: structural properties and mechanistic aspects, *Electrochim. Acta* 207 (2016) 76–86.
- [27] M. Farzaneh, K. Raeissi, M. Golozar, Effect of current density on deposition process and properties of nanocrystalline Ni-Co-W alloy coatings, *J. Alloy. Comp.* 489 (2010) 488–492.

- [28] S. Kabi, K. Raeissi, A. Saatchi, Effect of polarization type on properties of Ni–W nanocrystalline electrodeposits, *J. Appl. Electrochem.* 39 (2009) 1279–1285.
- [29] G.R. Malpass, M. Kalaji, E.C. Venancio, A.J. Motheo, Electrodeposition of nickel on carbon felt, *Electrochim. Acta* 49 (2004) 4933–4938.
- [30] L. Wang, Y. Gao, T. Xu, Q. Xue, A comparative study on the tribological behavior of nanocrystalline nickel and cobalt coatings correlated with grain size and phase structure, *Mater. Chem. Phys.* 99 (2006) 96–103.
- [31] M. Holm, T. O'keefe, Evaluation of nickel deposition by electrochemical impedance spectroscopy, *J. Appl. Electrochem.* 30 (2000) 1125–1132.
- [32] A. Radisic, P.M. Vereecken, J.B. Hannon, P.C. Searson, F.M. Ross, Quantifying electrochemical nucleation and growth of nanoscale clusters using real-time kinetic data, *Nano Lett.* 6 (2006) 238–242.
- [33] A. Martínez-Ruiz, M. Palomar-Pardavé, N. Batina, Overpotential deposition of copper on an iodine-modified Au (1 1 1) electrode, *Electrochim. Acta* 53 (2008) 2115–2120.
- [34] A. Milchev, T. Zapryanova, Nucleation and growth of copper under combined charge transfer and diffusion limitations: Part I, *Electrochim. Acta* 51 (2006) 2926–2933.
- [35] A. Kelaidopoulou, G. Kokkinidis, A. Milchev, Nucleation and growth of metal catalysts. Part I. Electrodeposition of platinum on tungsten, *J. Electroanal. Chem.* 444 (1998) 195–201.
- [36] R. Barradas, E. Bosco, A kinetic model of multilayer adsorption in electrochemical phase formation, *J. Electroanal. Chem. Interfacial Electrochem.* 193 (1985) 23–26.
- [37] A. Bewick, M. Fleischmann, H. Thirsk, Kinetics of the electrocrystallization of thin films of calomel, *Trans. Faraday Soc.* 58 (1962) 2200–2216.
- [38] R. Armstrong, M. Fleischmann, H. Thirsk, The anodic behaviour of mercury in hydroxide ion solutions, *J. Electroanal. Chem.* 11 (1966) (1959) 208–223.