

## Electrochemical impedance spectroscopy study of Ni coating electroplated from deep eutectic solvent at different current densities of pulse electrodeposition

Department of Chemistry, York University, Toronto, Ontario, M3J 1P3 Canada

Mehry Fattah and Sylvie Morin

### Abstract

A choline chloride-ethylene glycol (ChCl:2EG)-based DES electrolyte, was employed to fabricate Ni coatings through electrodeposition at different current densities of 2, 4, 8 and 16 mA cm<sup>-2</sup>. Microstructure, morphology and composition of the coatings were studied employing scanning electron microscopy (SEM), X-ray diffraction (XRD), and surface texture measurements. Electrochemical impedance spectroscopy was used to analyse the effect of the electrodeposition current density on the electrochemical behaviour of the coatings. XRD results showed face-centred cubic (fcc) Ni with identical crystallographic planes of (111), (200) and (220). A spherical granular growth with thin platelets oriented perpendicular to the films for all coatings. The appearance of the platelets was not affected by electrodeposition current density. EIS responses for the coatings electroplated at 2, 4 and 8 mA cm<sup>-2</sup> were found to contain one constant-phase element and these responses were fitted to an R(QR) equivalent circuit (EEC). The maximum coating resistance and the minimum coating capacitance were related to the sample electroplated at 4 mA cm<sup>-2</sup>. This behaviour can be linked to the influential effect of the electrodeposition current density on the characteristics and microstructure of the coatings.

## 1. Introduction

Electrodeposition of Ni and Ni-based composites from different electrolytes has been a subject of interest for a long time in improving surface properties [1–3]. Aqueous solutions and Watts electrolytes have been used widely for metal electrodeposition on the surface of engineered components. However, there are some shortcomings, such as low current efficiency and hydrogen embrittlement for metals with high reduction negative potential, such as Zn and Cr [4], side reactions due to the narrow potential window, the complexity of bath and additives, high sensitivity of coating properties and morphology to the composition and pH of the electrolyte, difficulties of the electrodeposition process on the high reactive surfaces with water such as aluminum due to the formation of a passive layer on the substrate surface [5]. Environmentally friendly deep eutectic solvents (DESs) were introduced recently by Abbott et al. [6] as a new environmentally friendly ionic liquid and have been used since for electrodeposition of pure metals [7, 8, 9, 10] and nanocomposites [11, 12] because of their superior stability with respect to composition, moisture, and air [12], dispersion [11], as well as being green [12]. In this study, we investigated the electrodeposition of Ni coating from an ethaline-based (choline chloride-ethylene glycol (ChCl:2EG)-based DES electrolyte containing NiCl<sub>2</sub>•6H<sub>2</sub>O on medium carbon steel AISI 1045, which is being used widely in industry. This paper aims to understand the effect of electrodeposition current density on the microstructural and compositional properties of the Ni coating. Afterwards, the relationship between Ni coating surface characteristics and surface electrochemical behaviour was obtained.

## 2. Experimental

### 2.1 Materials and Sample Preparation

- Substrate:** Disc-shaped AISI 1045 (CK45) medium carbon steel (0.45 wt.% carbon, Metal Supermarkets)

All samples were prepared through the following steps:

- Grinding**
- Degreasing** (NaOH (3%. wt.) at 80 °C for 5 min).
- Activation:** (H<sub>2</sub>SO<sub>4</sub> (10%) solution at 50 °C for 50 sec).

### 2.2 Electrolyte Preparation and Electrodeposition

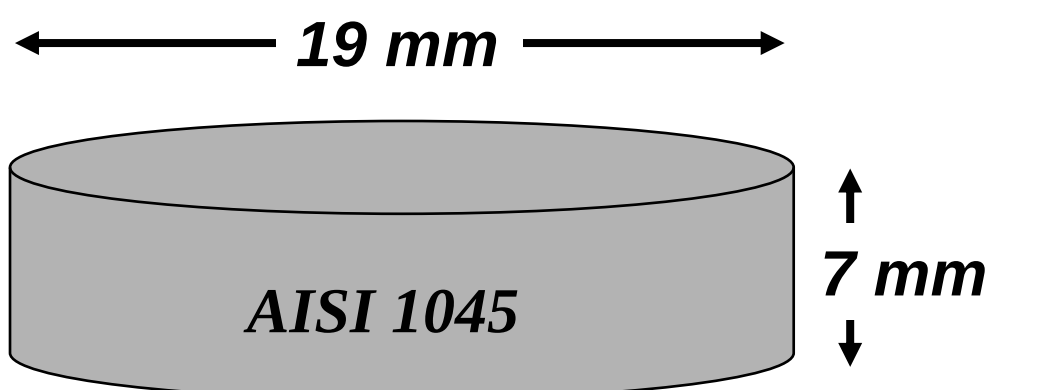


Table 1. Electrodeposition Conditions.

| Experimental parameters for electrodeposition of Ni coatings  |                     |
|---------------------------------------------------------------|---------------------|
| <b>• Deep Eutectic Electrolyte Composition</b>                |                     |
| Choline chloride/ethylene glycol mixture at 70 (°C) (ChCl/EG) | 1/2 (molar ratio)   |
| NiCl <sub>2</sub> •6H <sub>2</sub> O                          | 0.2 (M)             |
| <b>• Electrodeposition Conditions</b>                         |                     |
| Current Density (mA cm <sup>-2</sup> ) ± 0.2                  | 2.0, 4.0, 8.0, 16.0 |
| Frequency (Hz) ± 10                                           | 1000                |
| Duty Cycle (%) ± 0.2                                          | 27.7                |
| Temperature (°C) ± 2                                          | 70                  |
| PH ± 0.2                                                      | 5                   |
| Stirring rate (rpm) ± 5%                                      | 1000                |
| Time (min) ± 0.2                                              | 90                  |

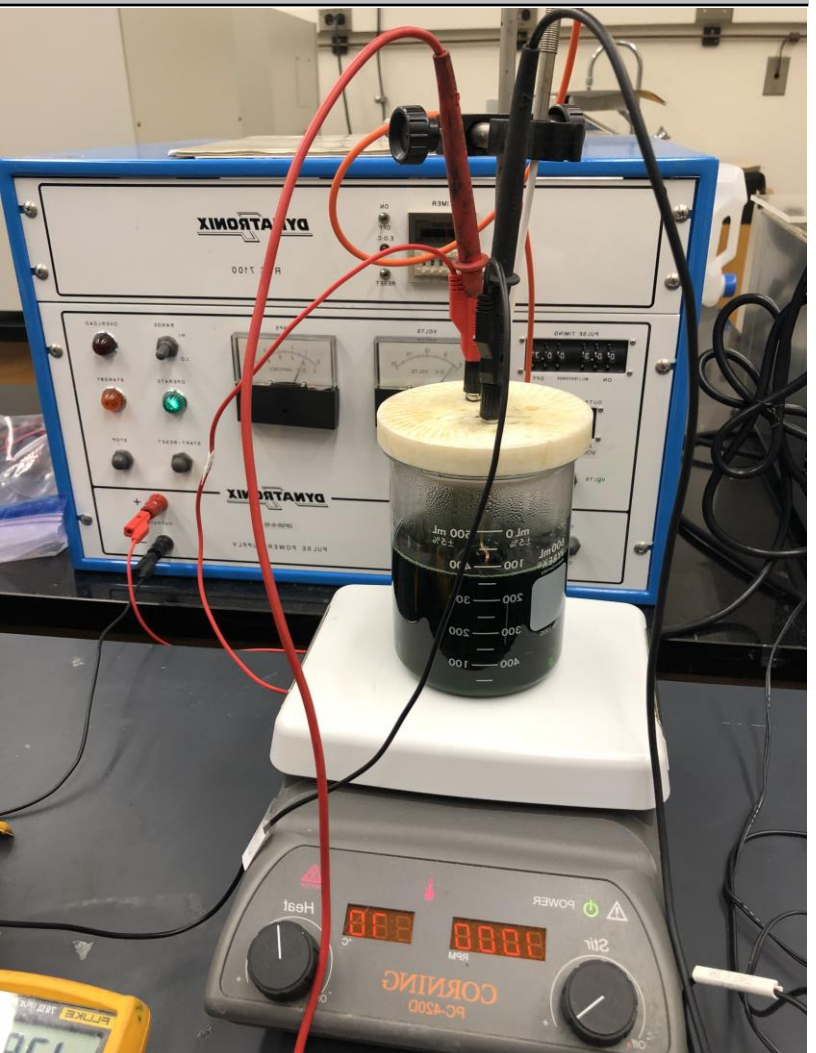


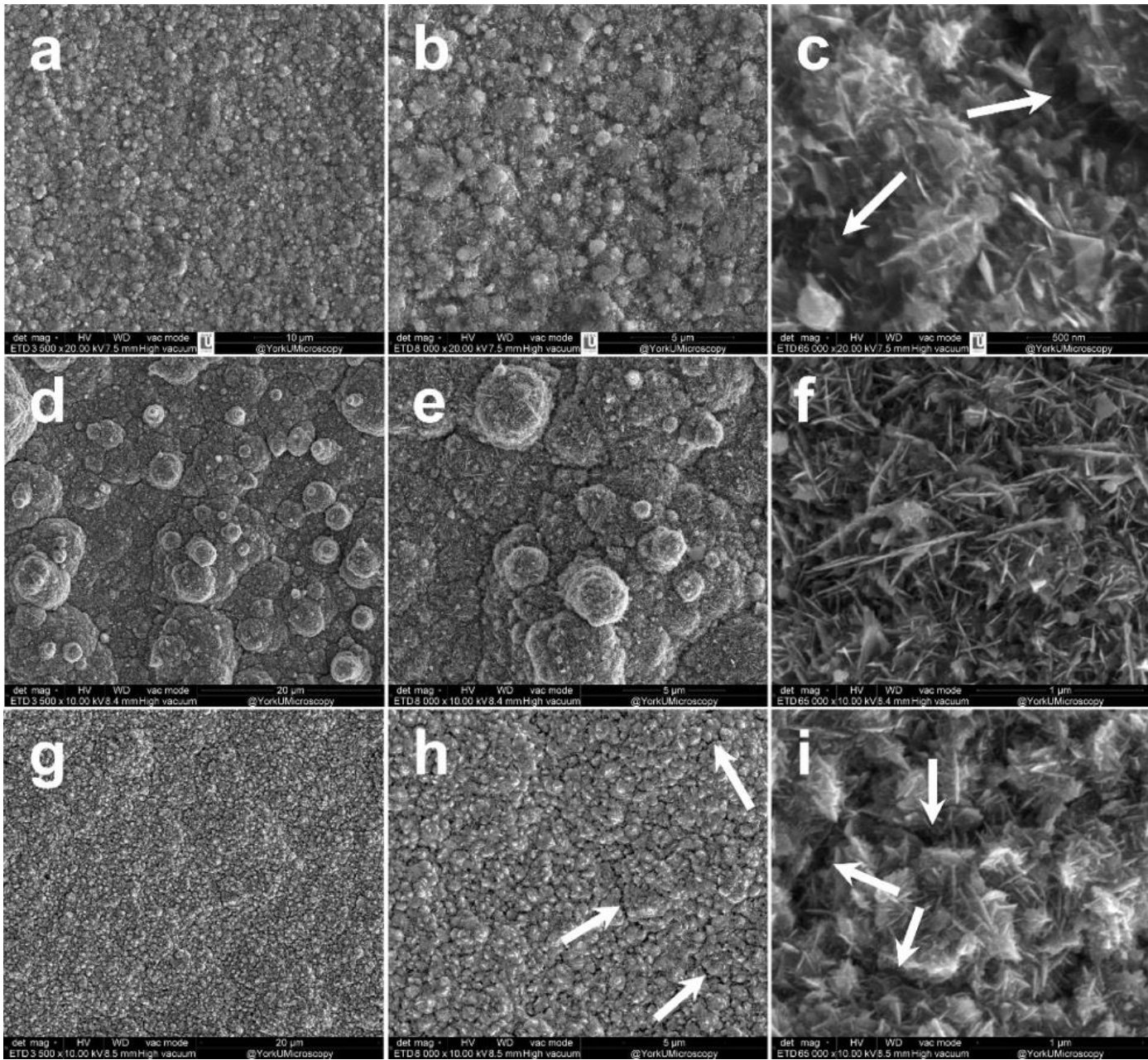
Fig. 1 Ni electrodeposition set up.

## 3. Results and Discussion

### 3.1 SEM

- Spherical granular growth with thin platelets oriented perpendicular to the films.
- The appearance of the platelets was not affected by electrodeposition current density.
- The Ni cluster size in the coatings was affected by the electrodeposition current density.

Figure 2: SEM images of Ni coating layers electrodeposited at different current densities of: (a, b, c) 4 mA cm<sup>-2</sup>; (d, e, f) 8 mA cm<sup>-2</sup> and (g, h, i) 16 mA cm<sup>-2</sup> at different magnifications. White arrows show the space between clusters in the surface of the coating electroplated at 4 mA cm<sup>-2</sup> (c), and intergranular space and microcracks in the coating surface electroplated at 16 mA cm<sup>-2</sup> (h and i).



### 3.2 XRD

- Iron peaks shown in Fig. 3 are related to the substrate material which is probably detected due to the low thickness of the coating.
- Ni microstructure in all Ni coatings is face-centered cubic (fcc) and the diffraction peaks detected at 2θ=52.2°, 61.0° and 91.8° are related to the (111), (200) and (220) Ni planes, respectively.
- Crystallographic planes and grain size were not affected by electrodeposition current density.

#### 3.2.1 Grain Size

- Debye-Scherrer**

Table 2. Ni crystallite size.

| Electrodeposition Current Density (mA cm <sup>-2</sup> ) | Ni Crystallite Size (nm) |
|----------------------------------------------------------|--------------------------|
| 4                                                        | 13 ± 0.2                 |
| 8                                                        | 12.3 ± 0.2               |
| 16                                                       | 12.5 ± 0.1               |

Where

**D:** Crystalline size (nm).

**λ:** Incident radiation wavelength = 0.179 nm for Co.

**B:** Peak width at half-maximum intensity (FWHM in rad).

**Θ:** Peak angle (rad).

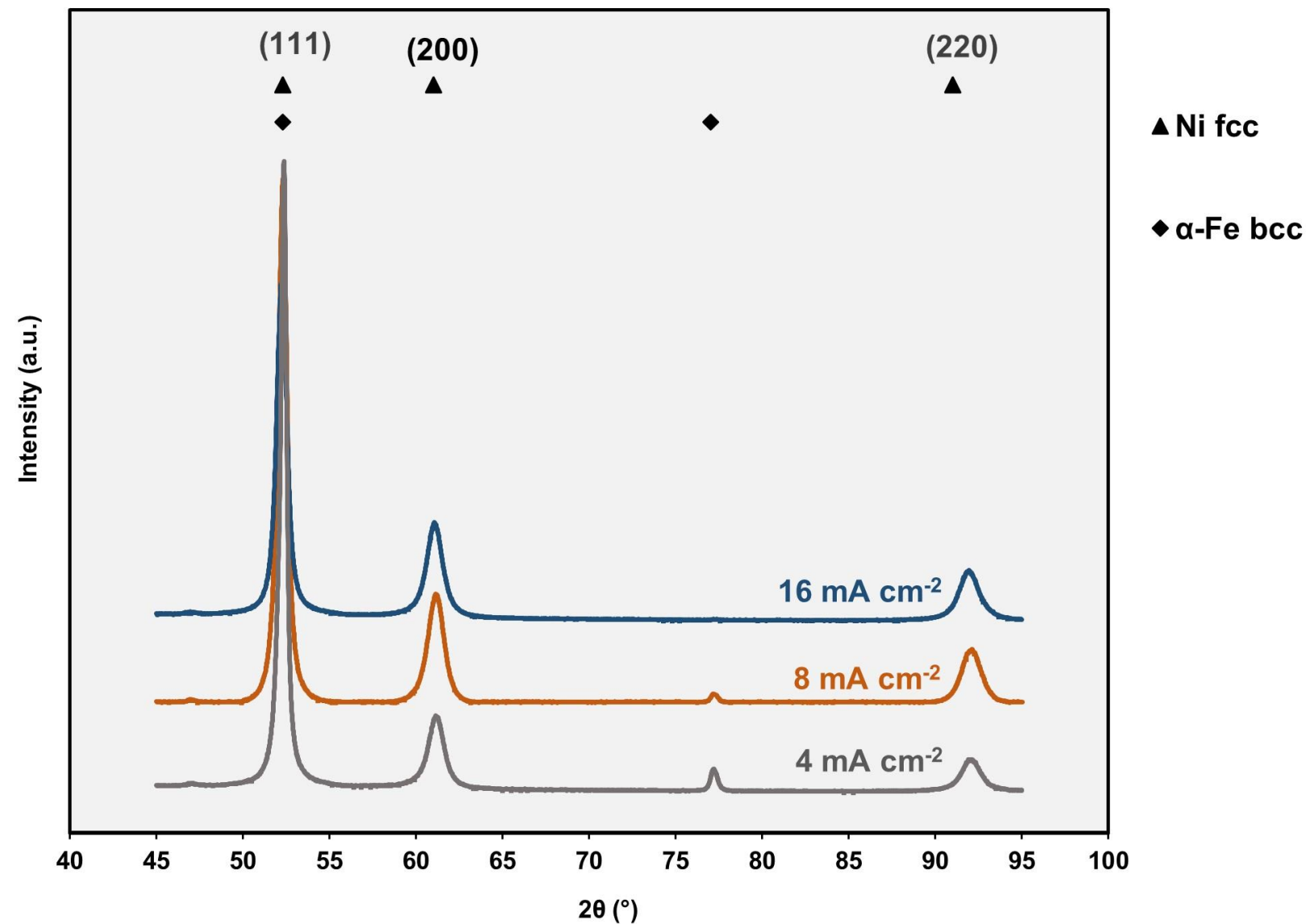


Figure 3: XRD pattern of Ni coatings electroplated at different electrodeposition current densities of 4, 8 and 16 mA cm<sup>-2</sup>. (111), (200), and (220) are crystallographic planes for Ni fcc.

## 3.3 Electrochemical Impedance Spectroscopy (EIS)

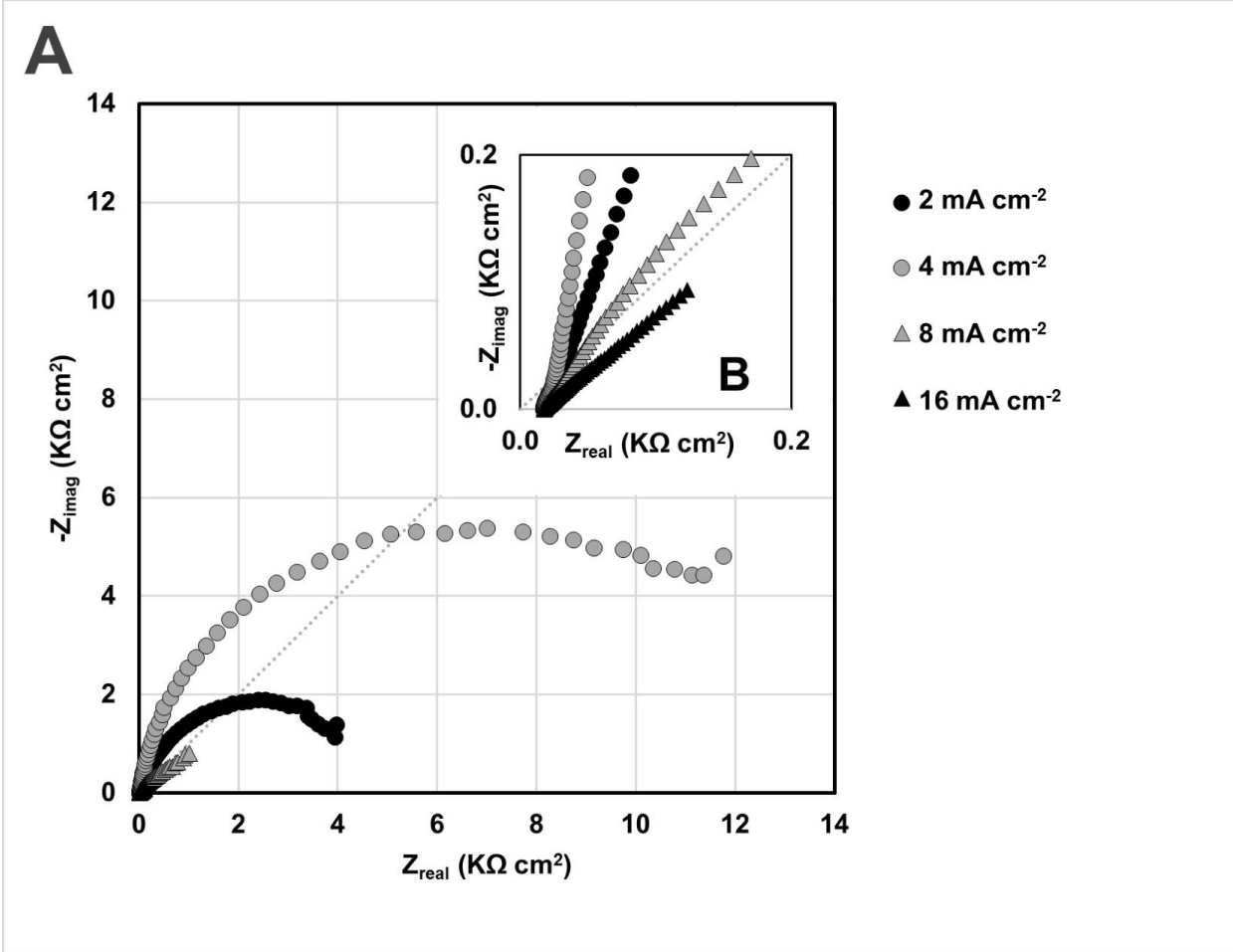


Figure 4. A) Nyquist plots for Ni coatings electroplated at different current densities of 2, 4, 8 and 16 mA cm<sup>-2</sup>. High frequency responses are magnified in (B). Broken line is the line with 45° angle and Nyquist plot for coating electroplated at 16 mA cm<sup>-2</sup> is linear and parallel to this line.

Figure 5. A) and B) Nyquist, and C) Bode plots along with the fitting curves for the coatings electroplated at (a) 2, (b) 4 and (c) 8 mA cm<sup>-2</sup>. High-frequency responses for Nyquist plots are magnified in (B). Line (a), (b) and (c) in (C) show the frequency line at the minimum phase angles for the fittings of the coatings electroplated at 2, 4 and 8 mA cm<sup>-2</sup> respectively. The equivalent circuit (EEC (a)), used to model measured data, is shown in (A).

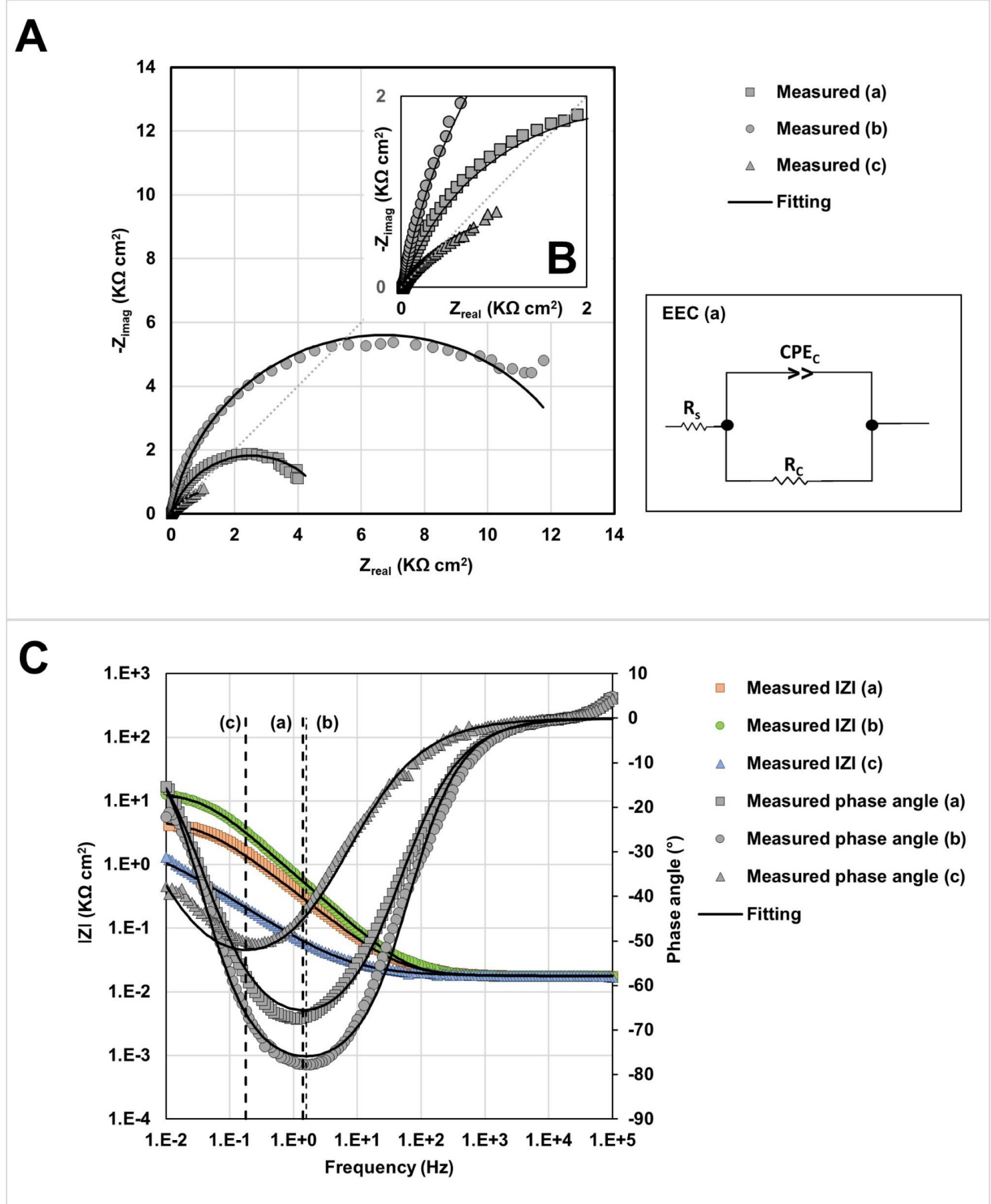


Table 3. Results obtained from EEC.

| Electrodeposition Current density (mA cm <sup>-2</sup> ) | R <sub>s</sub> (Ω cm <sup>2</sup> ) | CPE <sub>C</sub> (μF cm <sup>-2</sup> ) | CPE-n       | R <sub>c</sub> (Ω cm <sup>2</sup> ) |
|----------------------------------------------------------|-------------------------------------|-----------------------------------------|-------------|-------------------------------------|
| 2                                                        | 17.580 ± 0.009                      | 594.130 ± 0.007                         | 0.79 ± 0.04 | 5027.77 ± 0.14                      |
| 4                                                        | 17.827 ± 0.008                      | 266.485 ± 0.002                         | 0.89 ± 0.04 | 13369.94 ± 0.13                     |
| 8                                                        | 18.01 ± 0.01                        | 4392.63 ± 0.42                          | 0.67 ± 0.04 | 2365.06 ± 1.44                      |

## 4. Conclusions

- Nano-sized Ni crystallite obtained at current densities of 4, 8 and 16 mA cm<sup>-2</sup>.
- The electrodeposition current density had no appreciable effect on Ni crystallite size, and it remained around 12.6 ± 0.3 nm.
- Spherical granular growth with thin platelets oriented perpendicular to the films was observed for all coatings electroplated at different current densities.
- The appearance of the platelets was not affected by electrodeposition current density.
- XRD results of the coatings electroplated at 4, 8 and 16 mA cm<sup>-2</sup> indicated fcc Ni crystallites with peaks detected at (111), (200) and (220) crystallographic planes.
- Microstructure and compactness, layer thickness, and permittivity, as well as surface texture are the parameters controlling and electrochemical behaviour of the studied Ni coatings
- For coatings electroplated at current densities less than 4 mA cm<sup>-2</sup>, the thickness of the layers, controlled the electrochemical behaviour of the layers, while for the coatings electroplated at current densities above 4 mA cm<sup>-2</sup>, dense packing, permittivity, and surface texture were the dominant factors.

## References

- Vaezi, M.R.; Sadrnezhad, S.K.; Nikzad, L. Colloids Surf A Physicochem Eng Asp. 2008, 315, 176–182.
- Zemanová, M.; Krivosudská, M.; Chovancová, M.; Jorík, V. Int J. Appl. Electrochem. 2011, 1077–1085.
- Wang, Y.; Zhou, Q.; Li, K.; Zhong, Q.; Bui, Q.B. Ceram Int. 2015, 41, 79–84.
- Abbott, A.P.; McKenzie, K.J. Physical Chemistry Chemical Physics 2006, 8, 4265–4279.
- Bernasconi, R.; Magagnin, L. Surface Engineering 2017, 33, 131–135.
- Lekka, M.; Offoach, R.; Revelant, F.; Fedrizzi, L. Trans. IMF 2019, 97, 73-81.
- Mohajeri, S.; Dolati, A.; Ghorbani, M. J. Ultrafine Grained Nanostruct. Mater. 2016, 49, 51-63.
- Danilov, F. I. et al. Surf. Eng. Appl. Electrochem. 2019, 55, 138–149.
- Lanzutti, A. et al. Tribol. Int. 2019, 132, 50-61.
- Zhou, Y.; Xie, F. Q.; Wu, X. Q.; Zhao, W. D.; Chen, X. J. Alloys Compd. 2017, 699, 366-377.
- Li, R.; Hou, Y.; Liu, B.; Wang, D.; Liang, J. Electrochim. Acta 2016, 222, 1272–1280.
- Ratajski, T. et al. Mater. Charact. 2018, 142, 478-491.