

V. PROTSENKO^{1*}, T. BUTYRINA¹, D. MAKHOTA¹, S. KORNIY^{1,2}, F. DANILOV¹**MODIFICATION OF SURFACE MORPHOLOGY AND SURFACE PROPERTIES OF COPPER-NICKEL ALLOY BY ANODIC TREATMENT IN A DEEP EUTECTIC SOLVENT (ETHALINE)**

A deep eutectic solvent, ethaline (as a typical representative of new-generation room temperature ionic liquids), was used to anodically treat the surface of copper-nickel alloy (55 wt.% Cu). Anodic treatment in ethaline allows flexibly affecting the patterns of surface morphology: formation of stellated crystallites and surface smoothing (i.e. electropolishing) are observed depending on the applied electrode potential. The measured values of roughness coefficient (R_a) well correlate with the changes in surface morphology. Anodic treatment of Cu-Ni alloy in ethaline contributes to a considerable increase in the electrocatalytic activity towards the hydrogen evolution reaction in an alkaline aqueous medium, which can be used to develop new high-efficient and inexpensive electrocatalysts within the framework of the concept of carbon-free hydrogen economy.

Keywords: copper-nickel alloy; anodic treatment; deep eutectic solvent; surface morphology; hydrogen production

1. Introduction

Anodic surface treatment of metal surfaces is extremely widely used to modify the microstructure, chemical composition and properties of different metals and alloys [1-4]. Electrochemical anodic treatment allows electropolishing the surface [5,6] and forming surface layers with increased catalytic or electrocatalytic activity [7-9]. For the anodic modification of the surface of metals and alloys, in principle, various types of electrolytes can be used: solutions based on water, organic solvents and ionic liquids. Currently, much attention is paid to the development of new technologies for electrochemical treatment of metal surfaces using next-generation room temperature ionic liquids, deep eutectic solvents (DESs) [10]. DESs, which are eutectic mixtures of a number of organic and/or inorganic substances, exhibit ionic conductivity and a liquid aggregate state at temperatures close to room temperature [11-13]. DESs are characterized by practically zero saturated vapor pressure, non-toxicity, environmental safety and non-combustibility. They are relatively cheap and available. The intrinsic electrical conductivity of DESs is much higher than that of organic solvents and water. All these favorable properties, as well as a number of other advantages, make it possible to consider DESs as very promising solvents

for creating a variety of electrochemical processes for metal processing and metal finishing, including metal electrodeposition and dissolution [14]. In particular, a number of recent studies have shown that electrolytes based on DESs can be successfully used for electrochemical polishing of steel [15-17], nickel and cobalt [18-20], aluminum [21,22], titanium [23,24], bronze [25] and some other metals and alloys [5].

In this context, it should be noted that, to date, the electrochemical treatment of a copper-nickel alloy using DESs is clearly insufficiently studied, although this alloy is widely used in industry and it can be assumed that anodic treatment of its surface in DESs could significantly improve its surface properties. As far as we know, only one publication [26] reported anodization of the Cu-Ni alloy in a DES to produce an electrode for detection and analytical determination of L-carnitine. In addition, study [27] should be mentioned in which 3D nanoporous layers were synthesized by anodic processing of copper-zinc alloy in DESs to fabricate a surface structure with enhanced electrocatalytic activity towards the electroreduction of nitrate ions.

Therefore, the purpose of this work was to establish patterns of the effect of anodic treatment of Cu-Ni alloy in a deep eutectic solvent on surface morphology, surface roughness, and electrocatalytic properties.

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2. Experimental

In this work, the so-called ethaline was used as a deep eutectic solvent. It was prepared by mixing ethylene glycol (99.9%, AR, Belgium) and choline chloride (99%, Acros Organics) at the temperature of 70–80°C in a molar ratio of 2:1, respectively [11]. All chemicals were used as received. The water content in this solvent, determined by the Fisher method, did not exceed 1–1.5%.

For anodic treatment, 1 mm thick copper-nickel alloy plates were used. The content of the main components in the alloy according to the manufacturer's certificate was (wt.%): Cu 54.85±0.08, Ni 44.40±0.60%. Before the experiments, the alloy samples (working electrode) with a visible surface area of 1 cm² were degreased with MgO water slurry, etched in a hydrochloric acid solution for 10 s, thoroughly washed with water, and dried in an air flow. During the anodic treatment, a graphite electrode was used as an auxiliary electrode. Electrode potentials in ethaline medium were measured relative to a silver quasi-reference electrode. Anodic treatment of the Cu-Ni alloy in the electrolyte under consideration was carried out in a thermostated (298 K) glass cell using a Reference 3000 potentiostat (Gamry, USA).

Surface roughness (R_a) was evaluated using a Surface Roughness Tester SRT 6210 (PRC). The path length of a diamond stylus moving over the surface was 4.8 mm. The averaged results of five measurements on each sample are shown.

Surface morphology was studied by scanning electron microscope Zeiss EVO 40XVP.

The electrocatalytic activity of the samples with respect to the reaction of cathodic hydrogen evolution was determined by linear voltammetry technique in an aqueous solution of 1 M NaOH (99.99%, Sigma-Aldrich) at the temperature of 298 K and a potential sweep rate of 50 mV s⁻¹. In these experiments, a platinum grid served as an auxiliary electrode; electrode potentials were measured relative to a saturated silver chloride reference electrode and converted to the scale of a standard hydrogen electrode.

The experiments (potentiodynamic scans, study of surface morphology, surface roughness measurements and investigation of electrocatalytic activity) were repeated under specified conditions of anodic treatment at least five times. Each parallel experiment was performed with a new sample of the Cu-Ni alloy.

3. Results and discussion

3.1. Anodic treatment of Cu-Ni alloy in ethaline

The polarization curves of anodic dissolution of the Cu-Ni alloy in the used DES are shown in Fig. 1, from which it can be seen that two overlapping anodic current peaks are formed on the polarization curve (the first peak at ~0.1 ... 0.2 V and the second peak at ~0.5 V). With imposition of sequential scans of electrode potential, a decrease in anodic dissolution currents is observed (this effect is especially pronounced on the second

and third scans). On the sixth scan, the anode currents cease to change significantly and a quasi-stationary state is achieved.

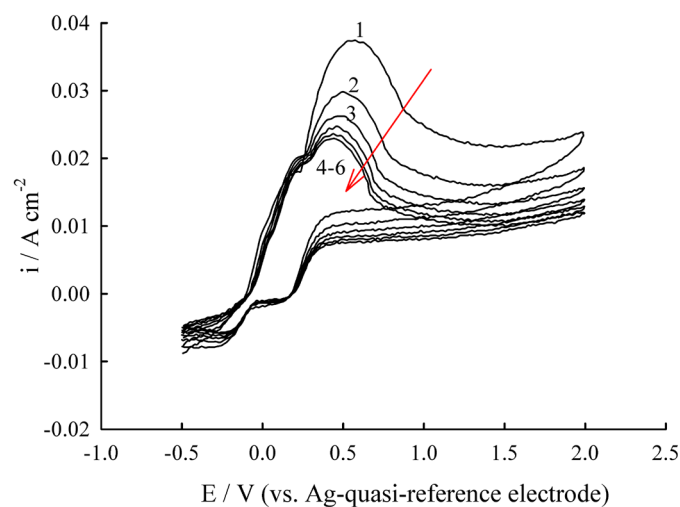


Fig. 1. Cyclic voltammograms characterizing behavior of the Cu-Ni alloy electrode in ethaline recorded for six consecutive potential scans. The arrow and numbering near the curves indicate the numbers of consecutive potential scans on the same sample. Potential scan rate is 100 mV s⁻¹.

Comparison of the potentials corresponding to the registered two current peaks with numerous data obtained in case of dissolution of individual copper and nickel in ethaline [18,19,28–31] suggests that the first of these peaks (at more negative potentials) is related to the anodic dissolution of copper, and the second peak (at more positive potentials) corresponds to the anodic dissolution of nickel. Thus, in the solvent under consideration, there is an unusual change in the arrangement of nickel and copper in the electronegativity scale of metals: nickel in ethaline is a more electropositive metal than copper, although in traditional aqueous solutions the ratio between the standard potentials of these metals is exactly the opposite. It should be noted that this unconventional relationship between the potentials of cathodic deposition/anodic dissolution of nickel and copper in DESs has been already reported in the literature [28,32,33].

Segregation of two current peaks of the anodic dissolution of copper-nickel alloy is another specific feature of cyclic voltammograms recorded in ethaline. In aqueous solutions, this effect is usually not observed, and the anodic dissolution of the Cu-Ni alloy is accompanied by the formation of one unsplit anodic current peak in the voltammogram [34,35]. It is significant that on the back scan (cathodic currents), the voltammogram also shows two plateaus of electroreduction, which obviously correspond to the discharge of nickel and copper ions accumulated in the near-electrode layer on the anode scan.

When studying the anodic dissolution of pure copper and nickel in ethaline, it was previously found that a decrease in the anodic current after reaching a maximum in the voltammograms (i.e. surface passivation) is caused by the so-called salt passivation rather than by the formation of oxide passivating film [19,28–30]. This phenomenon is due to the fact that chloride

salts of nickel and especially copper (in particular, CuCl) have only moderate solubility in ethaline. Under the conditions of anodic dissolution in a given DES, the concentration of metal salts quickly reaches a limiting value in the near-electrode layer, and a loose porous layer of poorly soluble salt is formed on the electrode surface and in the near-electrode zone, which partially blocks the anode, causing a decrease in the current recorded on the voltammograms. We assume that the formation of a film of poorly soluble salts can also occur during the anodic dissolution of a copper-nickel alloy in ethaline. An indirect confirmation of this conclusion can be a gradual decrease in the dissolution currents in the first few potential scans on the same sample and the achievement of a certain quasi-stationary state in 5-6 scans (a certain time is certainly required for the formation of a film of a poorly soluble salt in the near-electrode zone). The kinetics and mechanism of the anodic dissolution of the Cu-Ni alloy in ethaline will be considered in more detail in a separate communication.

Obviously, an important factor determining the patterns of changes in the morphological features of the surface and their physicochemical properties is the duration of the anodic treatment. At short processing times, the evolution of the surface morphology can be insignificant and ineffective. With prolonged processing, excessive etching (dissolution) of the metal may occur. In a series of preliminary experiments, we have shown that if the duration of anodic treatment is less than 2 hours, the effects associated with changes in surface morphology, its roughness, and electrocatalytic characteristics (see below) are very poorly reproducible. Therefore, the anodic treatment time was 2.5 hours in all further studies. Calculations carried out using Faraday's law have shown that during this time, the thickness of the dissolved alloy does not exceed $\sim 30 \mu\text{m}$ (depending on the applied potential). In our opinion, this value is acceptable in the context of the objectives of this study.

For the anodic treatment of the Cu-Ni alloy, the following values of the electrode potential (vs. Ag quasi-reference electrode) were chosen: 0.1 V (at the foot of the first peak in the anodic voltammogram in Fig. 1), 0.5 V (near the second peak of anodic dissolution), 1.35 V, and 1.7 V (the last two values correspond to the passive state region).

Studies carried out using the energy-dispersive X-ray (EDX) analysis method revealed another specific feature of the anodic dissolution of copper-nickel alloy in ethaline. In several dozen independent parallel experiments, it was found that, regardless of the applied anodic potential, the chemical composition of the surface layer after 2.5-hour anodic treatment in this deep eutectic solvent practically does not change and remains the same as for an untreated «fresh» surface ($\sim 45 \text{ wt.}\% \text{ Ni}$ and $\sim 55 \text{ wt.}\% \text{ Cu}$). The deviations of the chemical composition of the surface observed after anodic treatment in ethaline did not exceed 0.5%, which is at the limit of the method sensitivity. An earlier study [26] also reported that the Cu/Ni ratio remained unchanged after the anodizing of the Cu-Ni alloy in ethaline. At the same time, the anodic dissolution of the Cu-Ni alloy in aqueous electrolytes is commonly accompanied by selective etching of one

of the components (copper) due to the formation of nickel oxide passivating layers [36]. Obviously, in a deep eutectic solvent medium under conditions of a high concentration of chloride ions and the absence of water, the formation of nickel oxides does not occur (the absence of a noticeable amount of oxygen in the surface layers was confirmed by the EDX analysis). It was also shown earlier that even during the anodic dissolution of a copper-nickel alloy in an aqueous solution of hydrochloric acid of a sufficiently high concentration, which prevents passivation, under conditions of prolonged stationary electrolysis, no change in the chemical composition of the surface layer is also observed (i.e. no selective etching of one of the components) [37].

3.2. Evolution of surface morphology of Cu-Ni alloy

Scanning electron microscopy (SEM) images show that the surface of the Cu-Ni alloy is featureless prior to anodic treatment in ethaline; there are only some stripes, irregularities and cavities associated with rolling the surface of the sheet during its manufacture (Fig. 2a). The features of surface profile change significantly after anodic etching in ethaline. Even at the treatment potential of 0.1 V, the strips almost completely disappear; however, characteristic cavities on the surface associated with the etching of individual crystallites as well as single etching holes are observed (Fig. 2b). A further increase in the applied potential (up to 0.5 V) radically changes the patterns of surface morphology. The main feature is the appearance of irregular star-shaped crystallites with pointed rays on the surface (Fig. 2c). These star-shaped crystallites have an average size of 15-25 μm and overlap with each other. It should be mentioned that the areas of the surface between these protruding crystallites are perfectly homogeneous, which is characteristic of an electrochemically polished surface. With a further increase in the anodic potential of alloy processing in ethaline (1.35 V), a clear decrease in the number of stellated crystallites is observed, and the share of a smoothed flat surface increases markedly (Fig. 2d). Finally, at the largest of the studied values of the anodic potential (1.7 V), only single star-shaped crystallites with a size of up to 10-15 μm are detected on the surface, and the surface areas between them are smooth and defect-free; thus, the electrochemical polishing occurs (Fig. 2e).

Let us mention that the study [26] reported formation of spherical nanoparticles on the surface of Cu-Ni alloy after its anodization in ethaline. However, those findings is difficult to compare with the results obtained in our work because the anodic treatment in work [26] was performed at an elevated temperature (70°C) and the dependence on electrode potential was not investigated. It should also be noted that the formation of star-like structures on the surface of Cu-Ni alloy after its anodic etching was not previously described in the literature and was observed for the first time.

We assume that the origin of specific patterns of surface morphology (star-like crystallites with pointed rays) after the anodic etching of a copper-nickel alloy in a DES is caused by

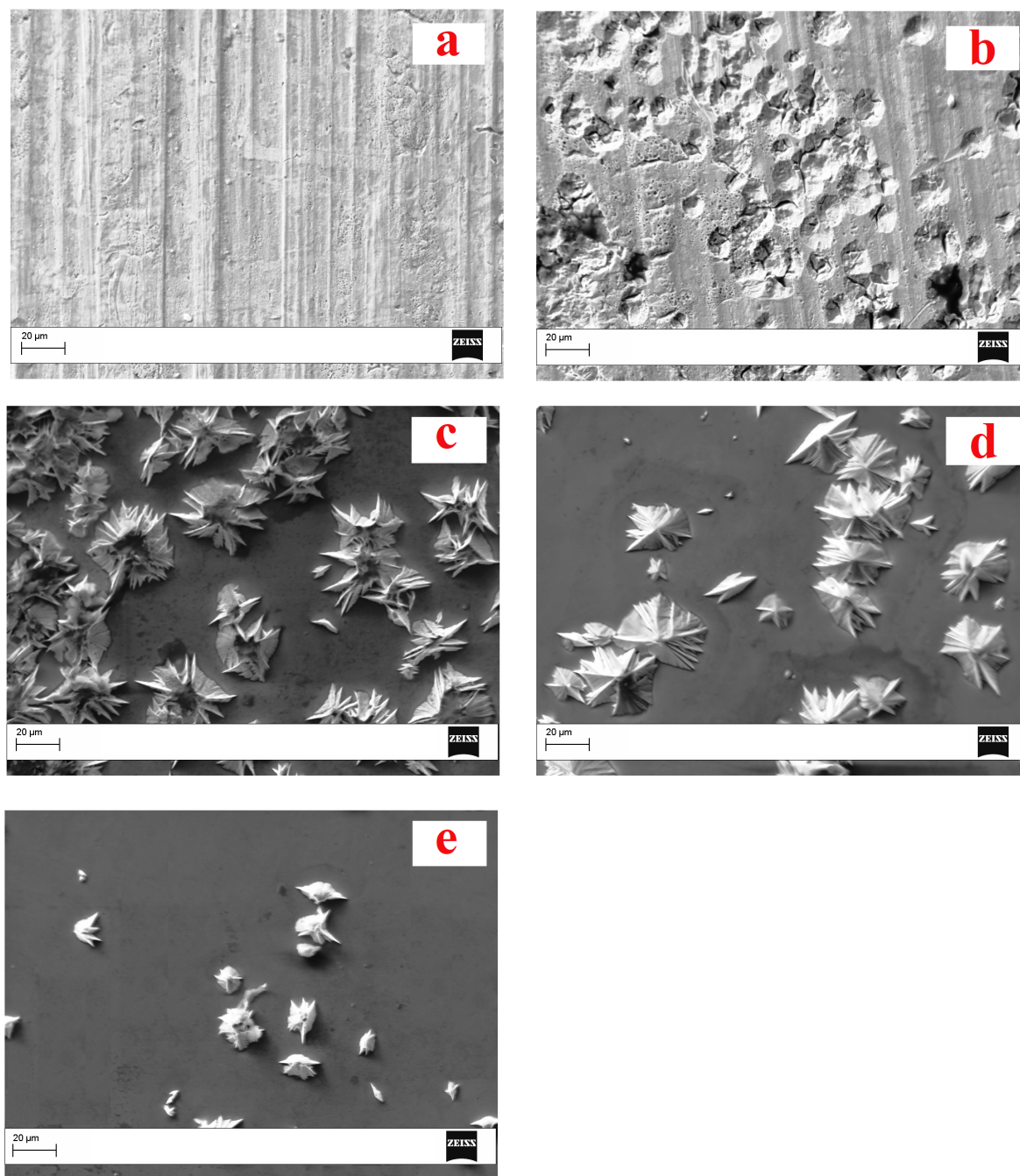


Fig. 2. SEM images of the Cu-Ni alloys before anodic processing (a) and after anodic treatment in ethaline (b)-(e) at the following electrode potentials (V): (b) 0.1, (c) 0.5, (d) 1.35, and (e) 1.7

strong adsorption of some organic components of the electrolyte on the electrode surface. Selective adsorption on the surface of specific crystal faces can lead to some local inhibition of anodic dissolution and increased etching of those faces on which adsorption is less pronounced. However, it is obvious that this issue requires a deeper and more detailed consideration. Leveling the surface profile (electrochemical polishing) at sufficiently high anodic potentials is usually associated with the occurrence of an anodic reaction under conditions of the existence of a viscous electrolyte layer on the surface, which is formed, for example, as a result of the formation of a dispersed phase of a metal salt in the near-electrode layer [19,29,30,38,39].

3.3. Surface roughness

To assess the effect of anodic treatment in ethaline on the surface roughness of the Cu-Ni alloy, the values of roughness coefficient (R_a) were determined (TABLE 1). As can be seen, the experimentally determined values of the roughness coefficient correlate well with the changes in the surface morphology assessed by the SEM analysis (Fig. 2). Thus, after anodic treatment at the lowest of the applied potentials (0.1 V), the roughness practically does not change in comparison with the untreated alloy surface. At the same time, the formation of stellated crystallites with elongated sharp rays on the surface leads

to a predicted noticeable increase in roughness due to an increase in the inhomogeneity of the surface morphology. The surface treatment of the Cu-Ni alloy at the highest anodic potential (1.7 V), as can be clearly seen from the SEM images, leads to a smoothing (leveling) of the surface profile, which is reflected in an almost twofold decrease in the R_a coefficient (in comparison with the untreated surface). Thus, the anodic treatment of a copper-nickel alloy in ethaline allows flexibly controlling the degree of surface roughness, opening up the possibility of both increasing and decreasing the value of the roughness coefficient by tuning the applied electrode potential.

TABLE 1

Dependence of roughness coefficient (R_a , mean and experimental standard deviation based on five measurements) on the applied potential at the anodic treatment of Cu-Ni alloy in ethaline (2.5 h, 298 K)

Electrode potential of anodic treatment in ethaline (V)	R_a (μm)
— (before anodic processing)	0.55±0.06
0.1	0.50±0.04
0.5	3.53±0.24
1.35	2.29±0.22
1.7	0.33±0.03

3.4. Electrocatalytic properties

Anodic modification of the copper-nickel alloy surface in ethaline causes a significant change in electrocatalytic behavior in the hydrogen evolution reaction in aqueous 1 M NaOH solution (Fig. 3). For comparison, the same figure shows the polarization

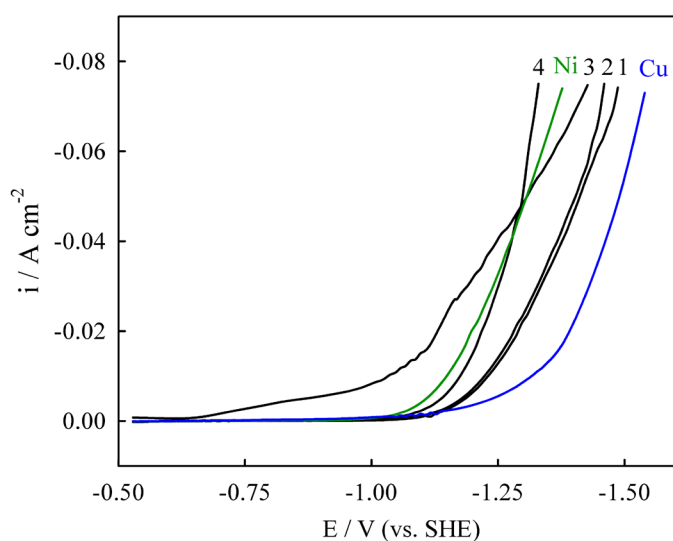


Fig. 3. Polarization curves characterizing hydrogen evolution reaction in 1 M NaOH on Ni, Cu and Ni-Cu alloys: before electrochemical processing (1) and after anodic treatment in ethaline (2)-(4) at the following electrode potentials (V): 0.1 (1), 0.5 (2), 1.35 (3), and 1.7 (4). The curves relating to “pure” nickel and copper are designated by respective chemical symbols

curves for „pure“ nickel and copper (without anodic surface treatment). Anodic treatment of the Cu-Ni alloy in a DES at the lowest of the applied potentials (0.1 V) has practically no effect on the activity with respect to the hydrogen evolution reaction (both for an untreated alloy sample and for a sample treated at 0.1 V, the same curve corresponds in Fig. 3 (curve 1)). As the potential increases to 0.5 V, a slight decrease in the polarization of the electrode process is observed (curve 2). The most significant decrease in the polarization of hydrogen evolution (reaching at certain current densities up to ~ 100 mV and more) occurs when using anodic potentials of 1.35 and 1.7 V (curves 3 and 4). The noted decrease in polarization in a number of cases is so significant that the electrocatalytic activity of the anodically treated Cu-Ni alloy is comparable and even exceeds the activity of the „pure“ nickel electrode. It is noteworthy that the modification of the alloy surface resulted from its anodic treatment in ethaline leads to a change in the slope of the polarization curves in such a way that curves 3 and 4 have an intersection point. As a result, in the region of cathodic current densities up to ~ 0.05 A cm $^{-2}$, the electrocatalytic activity of the surface treated at 1.35 V exceeds the corresponding characteristic of the sample after treatment at 1.7 V, while in the region of higher current densities, an opposite relationship between the catalytic activities is observed. We assume that the observed change in electrocatalytic activity is due to a deep evolution of the surface morphology of the alloy (Fig. 2).

4. Conclusions

Anodic treatment of the Cu-Ni alloys in a deep eutectic solvent (ethaline) was studied in this work for the first time. It was shown that anodic processing of copper-nickel alloy ensures peculiar evolution of surface morphology: appearance of star-shaped crystallites and further surface smoothing are observed with increasing anode potential. Thus, surface roughness can be controllably tuned by changing the potential of anodic processing of the copper-nickel alloy in ethaline. The surface treated in a deep eutectic solvent exhibits enhanced electrocatalytic activity towards the hydrogen evolution reaction in an alkaline solution, which offers new opportunities for creation novel, high-efficient and relatively inexpensive electrocatalysts for water electrolysis.

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