Int. J. Electrochem. Sci., 8 **(2013)** 1382 - 1393

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Nickel Electrodeposition from Protic Ionic Liquids Based on Carboxylate Anions as Electrolyte: II. Electrodeposition from 2-hydroxyethyl Ammonium Propionate.

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Received: 16 October 2012 / *Accepted:* 13 December 2012 / *Published:* 1 January 2013

Ionic Liquids (ILs) are a new kind of solvents that can be used as alternative solvents in order to improve the chemical or environmental performances of aqueous electrodeposition processes, commonly based on the use of hazardous chemicals. In this work we study the feasibility to use 2-hydroxyethyl ammonium propionate as solvent for the electrodeposition of nickel. Results shown that in this reaction medium, it is possible to obtain pure and homogeneous deposits of nanocrystalline nickel. These deposits grow with an initial 3D- and after following a 2D-mechanism, with a roughness and crystal size, dependent on the electrodeposition conditions.

Keywords: protic ionic liquids; nickel electrodeposition; electrocrystallization.

1. INTRODUCTION

Ionic Liquids (ILs) are assumed as liquids with only ions in their structure, discovered by Walden in 1914 [1]; the major difference between ILs and aqueous electrolyte solutions is their internal composition because of ILs are conducting liquids where only free ions are present instead solvated ions with solvent molecules such as in conventional molecular solvents. By this reason it is assumed that ILs are a liquid medium formed only by charged ions either positive or negatively charged in the same proportion and in the absence of molecular species of a solvent [2].

In recent years, the possibility to use these liquids as solvents was increased because of both their physicochemical and electrochemical properties that make them a very interesting option as reaction media for several industrial processes where molecular organic solvents or even water are usually employed. In addition, their properties as low production cost, zero flammability, high solubility of a large number of organic and inorganic compounds and practically zero vapor pressure with no emission into the environment, makes them a good choice to develop clean process according to the basic principles of Green Chemistry to replace processes with common molecular solvents [3-10]. In account of these facts, the substitution of aqueous electrodeposition process by electrodeposition in ILs of nanocrystalline materials is one of the most interesting areas. In this context, electrodeposition of nanocrystalline Ni is of particular interest from the technological point of view for applications in the construction of solar energy panels and in the fabrication of new materials for energy storage [11-14]. The problem of conventional aqueous nickel electrodeposition process is associated to the use of organic compounds as inhibitors, levelers or accelerators [15-19] in order to control the crystal growth rate and the final properties of the deposits.

In a previous work [20], we demonstrate the feasibility to obtain nanocrystalline electrodeposit of nickel from 2-hydroxyethyl Ammonium Formate (2-HEAF), a protic ionic liquids based on carboxylate anions. However, when 2-HEAF is used as an electrodeposition medium, the presence of water can be difficult to avoid without a further purification step, because of water is present in formic acid used as precursor to prepare the IL; in this case, the presence of water has a negative effect on the observed electrochemical window due to the hydrogen evolution from water reduction as a secondary reaction that would also affect the efficiency during electrodeposition of metals.

In account of the similar properties of protic ionic liquids based on different carboxylate anions but with a common cation, it is interesting to evaluate the differences in the electrochemical behavior of selected metal of industrial or technological interest as nickel in IL of the same chemical family. For this reason, in this work we study the feasibility to develop alternative electrodeposition process to obtain well-controlled Ni deposits without the use of additives, based in the use of 2-hydroxyethylammonium propionate (2-HEAP) as electrolyte. This IL is similar to 2-HEAF but it is possible to prepare it from anhydrous precursors which allow to work without the presence of water and in consequence offer the possibility to carry out electrodeposits in well-controlled conditions of selectivity.

2. EXPERIMENTAL

2.1. Synthesis of the IL 2-HEAP

The studied IL was synthesized by a neutralization reaction between propionic acid and monoethanolamine, under conditions similar to those previously reported to prepare 2-HEAF [10]. This reaction was carried out in a jacket cell with inert atmosphere where ethanolamine was added dropwise to the propionic acid (1) until an equimolar mixture was obtained.

$$CH_3CH_2COOH + OH\text{-}CH_2CH_2\text{-}NH_2 \rightarrow [OH\text{-}CH_2CH_2\text{-}NH_3]^+[\,CH_3CH_2COO]^- + \triangle \qquad (1)$$

Since neutralization reaction is highly exothermic, the synthesis reaction was carried out with vigorous stirring and controlling the temperature at T < 5ºC with a recirculation system. After addition was finishing, stirring was continued for 24 hours at room temperature. All chemicals used were RA (ethanolamine > 99% Sigma Aldrich, propionic acid J.T. Baker 99%).

2.2. Electrochemical experiments

All the experiments were carried out in a conventional glass electrochemical jacked cell with a Teflon cover and a maximum capacity of 20mL. As electrolyte, the synthetized 2-HEAP was employed and as source of Ni(II) ions a nickel propionate salt, prepared according to methodology reported in literature [12]. The dissolution of the nickel salt was carried out by heating the mixture Ni(II) salt + 2-HEAP at 80°C and mixing vigorously for 24 hours. Temperature in all the experiments was controlled with a recirculation system. All the experiments were performed at atmospheric pressure.

Pure 2-HEAP and Ni(II) solutions in IL was studied with the cyclic voltammetry (CV). The electrodeposition process of Ni was also studied by chronoamperometric techniques. In all the cases, an Autolab Eco Chimie BV PGSTAT302 potentiostat was used. As working electrode, a glassy carbon electrode (GC) of 6mm of diameter was used; the pseudo-reference electrode and the counter electrode were a silver wire and a platinum mesh, respectively. Prior to each experiment, the surface of the electrode was polished until a mirror surface was obtained by using 0.05μm alumina. After each chronoamperometric experiment, samples were rinsed successively with deionized water and with acetone to be finally dried with air.

2.3. Characterisation of Ni deposits.

The obtained Ni deposits were observed by SEM and their surface were analyzed by EDS. In both cases a SEM JSM – 5400 LV Microscope was used. For the EDS analysis a electron beam acceleration of 15keV and a 2000 counts/seconds time for each microanalysis were used as experimental conditions.

AFM images of the Ni deposits were obtained with a Dimension Icon Atomic Force Microscope with Scanasyst in both Contact air and ScanAsyst air mode .

3. RESULTS AND DISCUSSION

3.1. Electrochemical studies.

Prior to the study of nickel electrodeposition, the redox couples ferrocene (Fc/Fc^+) and cobalticinium (Cc^+/Cc) were electrochemically characterized in the studied IL, 2-HEAP; these two redox couples were chosen as internal electrochemical references in order to evaluate the stability of the silver electrode, choosen as pseudoreference electrode in previous works and reported in previous work [20] .

A typical behavior of reversible redox couple is observed for both systems. From the obtained results (Figure 1) the corresponding standard potentials of these systems were evaluated as -0.925V vs Ag for $Cc^+ + e^- \rightarrow Cc$ and 0.21V vs Ag, for $Fc \rightarrow Fc^+ + e^-$, respectively, both of them in reference with the silver electrode used as pseudo-reference electrode [7].

These systems are commonly used as internal potential references for electrochemistry in organic solvents and when aqueous or pseudo-references electrodes could interfere or contaminate the studied solutions. In our case, the stability of the pseudo-reference Ag electrode is well reported in these solvents [21,22] and was verified by measuring the electrochemical response of of ferrocene (Fc/Fc^+) and cobalticinium (Cc^+/Cc) systems as a function of time; results obtained with these internal references allow to verify the stability of the pseudo-reference Ag electrode in 2-HEAP and also to determine the potential scales in the studied solvent to further comparison with another solvents. Even if these systems are reported to be used as internal reference systems in other IL [23-28] mainly in aprotic IL, there is no reference to their use in these kind of protic carboxilated IL.

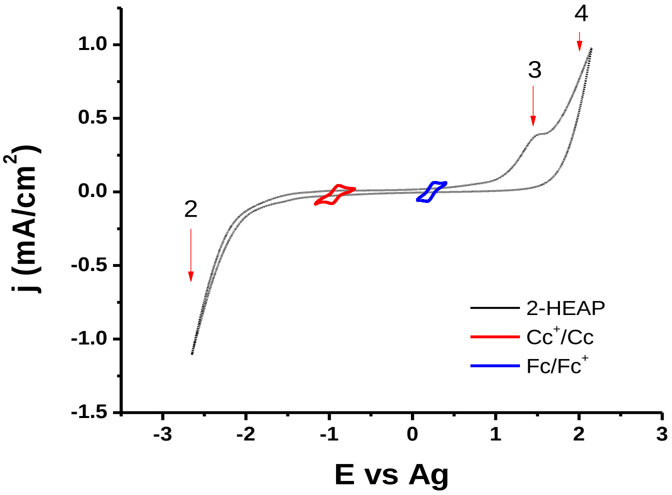


Figure 1. Cyclic voltammetry response of the 2-HEAP IL with internal reference of cobaltocinium and ferrocene 5mM in each case. 20mV/s. 25°C.

In figure 1, the electrochemical behavior of 2-HEAP is also shown. From this figure, the analysis of the electrochemical response of 2-HEAP shows that the electrochemical stability of this IL is observed at E<-2V and the corresponding limiting reactions are associated to the reduction of the 2-hydroxyethylammonium cation in the cathodic side (2) and to the oxidation of the propionate anion in the anodic side (3), (4), similarly to results observed with 2-HEAF [20] but involving the corresponding ions forming the ionic liquid. Another authors report these behavior as associated to the preadsorption of the carboxylic anion and its consecutive decarboxilation as a typical two steps Kolbe electrooxidation [29-31] or a global one step reaction involving the osidation of carboxilates to CO2 [32,33]. Further experiments are necessary to corroborate the consecutive mechanism of propionate oxidation in our ionic liquids.

$$2NH_3^{+}ROH + 2e^{-} \rightarrow 2NH_2ROH + H_2 \qquad (2)$$

$$R'COO^{-} - e^{-} \rightarrow R^{\cdot} + CO_2 \qquad (3)$$

$$R^{\cdot} - 1e^{-} \rightarrow R^{+} \qquad (4)$$

In figure 2, the corresponding CV responses at 80°C of Ni propionate solutions in 2-HEAP at several concentrations are shown. A reduction in the electrochemical window is observed in both the cathodic and the anodic sides when Ni(II) concentration is increased.

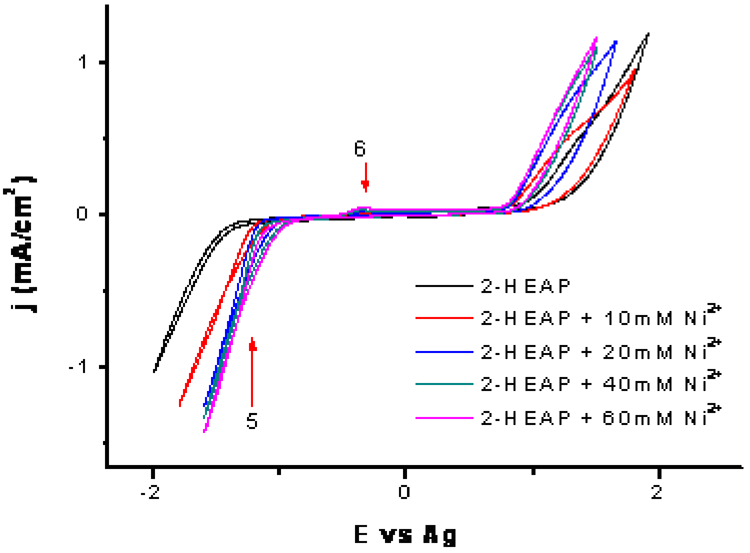


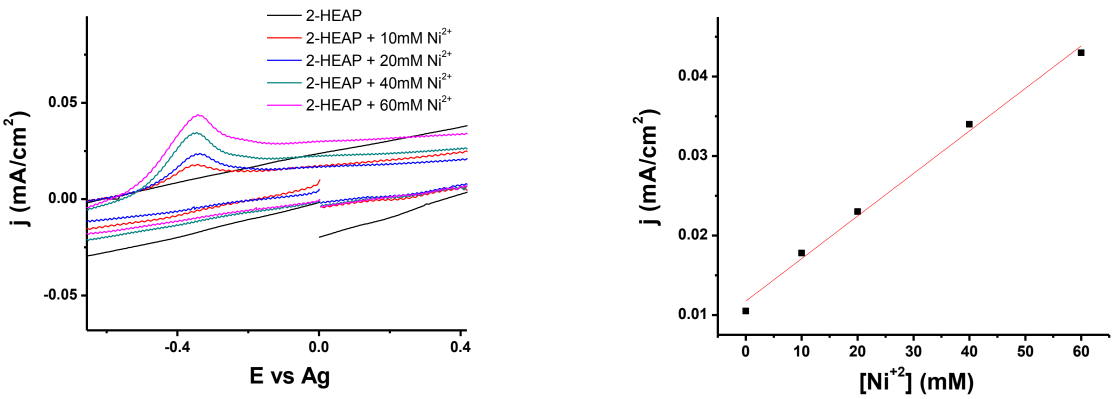
Figure 2. Cyclic voltametry of the 2-HEAP IL for solutions at variable Ni(II) propionate concentration. 20mV/s. 80°C. WE:GC; pRE: Ag; CE: Pt.

In addition a small anodic peak is observed in the presence of Ni propionate. The observed effect in the cathodic side is attributed to the reduction of Ni(II) (5) that is carried out simultaneously with the hydrogen evolution from the reduction of the cation of IL. This behavior is similar to that observed on a similar IL [20], the main difference corresponding to the potential range where these reactions are obseved and it is associated to the influence of the viscosity and conductivity on the electrochemical behavior of the IL because of the electrochemical proposed reactions are the same involving in both cases identical chemical species (monoethaolammonium and nickel ions)

$$Ni^{II+}\ 2e^{-} \rightarrow Ni^{0} \qquad (5)$$
$$Ni - 2e^{-} \rightarrow Ni^{+II} \qquad (6)$$

Results observed at the anodic side are attributed to the effect of the oxidized Ni (in solution or as oxide layer) on the electrochemical oxidation of carboxilates. This effect has been reported when the effect of the metallic ions on the electrooxidation Kolbe reaction was studied [34,35]

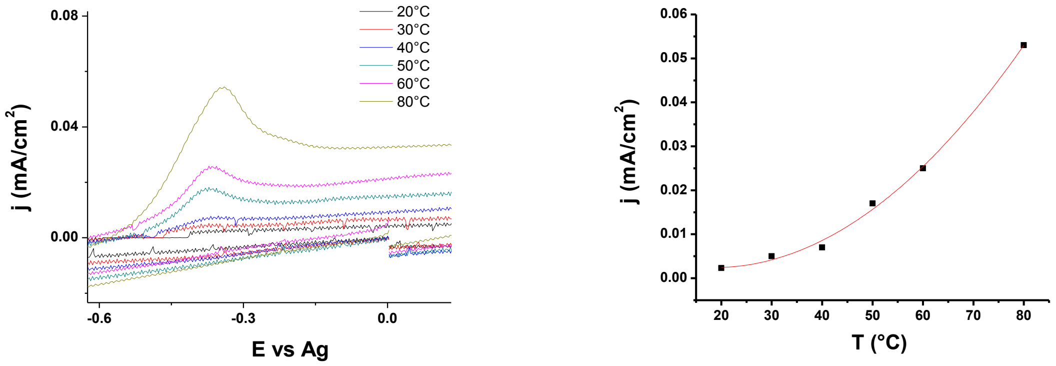
Concerning the oxidation peak (reaction 6, figure 2), in Figure 3a a detail of this signal is shown: the peak is clearly observed at -0.34V vs Ag and is associated to the oxidation process of the previously deposited Ni (5). The current density associated to this signal is linearly dependent on the Ni(II) concentration in the deposition solutions and allow to confirm that is associated to the Ni formed during the reduction scan (figure 3b).



a) b)

Figure 3. a) CV of the 2-HEAP IL with different quantities of nickel propionate at 80°C and b) the dependence of the quantity of nickel ions in the solution with the current peak found in the CV a -0.34V vs Ag. 20mVs. 80°C. WE:GC; pRE: Ag; CE: Pt.

In figure 4a and 4b, the effect of the temperature on the current density of this peak is shown. An exponential decrease of the current density is observed temperature of the electrodeposition system is decreased.



a) b)

Figure 4. a) CV of the 2-HEAP IL at different temperatures and b) dependence of the signal of current with respect to the temperature 20mVs. 30mM of nickel propionate. WE:GC; pRE: Ag; CE: Pt.

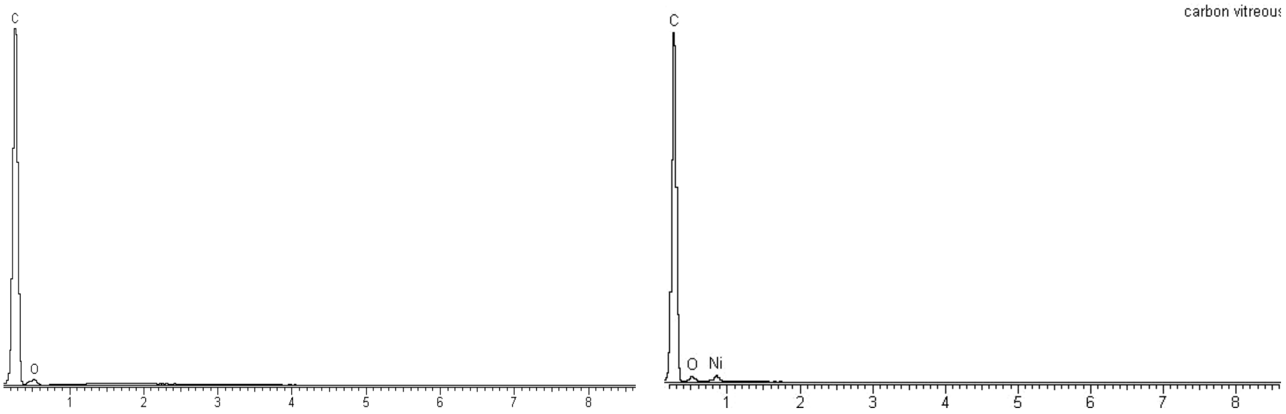
This effect may be associate to effect of the temperature on both the conductivity and the viscosity of 2-HEAP that depends exponentially on the temperature as predicted by the empirical Vogel-Tammann-Fulcher (VTF) Equation (equation 1) to explain the behavior of ILs as fluid as a function of the temperature [36-38]:

$$\kappa = AT^{-\frac{1}{2}}\exp\left[-\frac{B}{T-T_0}\right] \qquad \text{Equation 1}$$

where A and B are constants, and T_0 is the temperature when conductivity (κ) tends to zero [39].

3.2. Characterization of Ni electrodeposits

Since Ni deposits were qualitative observed at the electrode surface, the obtained samples were analyzed by SEM-EDS techniques to confirm this fact. However, it was no possible to demonstrate the presence of a deposit by SEM because of the involved nanometric grain size of the obtained electrodeposits. In counterpart, the elemental analysis by EDS of the same samples allows to evidence the presence of Ni over the glassy carbon electrode (figure 5).



a) b)

Figure 5. Elemental analysis over glassy carbon electrode a) blank and b) with nickel coating.

Further analysis of those deposits by AFM (figure 6) clearly shows the evolution of the shape of the nanoparticles forming the deposit obtained at -1.5V vs Ag on the glassy carbon electrode, as a function of the deposition time.

These results allow to propose a mechanism of nucleation/growth of the nickel coating at this potential because the reduction of nickel at the electrode is carried out simultaneously with the reduction of the cation of IL to generate hydrogen.

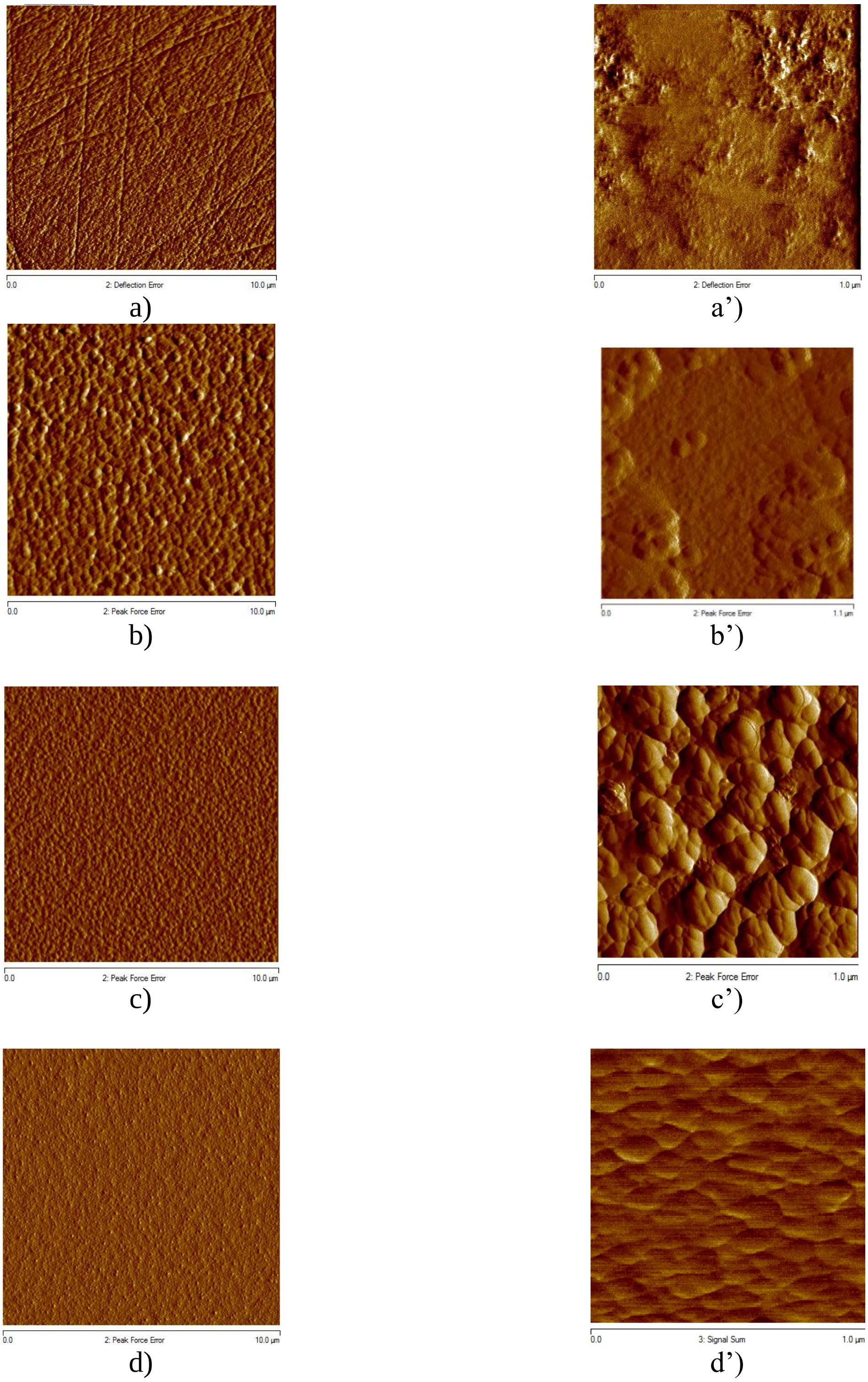


Figure 6. AFM images at a) 0, b) 45, c) 90 and d) 180 min deposition time at -1.5 V vs Ag over GC electrode. Images at 10 and 1um.

Table I. Roughness coefficients, grain size and roughness profile estimated by the mix of the roughness factor.

Time (s)	Roughness Rq	Roughness Sk	Roughness Ks	Grain size (nm)
0	2.51	-0.22	2.88	---
45	17.50	0.55	2.20	42.4 + 1.2
90	17.00	0.09	2.74	54.9 + 4.1
180	3.95	-0.24	3.40	13.8 + 0.3

From images obtained using the AFM and with the help of the NanoScope Analysis 1.40 Software, it was possible to obtain the roughness values of the surface particles (average, surkosis and kurtosis) to evidence the lateral behavior of the surface at different times [40] (Tabe I). Combination of these results with the AFM images, it is possible to propose that the surface of the eletrodeposit changes from a plain background (0 min) to an homogeneous grain crystal background surface including granular crystals (45 and 90 min) and at the final time (180 min), a plain background compress is again observed specially by smooth nanocrystals.

Figure 7 and 8 clearly show the behavior of nanocrystals growth formed on the surface of the electrode and their impact on the roughness of the electrode. The observed behavior allows to propose that a totally homogeneous growth of the nanocrystals is carried out over the glassy carbon electrode at all times.

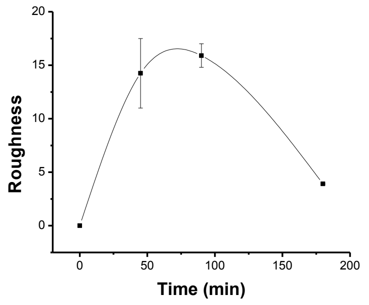


Figure 7. Evolution of the roughness at different electrodeposition times.

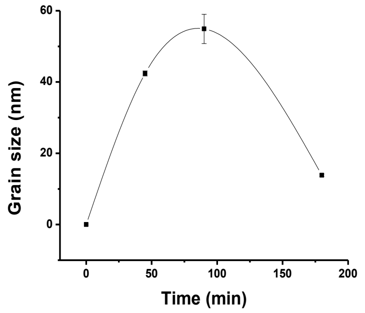


Figure 8. Evolution of the grain size at different electrodeposition times.

Results obtained from the characterization and analysis (SEM-EDX, AFM, roughness and grain size) of the obtained deposits allow to confirm that the electrodeposition of nickel from 2-HEAP depends both on the electrolyte nature and on the substrate surface because of deposits obtained from 2-HEAF are smaller and with a size independent on the deposition time [20].

In our case, the Ni electrodeposit obtained from 2-HEAP is produced simultaneously with the decomposition of the IL to generate molecular hydrogen. Despite the generation of hydrogen at the electrode, it was possible to generate nanocrystals that growth at the more energetic sites of the electrode from a 3D to a 2D mechanism due to the further growth of crystals on the less energetic sites of the electrode surface (figure 9).

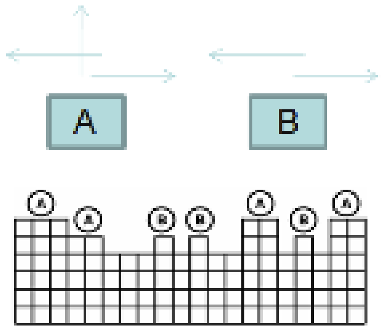


Figure 9. Crystal growth of the nickel nanocrystals over the electrode.

Growth of crystals in 2D allows to obtain a smooth plain background that covers all the surface of the electrode. These results are similar to those obtained from other ILs as electrolytes and GC as electrode where a three dimensional nucleation processes followed by hemispherical diffusion controlled growth of the nuclei [16] where usually observed and at higher electrodeposition times these nuclei gradually growth and are overlaped [17]. In our case it is not possible to differentiate between an instantaneous or a progressive nucleation process because it was no possible to obtain the chronoamperometric curves due to the simultaneous deposition process and reduction of 2-HEAP.

4. CONCLUSIONS

In this work, we present the results obtained of the study of nickel electrodeposition by using nickel propionate as the source of nickel ions and the 2-HEAP IL as the electrolyte media to obtain nickel nanocrystals without the use of additives in the media. This study shows that it is possible to obtain nickel nanocrystals at the same time that the generation of molecular hydrogen because of the reduction of nickel ions and the decomposition of the IL are carried out simultaneously. Size of the nuclei are dependent on the deposition time and an evolution to a surface growing from a 3D- to a 2D-mechanism is observed, allowing to obtain a smooth and homogenous deposit formed by nanometric nuclei. Similarly to results obtained with 2-HEAF, Ni electrodeposits from 2-HEAP are homogeneous, smooth and no additives are required which allows to work with less complex solutions than that used to electrodeposit from aqueous electrolytes.

ACKNOWLEDGEMENTS

The financial support provided by CONACYT (Mexico), project CB 2011 – 168032 and The Engineering Research Council of Canada (NSERC) are gratefully acknowledged.

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