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STATEMENT LETTER OF THE ARTICLE:

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Dear Editor

It is stated, in this letter, that the submitted paper has not been published previously, is not under consideration for publication elsewhere, and if accepted will not be published elsewhere in the same form, in English or in any other language, without the written consent of the publisher. The authors have no commercial associations or sources of support that might pose a conflict of interest. All authors have made substantive contributions to the study.

Sincerely

Dr. Alessandro Dell’Era

Electrodeposition of NiCoW alloys, from bath with and without Na citrate, for HER

Characterization of NiCoW deposits by SEM-EDS and XRD analyses

Electrochemical characterization of electrodeposited NiCoW alloys for HER

Comparison between performances of the ternary NiCoW and binary NiCo alloys for HER

# Effectiveness of sodium citrate on electrodeposition process of Ni-Co-W alloys for hydrogen evolution reaction

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## Abstract

In this study Ni-Co-W alloys have been produced by electrodeposition on Al net. Two electrolytic baths, with and without sodium citrate, having the same metal ion content (20g/l Ni, 8g/l Co and W in the range 2-8g/l) and boric acid content 20g/l, have been used. Temperature and current density operative conditions have been varied in the range 30-60°C and 260-350 A/m<sup>2</sup> respectively. The electrodeposition performed in the presence of sodium citrate presents always the best results in term of current efficiency and specific energy consumption, while W content in the alloy highlights different behavior: higher W content at higher temperature with citrate in solution, quite constant W content with temperature, without citrate. Morphological and structural analyses of deposits have been also performed to assess in which electrolysis conditions the best deposit was obtained. Preliminary electrochemical tests have been also carried out on Ni-Co-W deposits for establishing their ability to act as cathode for HER and to compare these ternary alloys with those binary Ni-Co, thus detecting W positive influence in both hydrogen overvoltage and exchange current density. The W presence in the alloys affects, in the same way, the HER independently of their production.

## 1. Introduction

Several engineering applications take advantage of Nickel, Cobalt and their alloys, as significant materials because of their unique properties among which: magnetism, wear-resistance, thermal conductivity and not less important electrocatalytic properties [1-7]. Ni-Co alloy electrodeposition have been thoroughly investigated by many authors [8-18]. There are several works describing the anomalous Ni-Co co-deposition, in which the bath Co/Ni ratio is considerably lower than that of the alloy, representing the anomalous nature of co-deposition process, where cobalt, that has the more negative standard potential, is preferentially deposited [19-23].

Literature has shown [24] that a combination of two or more metals from the two volcano curve branches could results in enhanced properties of electrodeposited alloy. As an example in a previous work [25,26] it has been demonstrated that in situ activation with Mo (left branch) of Ni-Co (right branch) alloys is effective for HER. Tungsten addition to the Ni-Co alloys improves their durability, hardness and resistance at high temperatures [1,4, 8-10]. Furthermore the tungsten electrodeposited together with Ni and/or Co has received, in the last decade, an increased interest because of the advantageous utilization as electrode for hydrogen evolution reaction (HER) [27-32] in alkaline media.

Tungsten can be easily electroplated together with iron group metals due to induced codeposition, while it is not from tungstate aqueous solutions because of the oxide layer growth on the cathode.

The mechanism of W electrodeposition differs depending on electrolyte composition; if organic polyacids like citrate are present the metal ions are complexed. The complex formation allows a more easily specie adsorption on the electrode surface, that could block the surface partially, acting as an inhibitor for hydrogen evolution, leading to an increasing the faradic efficiency [33]. There is also a reduction of the specific rate for metal deposition, producing a more uniform plating [33]. Aim of this work is comparing Ni-Co-W alloys electrodeposited in the same operative conditions from two electrolytic baths having the same metal ion content and differing only for the sodium citrate presence in one of these, in order to evaluate through compositional, morphological, structural and electrochemical analyses the effectiveness of such additive on alloy electrodeposition process [34-36]. An other objective is to compare the ability of these deposits to work as cathode in hydrogen evolution reaction.

## 2. Experimental

### 2.1- Experimental apparatus set-up

The alloy electrodeposition has been performed using a Plexiglas laboratory cell having separated cathodic and anodic compartments, 250 mL each, by a polypropylene membrane to hinder hydrogen ion migration from anode to cathode. Aluminium net cathode (2.5 cm x 3.5 cm), arranged on specific cathode-carriers, and Pb-8%Sb anode were spaced 30 mm apart. All experiments, lasting 6 h, have been carried out at 260 A/m<sup>2</sup> initial current density, by varying temperature in the range 30-60 °C. Due to OER (Oxygen Evolution Reaction) at anode, the electrolyte pH is decreasing during electrodeposition, thus to maintain the pH constant at 4.5, but at the same time to avoid hydroxides formation at cathode, KOH was added in the anodic compartment. Two different electrolytic baths, having the composition reported in table 1, have been prepared from analytical grade reagents and distilled water. The cathodic geometric surface has been evaluated equal to 5.9 cm<sup>2</sup>, after SEM magnification of a known small net portion, by using image analysis [12]. Alloy electrodeposition has been carried out by using an AMEL galvanostat (mod. 2053), at the end of each experiment the composition, and morphology and structure of cathodic deposits have been analysed by SEM Hitachi S2500 equipped with EDS quantitative analysis KEVEX apparatus SEM-EDS and XRD a PHILIPS PW 1830 diffractometer with Cu-K $\alpha$  radiation ( $\lambda=0.15418$  nm) apparatus.

Successively, some of Ni-Co-W electro-coated net and platinum net were used as electrodes in the water electrolysis for hydrogen evolution reaction (HER) in alkaline solution at 30% KOH, 25 °C temperature. They were spaced 30 mm apart in a beaker having a volume of 500 mL. In all electrochemical tests the Saturated Calomel Electrode (SCE) was used as reference electrode so as to monitor the behavior of the cathode only. In all tests the reference electrode, consisting of a cylinder having 10 mm diameter, was placed near to the working electrode in such a way the distance between the cathode and the sensing element of reference electrode can be assumed equal to 5 mm. An experimental apparatus constituted by

- an AMEL Galvanostat/potentiostat(mod. 2053) that has been utilized both in the galvanostatic and potentiodynamic mode,
- a 7800 AMEL interface,
- a FALC F70 ST hotplate magnetic stirrer,

has been used.

## 2.2 – Electrochemical phenomena description

The electrochemical phenomena occurring for the passage of current through the cell are closely associated to the used electrolyte type.

Considering the bath without sodium citrate, metal ions in solution are solvated by water molecules, and the reactions occurring can be described as follows:

CATHODE :

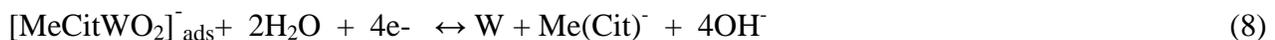


ANODE :



When sodium citrate is present in the electrolyte the Ni and Co are in the form of different complexes, depending their relatively quantity in solution on pH at which the test is performed. Thus pH affects both the quality of obtained deposit, due to the competition of hydrogen and other metals reduction, and the type of metal ion complexes in the bath. Considering 4.5 pH, Ni or Co citrate complexes are:  $\text{MeH}_2\text{Cit}^+$ ,  $\text{MeHCit}$  and  $\text{MeCit}^-$  (where Me stands for Ni or Co). Referring to the complex formed by W, an exact stoichiometric formula has not been yet determined, because it shows a great variability as a function of pH.

Considering for example the specie  $\text{MeCit}^-$ , the reactions occurring at cathode with citrate, as proposed by Podlaha and Landolt [37] are:



where Me stands for Co and Ni.

Indeed the complex formation allows a more easily specie adsorption on the electrode surface, blocking it partially and thus, slowing down, in the same operative conditions, the hydrogen evolution, and, thereby, leading to an increasing the faradic efficiency, and to a more uniform plating. It is reflected positively on most of the chemical and physical parameters characterizing deposition tests: trend of the cell voltage, current efficiency, overvoltage and specific energy consumption.

### 3. Results and Discussion

#### 3.1 Electrodeposition of Ni-Co-W alloys

Cell voltage behavior for both baths over time are characterized by a transient that occurs generally during the first 30 minutes of testing, in which the voltage from the higher values, moves asymptotically toward lower values (figure 1a),b). This is due to electrode depolarization phenomena because the cathode presents a thin oxide coating formed during the preparation phase of the experimental system. The cell voltage reduction as a function of the test temperature is evident and is due to: reduction of the ohmic drop, improvement of the cathodic reduction and anodic oxidation kinetics and overvoltage that each specie presents. The cell voltage decrease is mainly evident for tests carried out by using sodium citrate. In those tests the bath compositions differ only for the presence of sodium citrate and the concentration of metal ions in solution is: 40 g/l of  $\text{Ni}^{+2}$ , 8 g/l of  $\text{Co}^{+2}$  and 2g/l of  $\text{WO}_4^{-2}$ .

Referring to current efficiency the deposit obtained without sodium citrate shows current efficiency values of about 78%, while in presence of sodium citrate values grow even reaching 90%, whatever is the temperature. Figure 2 shows SEC trends for systems with and without sodium citrate. It can be noted that in both cases the qualitative trend with temperature is quite similar and particularly the specific energy consumption decreases with temperature increasing. Furthermore it can be noted that, at the same temperature, the bath with sodium citrate always provides a lower specific energy consumption.

Thinking that the improvement of the electrolytic bath conductivity, is due to the presence of sodium citrate a measurement of the two bath conductivity has been performed. From the measurements carried out at room temperature was found that the baths without and with sodium citrate have respectively a conductivity of 32 mS / cm, and 32.5 mS / cm. Given the low gain obtained with sodium citrate presence, it follows that the SEC reduction at the same temperature is only in small part due to the improvement of the bath conductivity, the fundamental contribution is related to metal complexation in solution which favors the electrodic surface adsorption with reduction of discharge overvoltage of the species present, thus requiring a lower voltage. As a consequence there is also an increase in the current efficiency for the bath with sodium citrate with values close to 90% and less hydrogen evolution, that further confirms the lower SEC. The deposit quality can be assessed by means of the chemical composition homogeneity and its physical appearance: the deposit must be as compact as possible, without cracking, porosity and with structural coherence. By SEM observation of deposits obtained using the bath with boric acid presence only, it has been possible to note that the deposits obtained at a lower temperature (figure 3a) had a greater quantity of cracks than those obtained at higher temperature (figure 3b). In general, an increase in bath temperature causes an increase in the crystal size [38]. The solubility of the metal salts increases, leading to an increase of solution conductivity and metal ions mobility, [38,39] while the solution viscosity decreases. In this situation the diffusion layer is more rapidly replenished, increasing the current density and the limiting current density obtained with a given voltage. The diffusion layer thickness decreases enabling metal ions to be rapidly replenished at the cathode surface, facilitating the replacement of the metal ions or complexes at the cathode surface, which consecutively help the plating of metal [38]. So, there is an advantage to elevated temperatures, having less adsorption of hydrogen in the deposits and then less stress, reducing in this way the tendency towards cracking [39].

Table 2 summarizes the electrodeposition preliminary results of the tests carried out without and with sodium citrate in the bath. The results obtained in this work show (table 2) a qualitative analogy if the alloys obtained by using bath containing sodium citrate are considered, while a behavior completely different is reached by using the electrolyte in which only boric acid acts as a buffer. This could be due to both the greater difficulty of pH control, which occurs if only boric acid is used and the totally different nature of the metal ions in solution that, with boric acid, are not complexed but only solvated by water molecules, therefore if sodium citrate is added to the electrolyte the pH control improves and metal ions are present in a complexed form. Indeed from table 2, it is possible to state that by using bath 1, without citrate, the quantity of Co decreases with temperature while for Ni the percentage increases. Differently, W concentration remains almost constant. Instead, for bath 2, with citrate, the content of Co and W increases with temperature, while Ni decreases. It could be possible that Co complexation is more favored by an increase of temperature in such a way that W concentration increases because  $\text{Co}(\text{Cit})^-$  complex is also more effective for W deposition than  $\text{Ni}(\text{Cit})^-$  complex. Finally, it is possible to state that performing deposition with sodium citrate guarantees lower overvoltages, higher current efficiencies, lower specific energy consumption at the same temperature and a greater buffering capacity of the system, boric acid / sodium citrate.

After defining the electrolyte to be used and the operating temperature, tests have been performed in order to obtain alloys having different W composition by changing the W electrolyte concentration in the range 3-8 g/l and leaving the Ni/Co ratio equal to 5/1. All the tests have been performed at 260 A/m<sup>2</sup> initial current density. Lastly an electrodeposition test has been performed at higher current density maintaining constant the electrolyte composition. The tests are broadly summarized in table 3 which reports the main operating conditions. The aim was to determine whether, by increasing only the W concentration in the electrolyte, it was possible to cause an increase in the W percentage of the deposit. Dealing of a ternary alloy, it can not immediately determine, as in the case of a binary alloy, what happens by increasing the concentration of one of the components inside the electrolyte due to the mutual interaction of the components.

The experimental results reported in Table 4 have shown behaviors comparable to that observed for the other depositions carried out with bath 2. The average value of the cell voltages, shown in table 4, are very near to the value obtained in the previous test at 60 °C (W-R3), the pH control was great and the current efficiency values are always closed to 90%. The percentage of W is almost constant while the percentage of Co increases significantly with decreasing presence of W, although the ratio Ni: Co in solution has been maintained equal to 5/1. In particular, the abnormal codeposition is progressively reduced with increasing the amount of dissolved W.

In solution there are many equilibrium reactions involving complex forms as  $\text{Co}(\text{Cit})^-$  or  $\text{Ni}(\text{Cit})^-$  and others, furthermore in agreement with Podlaha and Landolt reaction mechanism (6), (7) and (8), the deposition of W (as well as the deposition of Co and Ni) in the alloy is limited from  $\text{Co}(\text{Cit})^-$  and  $\text{Ni}(\text{Cit})^-$  (or  $\text{CoH}(\text{Cit})^-$ ,  $\text{NiH}(\text{Cit})^-$ ,  $\text{CoH}_2(\text{Cit})^+$ ,  $\text{NiH}_2(\text{Cit})^+$ ) presence. So, even increasing the  $\text{WO}_4^{2-}$  concentration in solution, a related enhancement of W in the alloy is not so noticeable.

Being Ni, Co and citrate constant in the solution treated and because of  $\text{Co}(\text{Cit})^-$  complex is more effective for W deposition than  $\text{Ni}(\text{Cit})^-$ , the cobalt complex is that more involved in W deposition, (considering the reactions (6), (7) and (8)). It is clear that to maintain the electrodic equilibrium (7)

among the complexes,  $\text{Co}(\text{Cit})^-$  is less involved to produce cobalt deposition respect to  $\text{Ni}(\text{Cit})^-$  for nickel deposition, therefore, the result is that there is an increase of Nickel content into the alloy. Summarizing, the comparison of the results obtained (table 2 and table 4) shows clearly that using a bath with sodium citrate and a temperature of  $60^\circ\text{C}$ , allows to reach the best conditions for electrodeposition.

### 3.2 Morphological and structural analysis of Ni-Co-W electrodeposited alloys

The morphology of electrodeposited Ni-Co-W alloys was analyzed by SEM observation in order to investigate its correlation with alloy composition. In particular, Fig. 4 shows the micrographs of alloys R6, R10, R12 and R3, all obtained with the same electrolytic bath containing sodium citrate (the best one) and also representative of morphology of the other alloys obtained in the different tests.

The morphology of alloy W-R6 containing 3.52 %w of W is shown in figure 4a), crystallite shape is almost spherical, even if some of them show a more elongated structure. Considering the alloy W-R10 W-R12 and W-R3 with a tungsten content of 7.93%w, 9.95%w and 9.4%w respectively, the micrograph in figure 4b), 4c) and 4d), highlights that the morphology becomes much more needle-like with crystallites increasingly elongated, each in a direction that appears completely random. The morphological change of the deposit appearance would seem, therefore, to be due to growth of tungsten content rather than to change of the Co/Ni composition ratio. It is noticed the homogeneity that each deposit presents. Images and EDS analysis provided by SEM showed a constancy of the composition and a homogeneous morphology, confirming complete coverage of the aluminum support and an absence of fractures due to distension of the internal stress state permitted by the  $60^\circ\text{C}$  test temperature.

As far as XRD analyses are concerned, it is worth stressing that Ni-Co-W films, as shown in figure 5, show different structures depending on the bath: films obtained by bath 1, without citrate, (figure 5 A) patterns a), b) and c)) show always the reflections [10-10] and [11-20] of Co hexagonal structure and in case of pattern b) also the reflection [10-11] appears, while those obtained by bath 2, with sodium citrate, also have the reflections [220] and [111] of Ni face centered cubic structure (figure 5 B); patterns d), e) and g)). Figure 5 C shows patterns a) and c) and patterns f) and h) of films obtained by both bath (without and with citrate respectively), with equal composition but at different temperature ( $30^\circ\text{C}$  and  $60^\circ\text{C}$  respectively). The temperature increase doesn't cause any structure change. It is possible to say that the main difference influencing pattern reflections is the presence of sodium citrate that, favors Ni fcc structure formation. Anyway, in all cases the deposit appears fairly amorphous, as it results from the peaks broadening.

### 3.3 Electrochemical tests on Ni-Co-W alloys for HER

The Ni-Co-W have been used as electrodes for hydrogen evolution reaction (HER) in an electrolysis cell, whose characteristics have been aforementioned. The determination of the overvoltage values, by using a current density of about  $30\text{ mA/cm}^2$  considering the electrode geometric area, has been performed, after the ohmic compensation, and the results have been reported in table 5.

Also an estimation of the real electrode surface has been carried out by using cyclic voltammetry technique [40,41]. Taking into account the cyclic voltammetry for the alloys at different scan rates (20, 50, 100 and 150 mV/s) as shown in figure 6a) for the alloy W-R2, the non-faradic current density has

been reported as a function of scan rate on the graph of figure 6b). In that region the pseudo-capacity is enough potential-independent. By fitting the points shown in figure 6b) a straight line is obtained, whose slope represents the capacity of electrode double layer.

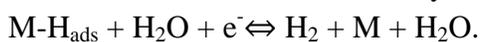
Then dividing by the pseudo-capacity reference of a smooth electrode surface for nickel and its alloys equal to  $1120 \cdot 10^6 \text{ F/cm}^2$ , as reported in literature [42], a roughness factor, ranging from 3.3 to 7.1, has been calculated and the real surface is therefore a value in between about 20 and  $42.5 \text{ cm}^2$ , for the different alloys obtained.

Other electrochemical parameters have been also determined by voltammetric tests to perform a complete comparison with the performance of the binary Ni-Co alloys.

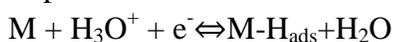
Indeed, the values of the exchange current density and the Tafel slopes for some alloys have been determined by graphs as those shown in figure 7 and reported in table 6. Those Tafel curves, with linear parts quite evident, were obtained by taking into account and eliminating the ohmic drop of the solutions. Finally, a comparison between ternary and binary alloys, with and without W, having the same Co content, has been performed, collecting the values of the electrode overvoltage, exchange current density and Tafel slopes and always reported in table 6.

It is possible to affirm that, for hydrogen evolution reaction, ternary alloys with tungsten, whatever is the used bath, work better than the binary ones without tungsten, considering the same cobalt content. Indeed they present a lower electrode overvoltage at  $30 \text{ mA/cm}^2$  and a bigger exchange current density, that have almost forty-fold higher value. Tafel slope values “*b*”, likely, highlights different mechanisms.

For binary alloys and for lower overvoltage, initially *b* change from about  $35 \text{ mVdec}^{-1}$  to about  $65 \text{ mVdec}^{-1}$ , characteristic of the Heyrovsky step:



For higher overvoltage Tafel slope increases up to about  $130 \text{ mVdec}^{-1}$  characteristic of the Volmer step:



indicating that the HER on this alloys takes place via the Volmer-Heyrovsky mechanism [43].

For Ni-Co-W ternary alloys there is only one Tafel slope for all overvoltage values indicating that, likely, the reaction takes place via Volmer-Heyrovsky-Tafel mechanism [26,44].

## Conclusions

On the base of the performed experimental work it is possible to affirm that sodium citrate actually affect the electrodeposition process of Ni-Co-W ternary alloy, while the samples obtained with and without sodium citrate present a similar behaviour for the HER.

Particularly at each temperature considered in the range  $30\text{-}60 \text{ }^\circ\text{C}$  current efficiency and specific energy consumption are better with bath containing sodium citrate, while the cell voltage is lower for temperature in the range  $40\text{-}60 \text{ }^\circ\text{C}$ . By using sodium citrate there is a different correlation among the compositions of Ni, Co and W in the alloy. Considering deposit X ray diffraction it is possible to affirm that the main difference influencing the pattern reflections of samples is that, those coming from sodium citrate containing electrolyte exhibit also Ni fcc structure formation.

Instead, considering the electrochemical tests, overvoltage, exchange current density and Tafel slope are almost similar regardless of how the samples were obtained. It should however be noted that

comparing, binary Ni-Co and ternary Ni-Co-W alloys with the same Co composition, the ternary alloys show the higher values of electrochemical parameters.

### Figure list

**Figure 1** - Cell voltage for electrodeposition tests performed a) with and b) without sodium citrate.

**Figure 2** - Specific energy consumption vs. temperature obtained with and without sodium citrate.

**Figure 3** - Effect of temperature on deposit morphology: a) low temperature, b) high temperature.

**Figure 4** - Morphology of deposits containing: a) 3.52 %W (W-R6), b) 7.93 %W (W-R10), c) 9.95 %W (W-R12) and d) 9.4 %W (W-R3).

**Figure 5** - A) Patterns a) b) and c) of alloys W-R8, W-R7 and W-R1 obtained at different temperature and using the same solution composition of bath 1; B) Patterns d) e) and g) of alloys W-R9, W-R11, W-R12 at the same temperature but different W solution concentration in bath 2; C) Patterns a) and c) for the alloys W-R8 and R1, obtained by bath 1 and f) and g) for the alloys W-R6 and W-R3 obtained by bath 2 at different temperature: 30°C and 60 °C.

**Figure 6** - Non-faradic region of voltammetric curves at different scan rates (a); current density as a function of scan rate (b).

**Figure 7**- Tafel curves for Ni-Co-W a) and Ni-Co alloy b) (48% Co).

### Table list

**Table 1** - Electrolytes composition.

**Table 2** - Results of electrowinning tests performed with and without sodium citrate.

**Table 3** - Operative conditions for tests performed with sodium citrate and different amount of W in the electrolyte.

**Table 4** - Results of tests performed at 60°C by using sodium citrate.

**Table 5** - Results of electrochemical tests performed at 30 mA/cm<sup>2</sup> current density on deposits obtained with and without citrate in bath solution.

**Table 6** - Electrochemical parameters for Ni-Co-W ternary alloys and Ni-Co binary alloys (42%, 48% and 63%Co).

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**Table 1 - Electrolytes composition**

Reagents	Bath N.1	Bath N.2
<i>Ni(II) (g/l)</i>	40	40
<i>Co(II) (g/l)</i>	8	8
<i>W(VI) (g/l)</i>	2-8	2-8
<i>H<sub>3</sub>BO<sub>3</sub> (g/l)</i>	20	20
<i>Na citrate (M)</i>	–	0.12

**Table 2 - Results of electrowinning tests performed with and without sodium citrate**

Alloy	T (°C)	Ni %	Co %	W %	$\eta$ (%)	V (Volt)	S.E.C. (KWh / Kg)
boric acid							
<b>W-R8</b>	30	26.77	63.60	9.63	84.30	3.47	4.23
<b>W-R7</b>	40	39.30	52.79	7.91	86.30	3.33	3.88
<b>W-R2</b>	50	44.16	48.02	7.82	87.30	3.16	3.72
<b>W-R1</b>	60	49.66	41.96	8.38	87.90	2.85	3.52
boric acid / Na citrate							
<b>W-R6</b>	30	46.65	49.83	3.52	89.30	3.17	3.51
<b>W-R5</b>	40	44.10	51.16	4.74	89.45	3.03	3.32
<b>W-R4</b>	50	39.15	52.90	7.95	89.60	2.88	3.05
<b>W-R3</b>	60	35.36	55.24	9.40	89.50	2.43	2.83

**Table 3 - Operative conditions for tests performed with sodium citrate and different amount of W in the electrolyte**

Alloy	T (°C)	Ni (g/l)	Co (g/l)	W (g/l)	Boric acid (g/l)	Na citrate (g/l)	J (A/m <sup>2</sup> )
<b>W-R9</b>	60	40	8	3	20	35.3	260
<b>W-R10</b>	60	40	8	4	20	35.3	260
<b>W-R11</b>	60	40	8	8	20	35.3	260
<b>W-R12</b>	60	40	8	8	20	35.3	350

**Table 4 - Results of tests performed at 60°C by using sodium citrate**

Alloy	T (°C)	%Ni	%Co	%W	$\eta$	V <sub>average</sub> [V]	S.E.C. (KWh / Kg)
<b>W-R3</b>	60	35.36	55.24	9.40	89.50	2.43	2.83
<b>W-R9</b>	60	27.31	65.09	7.60	89.7	2.46	2.47
<b>W-R10</b>	60	31.97	60.10	7.93	89.9	2.41	2.42
<b>W-R11</b>	60	41.96	48.47	9.57	89.5	2.34	2.38
<b>W-R12</b>	60	47.43	42.62	9.95	89.4	2.32	2.35

**Table 5 - Results of electrochemical tests performed at 30 mA/cm<sup>2</sup> current density on deposits obtained with and without citrate**

Alloy	% W	% Co	% Ni	$\eta$ [V] geom. surface at $i = 30 \text{ mA/cm}^2$	$i_0$ real surface A/cm <sup>2</sup>	TafelslopemV/dec
W-R8 (bath 1)	9.63	63.60	26.77	0.180	$6.5 \cdot 10^{-4}$	150
W-R7 (bath 1)	7.91	52.59	39.30	0.190	$2.5 \cdot 10^{-4}$	150
W-R1(bath 1)	8.38	41.96	49.66	0.195	$3.1 \cdot 10^{-4}$	175
W-R2 (bath 1)	7.82	48.02	44.16	0.210	$2.5 \cdot 10^{-4}$	175
W-R6 (bath 2)	3.52	49.83	46.65	0.195	$4 \cdot 10^{-4}$	150
W-R9 (bath2)	7.60	65.09	27.31	0.200	$6.5 \cdot 10^{-4}$	170
W-R11 (bath2)	9.57	48.47	41.96	0.190	$3.1 \cdot 10^{-4}$	155
W-R12 (bath2)	9.95	42.62	47.43	0.195	$3.1 \cdot 10^{-4}$	155

**Table 6 - Electrochemical parameters for Ni-Co-W ternary alloys and Ni-Co binary alloys (42%, 48% and 63% Co).**

Binary alloys	Ni-Co	Ni-Co	Ni-Co
Cobalt content	( $\approx 42\%$ Co)	( $\approx 48\%$ Co)	( $\approx 63\%$ Co)
Overvoltage [mV]	320	315	295
Exchange current density $i_0$ [A/cm <sup>2</sup> ]	$1 \cdot 10^{-5}$	$5.3 \cdot 10^{-6}$	$1.7 \cdot 10^{-5}$
Tafelslope [mV/dec]( $i < 0.4 \text{ mA/cm}^2$ )	35	35	35
Tafelslope [mV/dec] ( $0.4 < i < 10 \text{ mA/cm}^2$ )	60	65	65
Tafelslope [mV/dec] ( $i > 10 \text{ mA/cm}^2$ )	125	135	125
<b>Ternary alloys (Bath 1)</b>	<b>Ni-Co-W</b>	<b>Ni-Co-W</b>	<b>Ni-Co-W</b>
Cobalt content	( $\approx 42\%$ Co)	( $\approx 48\%$ Co)	( $\approx 63\%$ Co)
Overvoltage [mV]	195	210	180
Exchange current density $i_0$ [A/cm <sup>2</sup> ]	$3.1 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$
Tafel slope mV/dec	175	155	150
<b>Ternary alloys (Bath 2)</b>	<b>Ni-Co-W</b>	<b>Ni-Co-W</b>	<b>Ni-Co-W</b>
Cobalt content	( $\approx 42\%$ Co)	( $\approx 48\%$ Co)	( $\approx 63\%$ Co)
Overvoltage [mV]	190	190	200
Exchange current density $i_0$ [A/cm <sup>2</sup> ]	$3.1 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$
Tafel slope [mV/dec]	155	155	170

Figure 1  
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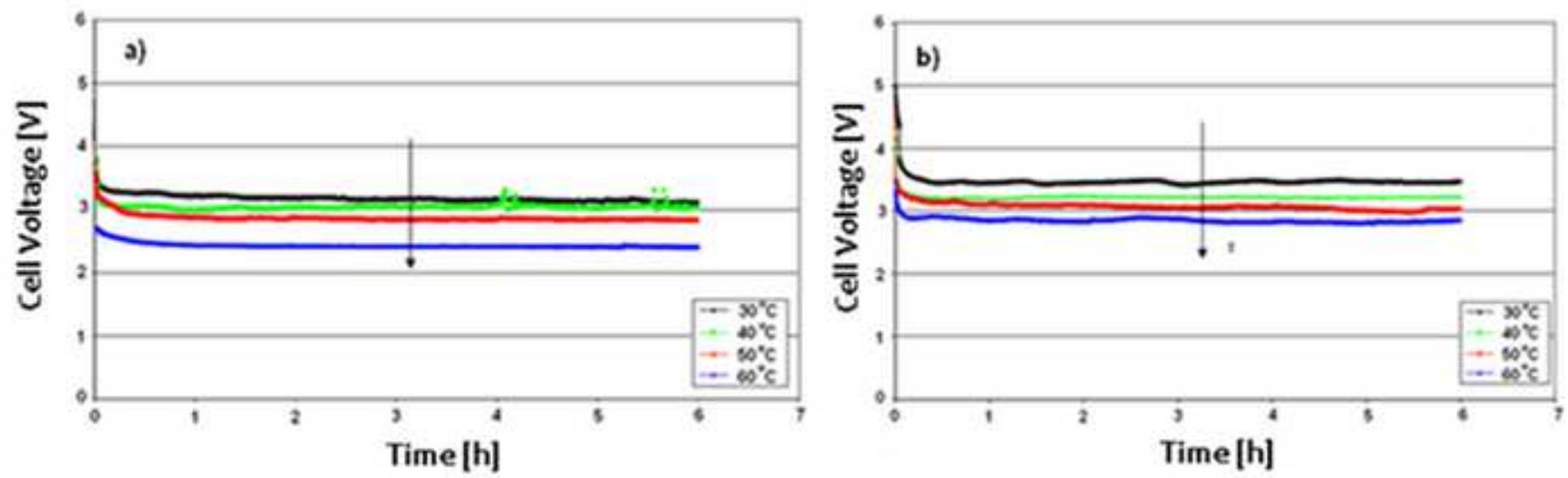


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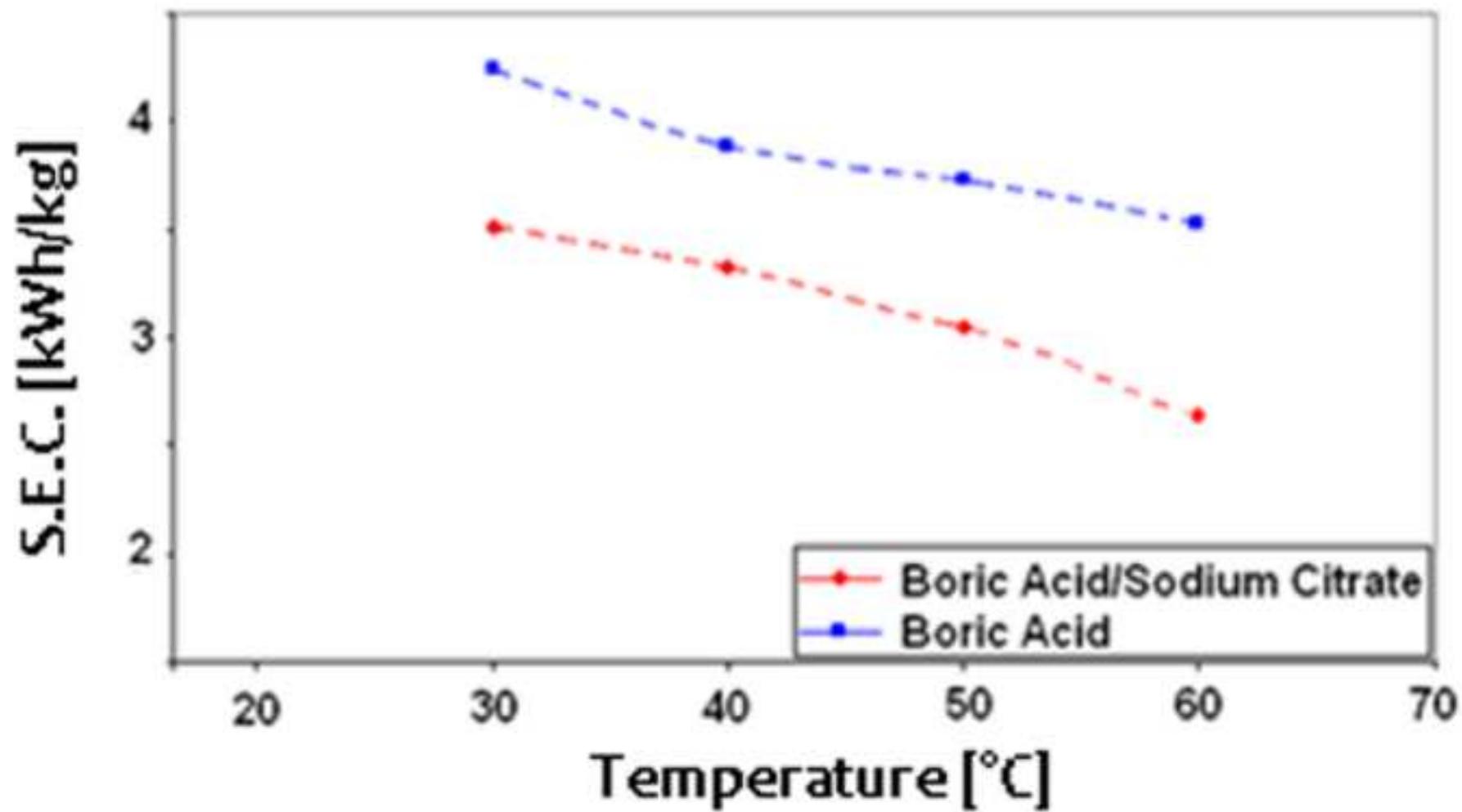


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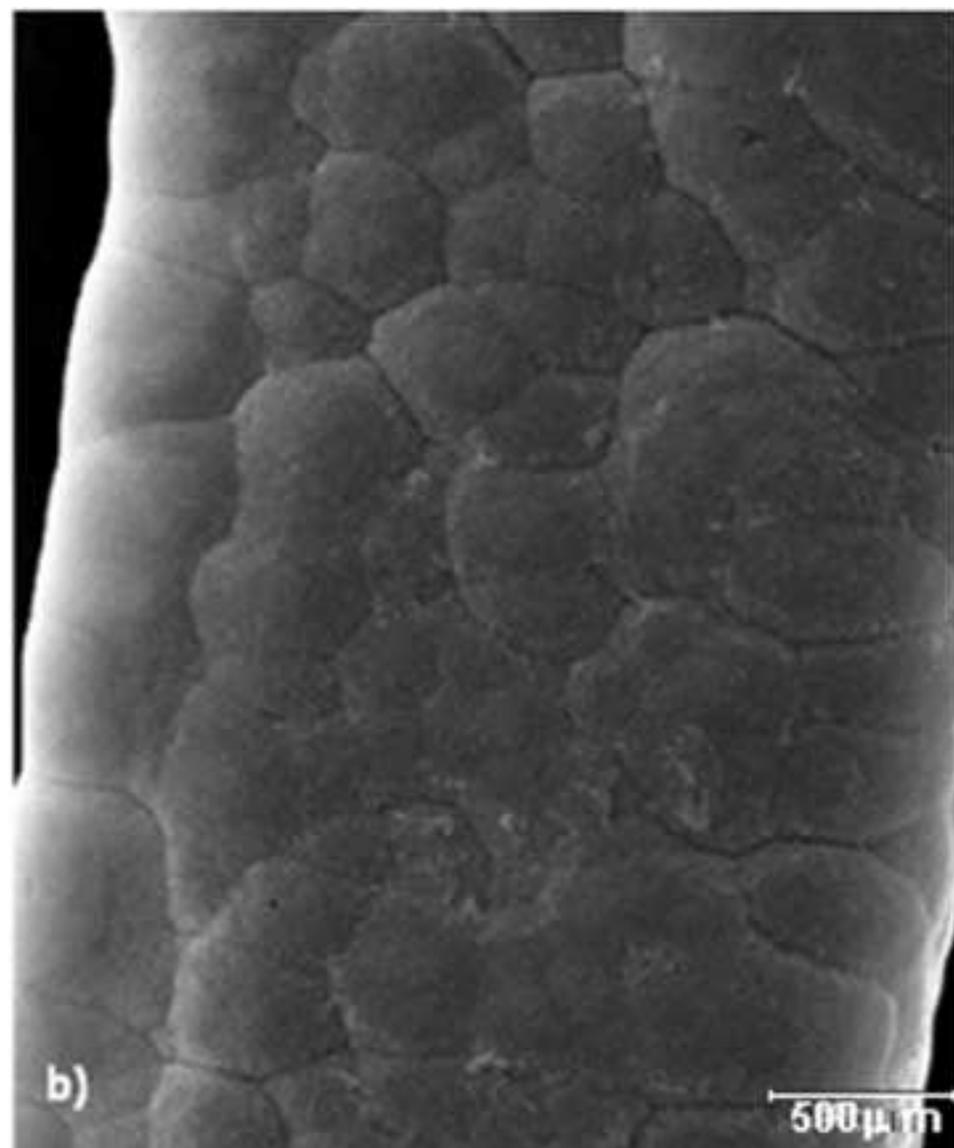
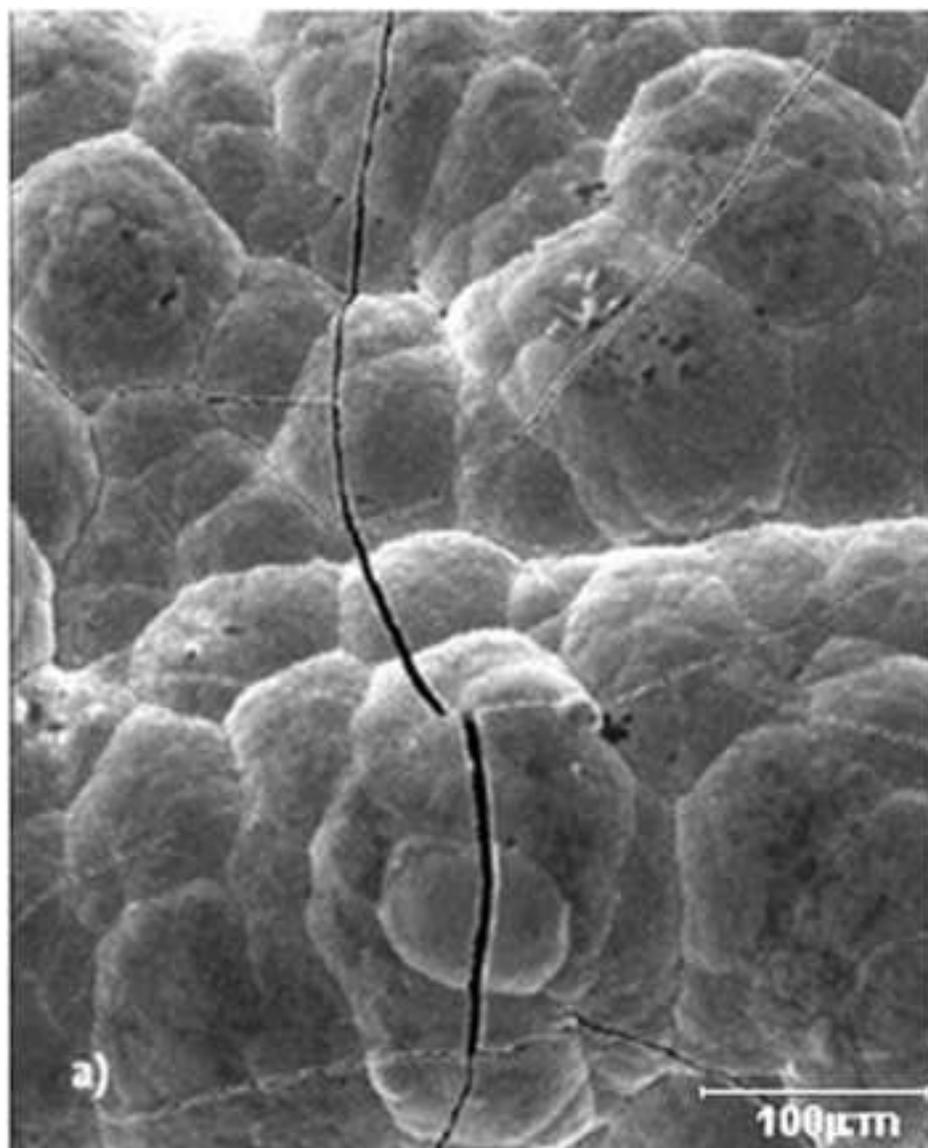


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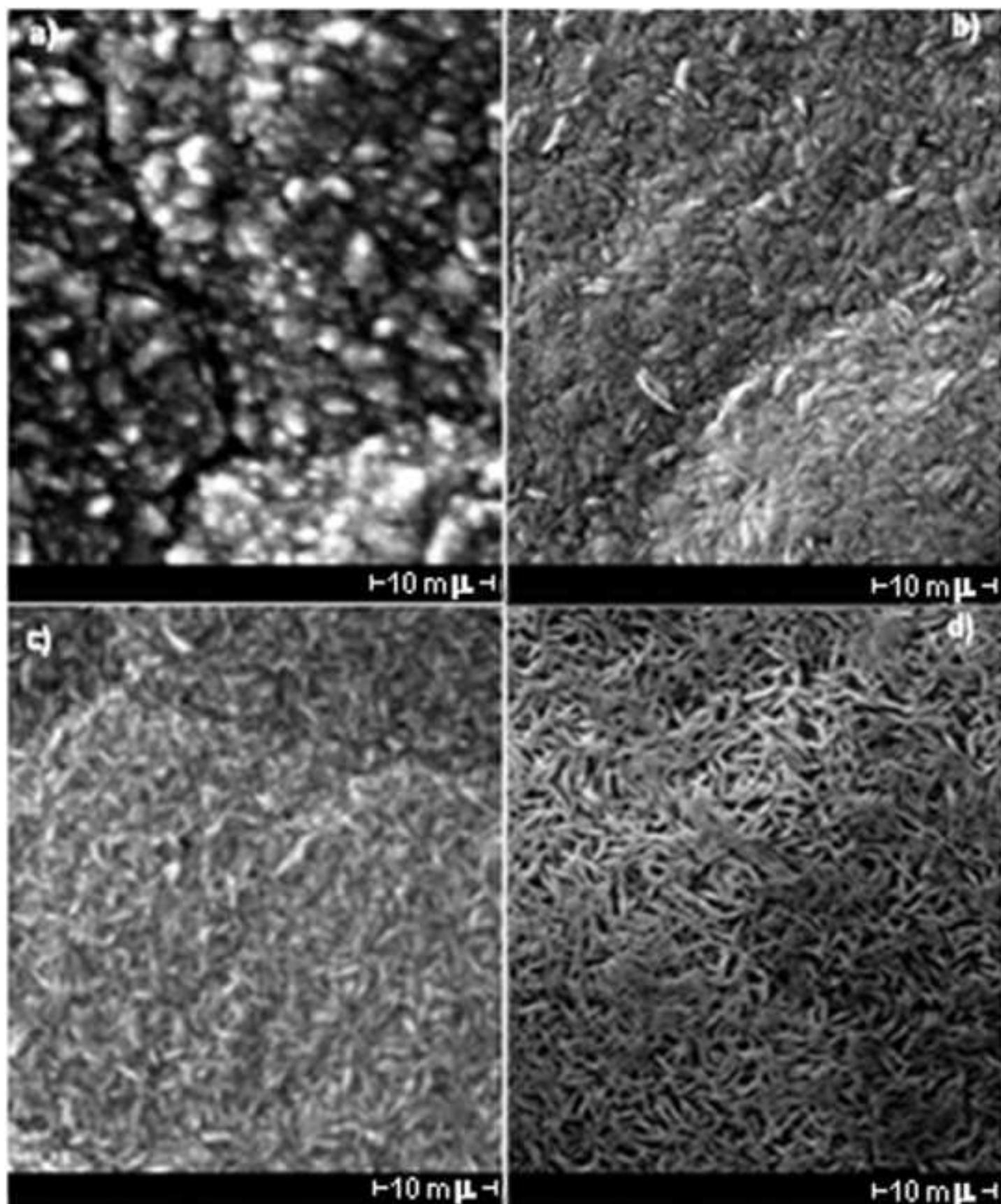


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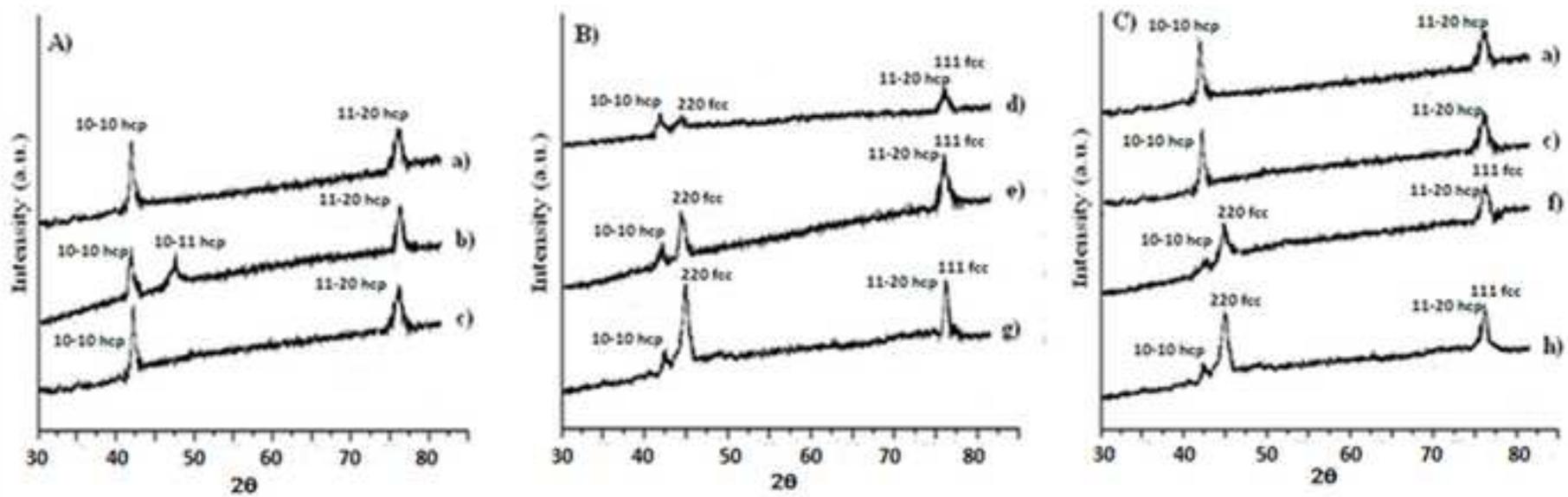


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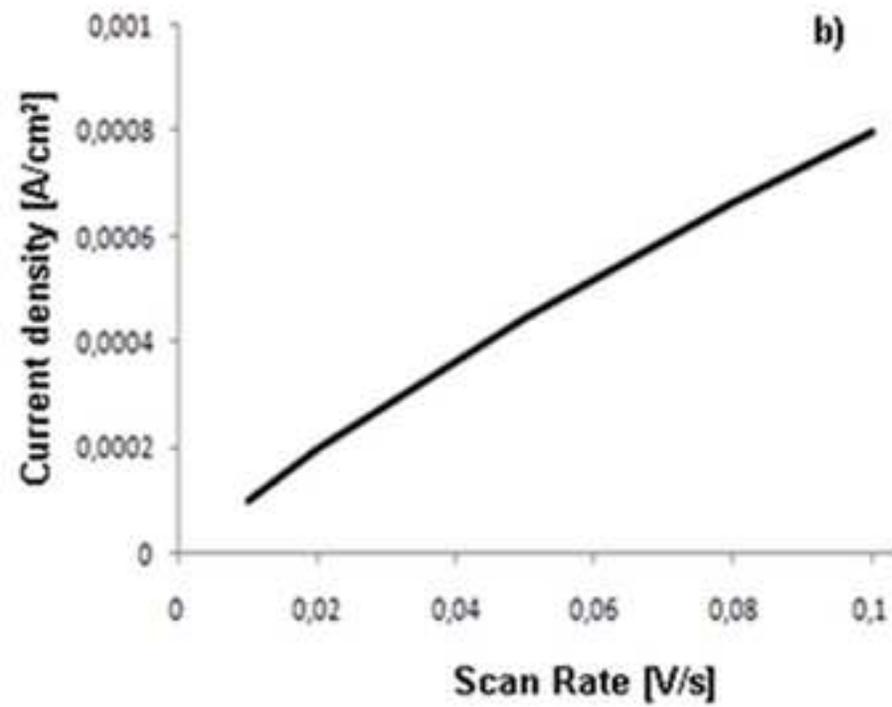
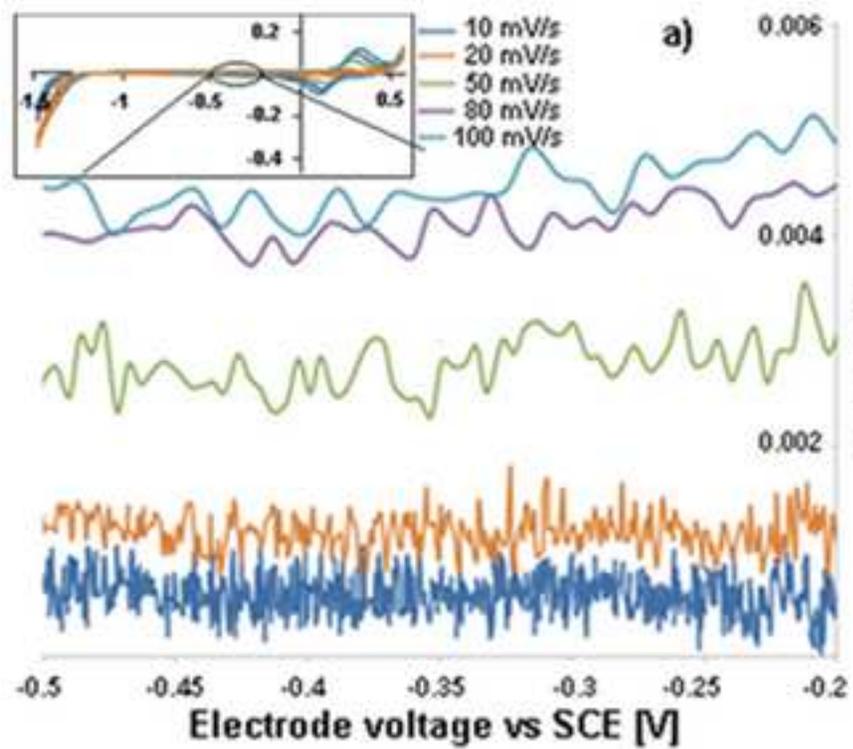


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