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Effect of Deposition Time and Temperature on the Performance of Electroless Ni-P Coatings

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In this study, electroless nickel-phosphorous (Ni-P) coatings were deposited on the copper (Cu) substrate in order to improve the electrolyte resistance of electrode tabs of lithium ion battery. The effects of treatment time and temperature on the surface morphology, composition and corrosion resistance of the deposited copper were investigated by scanning electron microscopy (SEM), energy diffraction spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and electrolyte immersion test. The results show that Ni-P coatings deposited at 75 - 80 °C for more than 10 min have much smoother surfaces, and Ni-P coating deposited at 75 °C for 25min has the best corrosion resistance. All Ni-P coatings have good electrolyte resistance and can endure the electrolyte at 80 °C for at least 48h.

Keywords: lithium ion battery; nickel-plated copper tab; corrosion resistance; electrolyte resistance

1. INTRODUCTION

The problems of oil shortage and environmental pollution have created an ever increasing demand for new high-energy and high power-density energy storage devices, among which lithium ion battery has attracted considerable research attention due to its high energy density and good cycle performance. However, although considerable efforts have been devoted to develop the key materials of lithium ion battery, such as electrodes [1-6] and electrolytes [7, 8], less research has focused on the electrode tabs, which are used to connect the anode and the cathode electrode on the current collector, and thus play an important role in improving the safety of lithium ion battery.

Nickel (Ni) is often used as the material of choice for negative tab. However, the conductivity of Ni is poorer than that of copper (Cu), thus Ni-plated Cu tabs have emerged to meet the increasing demand of conductivity of lithium ion battery. Ni-plated Cu material can be prepared using

electroplating or electroless plating technology. In comparison, electroless plating technology appears to be easier and more environmentally friendly [9, 10]. Electroless Ni plating has been previously used for the preparation of Ni-P alloys [11-13], Ni-B alloys [14-16] and Ni-based multicomponent alloys [17, 18]. Ni-B alloys are often used to improve abrasion resistance, and Ni-P alloys and Ni-based multicomponent alloys are often used to improve corrosion resistance.

The purpose of this study is to investigate the effects of deposition time and temperature on the surface properties, corrosion and electrolyte resistance of Ni-plated Cu tabs. The surface morphologies and compositions of samples were characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and x-ray photoelectric spectroscopy (XPS), the corrosion resistance was evaluated by electrochemical impedance spectroscopy (EIS), and electrolyte resistance was evaluated by immersing the samples in electrolyte.

2. EXPERIMENTAL

2.1. Materials

Cu foil was provided by Lianyungang Delixin Co. (Jiangsu, China). Nickel chloride, chromic nitrate, sodium hypophosphite, citric acid, and sodium acetate were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., (Shanghai, China).

2.2. Electroless plating process

Cu foil was first degreased at 40 ℃ in acetone for 10min, washed with water, and then immersed in an electroless plating solution containing nickel chloride (12g/l), chromic nitrate (9.6g/l), sodium hypophosphite (42g/l), citric acid (29g/l), and sodium acetate (30g/l), where pH was adjusted to 8 with $NH_3 \cdot H_2O$, temperature was set at 70-90 ℃, and time was set at 5-25 min, respectively. The resultant Ni-P coatings were washed with distilled water and dried in an oven.

2.3. Surface analysis

Surface analysis was carried out to identify the changes introduced to the Cu substrate by the electroless plating. Specifically, the surface morphologies of the resultant Ni-P coatings were observed using field emission scanning electron microscopy (S-4800; Hitachi Limited, Japan) operated at 10 kV; the changes in composition of Ni-P coatings were determined using EDS (QUANTAX 400-30; Bruker AXS, Germany); and the chemical states of Ni and P on the Ni-P coatings were determined using XPS (ESCALAB 250; Thermo Fisher, America) equipped with an Al anode. All XPS peaks were calibrated using the C-C/C-H C1s peak at a binding energy of 284.6 eV, and the XPS spectra were curve-fitted and decomposed using XPSPEAK software.

2.4. Electrochemical impedance spectroscopy (EIS)

EIS tests were performed in a conventional three-electrode system on a PARSTAT2273 electrochemical workstation (AMETEK, America), which consisted of a counter electrode (a platinum

sheet with a surface area of 1 cm^2), a reference electrode (a saturated calomel electrode), and a working electrode (samples with an exposed area of 1.0 cm^2). The corrosive medium was 3.5 wt% NaCl solution. Prior to the EIS test, samples were immersed in the electrolyte in the three-electrode glass cell for about 15min to reach a steady open circuit potential. The impedance data were collected over a frequency range of 100 kHz to 0.01 Hz under open circuit conditions, and analyzed by Zsimpwin software.

2.5. Electrolyte immersion test

Samples were immersed in the electrolyte at 80 °C for 48h to evaluate their resistance to electrolyte.

3. RESULTS AND DISCUSSION

3.1. Surface morphologies of Ni-P coatings

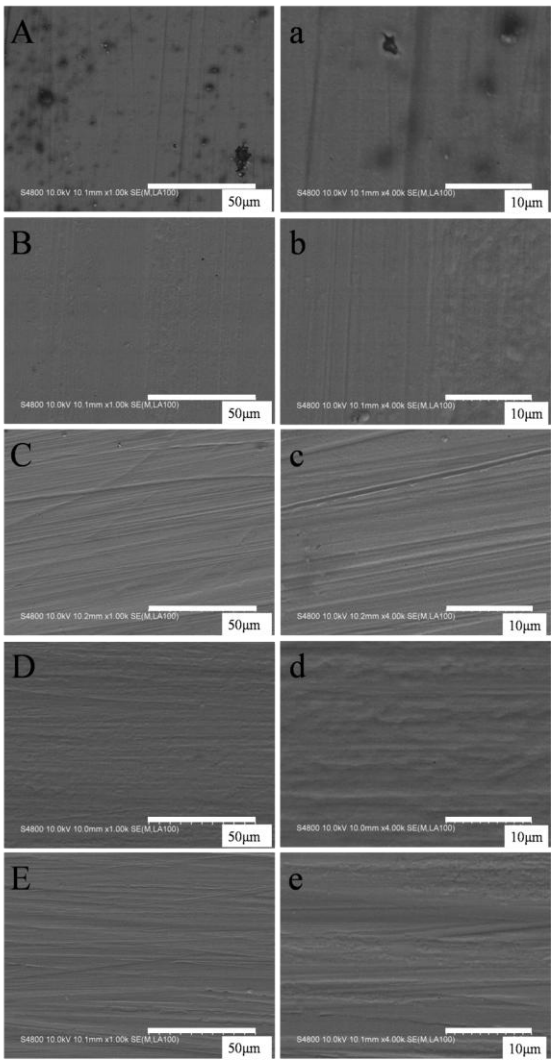

Figure 1. Surface morphologies of Ni-P coatings treated for 5 min (A, a), 10 min (B, b), 15 min (C, c), 20 min (D, d), and 25 min (E, e)

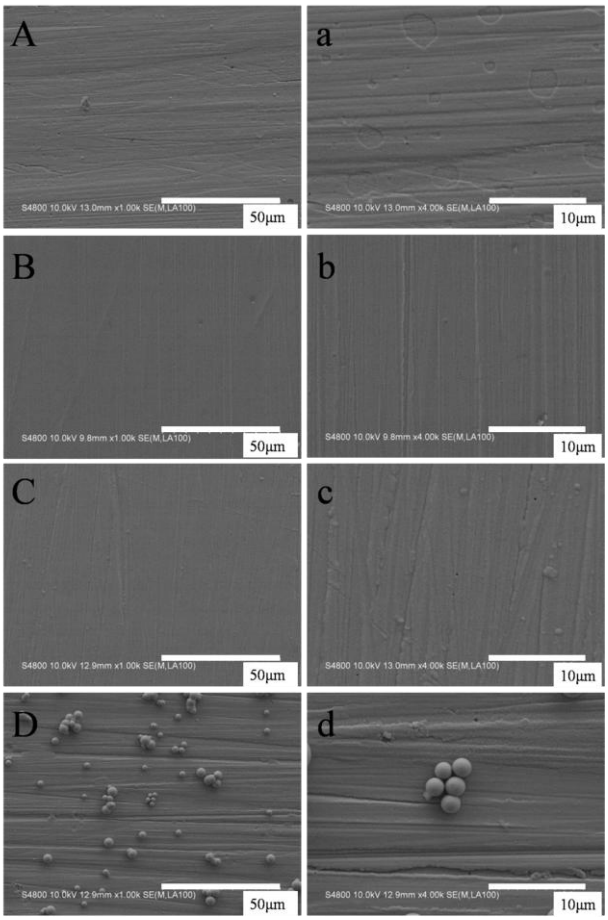

Figure 2. Surface morphologies of Ni-P coating treated at 70 ℃ (A, a), 75 ℃ (B, b), 80 ℃ (C, c), and 85 ℃ (D, d)

Fig.1 shows the SEM images of Ni-P coatings treated for different times. Fig. 1(A, a) shows many holes on the surface of Ni-P coating treated for 5min, indicating that electroless plating for 5min is insufficient to form a uniform surface.

The surfaces of Ni-P coatings become smoother with the increase of electroless plating time to 10-25min, but some regular scratches and rolling traces can be observed on the surface due to machining [19] (Fig. B-E, b-e).

Fig.2 shows the SEM images of Ni-P coatings treated at different temperatures. Fig. 2 (A, a) shows that there are some dents on the surface of Ni-P coating treated at 70 °C, probably because the temperature of plating solution is too low to form a stable surface. The surface becomes smoother and more homogeneous as the temperature increases to 75-80 °C. With further increase of temperature to 85 °C, many micro-nickel balls can be observed on the surface, because the plating solution is not stable at this temperature. When the temperature reaches 90 °C, Ni can not be plated on the Cu surface.

3.2. Chemical compositions of Ni-P coatings

The surface compositions of Ni-P coatings obtained under different conditions were determined by EDS, and the results are shown in Table 1 and Table 2. Table1 shows that the Ni and P content is

low in samples treated for 5min (74.88% and 11.48%, respectively), and increases to 77.12-77.71% and 14.32-14.88%, respectively, with the increase of electroless plating time. Table 2 shows the Ni and P content of Ni-P coatings obtained at different temperatures ranges from 76.38-78.11% and 14.87-15.10%, respectively.

Table 1. Effect of electroless plating time on the surface compositions of Ni-P coatings

Element	5min		10min		15min		20min		25min	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Ni	74.88	46.67	78.57	55.06	77.71	55.09	77.12	53.75	77.62	54.62
P	11.48	13.56	12.86	17.07	14.88	20.00	14.51	19.16	14.32	19.09
C	11.31	34.43	6.81	23.32	6.54	22.64	6.70	22.83	6.38	21.95
O	2.33	5.33	1.77	4.54	0.87	2.27	1.66	4.25	1.68	4.34

Table 2. Effect of temperature on the surface compositions of Ni-P coatings

Element	70 °C		75 °C		80 °C		85 °C	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Ni	76.38	52.58	77.83	55.44	77.71	55.09	78.11	56.23
P	14.92	19.47	14.87	20.07	14.88	20.00	15.10	20.59
C	7.16	24.07	6.25	21.76	6.54	22.64	5.97	20.99
O	1.54	3.88	1.05	2.74	0.87	2.27	0.83	2.19

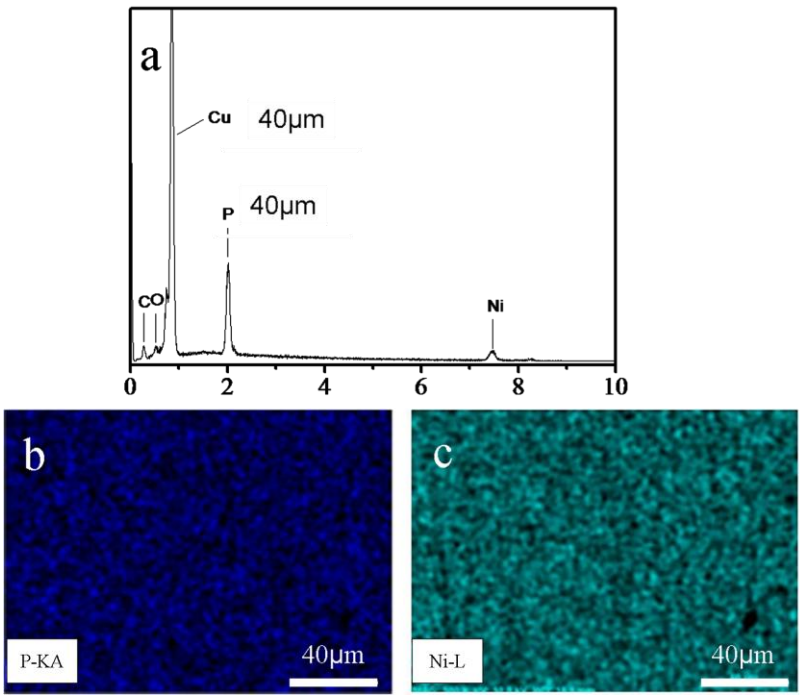

Figure 3. EDS spectra (a) and EDS mapping (b and c) of Ni-P coatings treated for 25 min

Fig. 3a shows the spectra of Ni-P coatings treated for 25min. It can be found that these Ni-P coatings are composed of Ni, P, C, O, and Cu. The presence of Ni and P can be attributed to the Ni plating process. Besides, the Ni-P coatings show an uniform distribution of Ni and P atoms, as shown by the EDS mapping images in Fig. 3b and Fig. 3c.

The chemical states of Ni and P on the Ni-P coatings were further determined using XPS. Fig.4 shows that Ni and P peaks can be clearly detected in the XPS spectra, thus indicating the formation of Ni-P coatings.

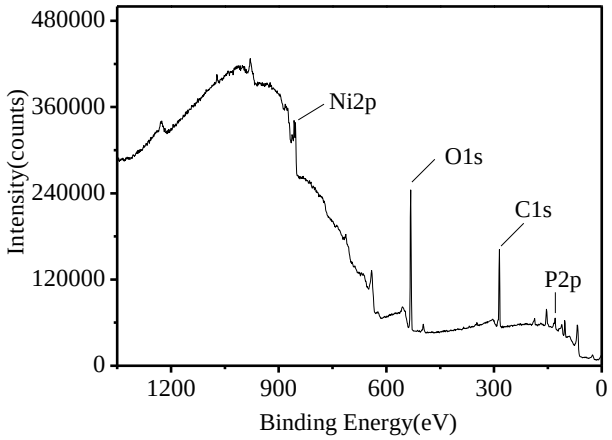

Figure 4. XPS spectra of Ni-P coating treated for 25min

The high-resolution spectra of Ni-P coatings deposited on the Cu substrate were also collected by XPS. Fig.5 shows the signals of P2p. The two peaks at 132.6 (2p3/2) and 133.3 eV (2p1/2) can be attributed to the presence of NaH_2PO_2 [20, 21]. The peak at 129.7eV can be assigned to P atoms in the bulk alloy, whose binding energy is very close to that of P in binary nickel phosphides [22]. The peak at 128.9eV can be attributed to P2p 1/2, which is identical to that of P atoms of Ni-P coating [23].

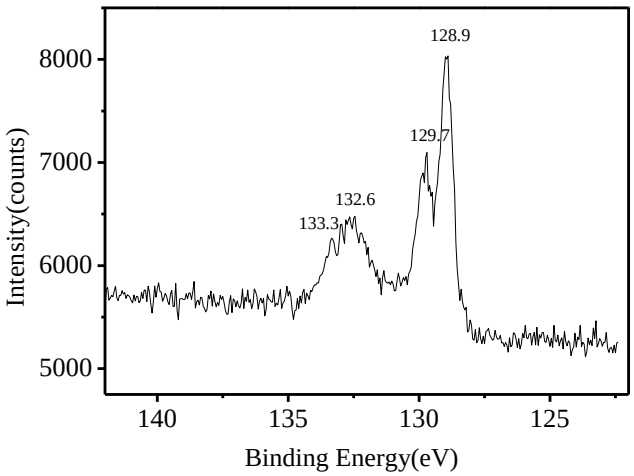

Figure 5. High resolution XPS P 2p spectra of electroless deposited Ni-P alloy

Fig. 6 shows the signals of Ni 2p. The peaks at 852.2 and 869.4eV can be attributed to metallic Ni 2p3/2 and 2p1/2, respectively [24]. The oxide/hydroxide state is observed at 855.9eV, with a shake-up satellite peak at 861.2eV [25]. The peak at 873.5eV is attributed to Ni_2O_3 [23].

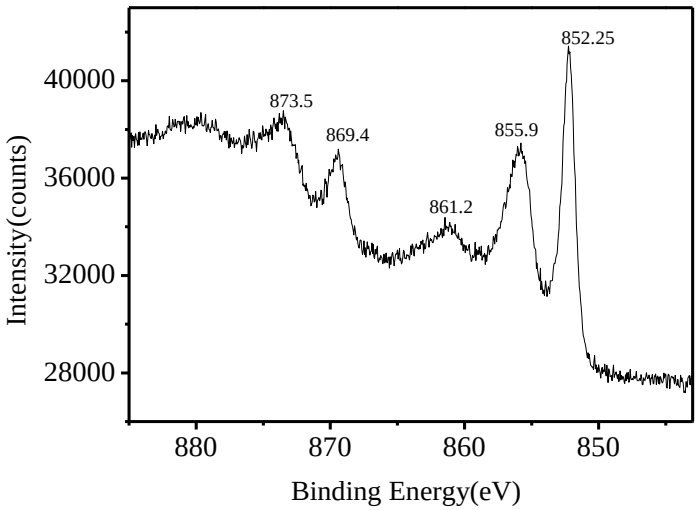

Figure 6. High resolution XPS Ni 2p spectra of electroless deposited Ni-P alloy

3.3. Corrosion resistance of Ni-P coatings

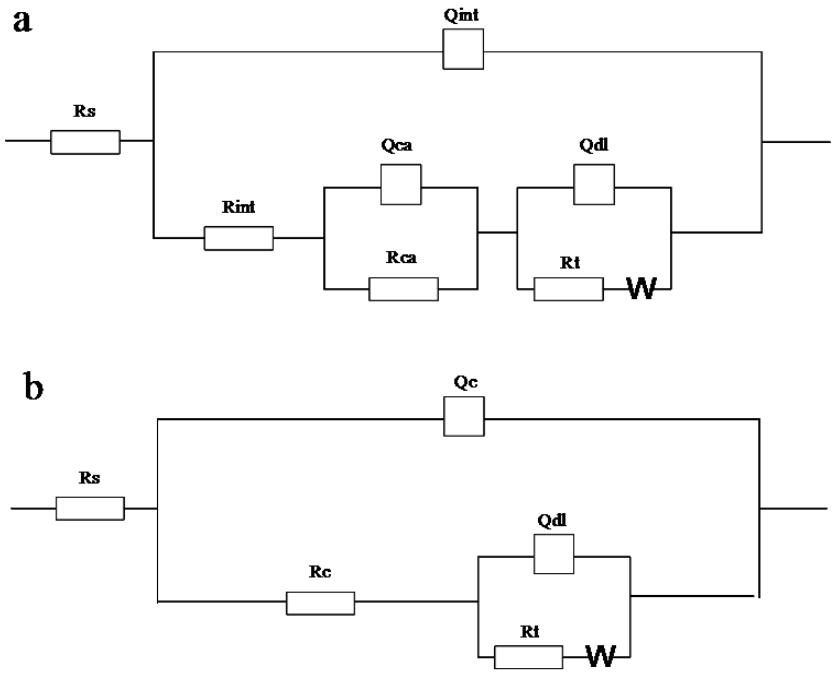

Figure 7. Equivalent circuits proposed for simulating the electrochemical response in NaCl for (a) untreated and (b) treated samples

The corrosion resistance of Ni-P coatings was evaluated by EIS measurements in 3.5% NaCl solution. Fig. 7a and 7b show the equivalent circuits used to represent the electrochemical response of untreated and treated samples. In Fig. 7a, Rs is the resistance of the electrolyte, Rint-Qint represents the reactions occurred around the intermetallics, Rca-Qca represents the response of the layer, Rt represents the loading transfer resistance, Qdl is the capacity of the double layer, and W is the Warburg diffusion resistance. In Fig. 7b, the Rint–Qint loop disappears, because the Ni-P coating can protect the Cu substrate and minimize the response corresponding to the intermetallics. The Rc–Qc loop represents the response of the mixed layer formed on Cu foil during the treatment.

The relationship between the circuits shown in Fig. 7a and Fig. 7b can be expressed as follows:

Qc = Qint + Qca

Rc = Rint + Rca

Fig. 8 shows the EIS characteristics of Ni-P coatings obtained at different temperatures, and the parameters obtained by fitting the experimental data to the equivalent circuit of Fig.7 using a software application are shown in Table 3. The nyquist diagram for different samples shows an arc of 75 °C > 80 °C > 85°C > copper >70 °C, indicating that the best corrosion resistance can be obtained at 75 °C. This is in agreement with the charge transfer resistance as the largest Rct is also obtained at 75 °C.

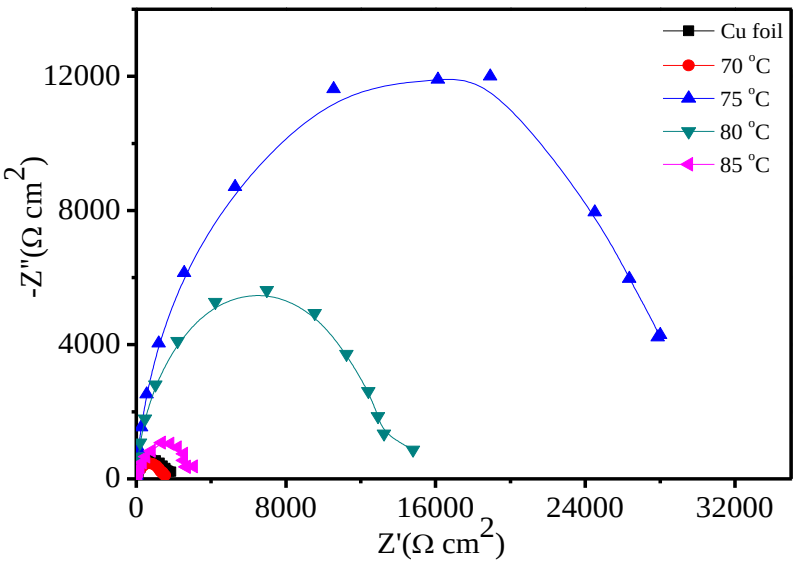

Figure 8. Nyquist curves in 3.5 % NaCl solution for Ni-plated Cu tabs obtained at different temperatures.

Table 3. Fitted parameters associated with the impedance diagrams for Ni-plated Cu tabs obtained at different temperatures.

	Rs (Ωcm^2)	Rc (Ωcm^2)	Rct (Ωcm^2)	Qc/Fcm^{-2}	Qdl/Fcm^{-2}	Error(%)
Untreated	3.114	11.96	1630	5.164E-5	1.244E-4	1.58
70°C	4.838	34.95	1358	6.938E-5	1.406E-4	2.13
75°C	4.821	0.02	26220	2.913E-5	4.972E-19	6.17
80°C	3.592	0.01	10230	1.034E-5	1.275E-5	4.17
85°C	3.175	238.00	2759	9.151E-5	1.013E-4	7.61

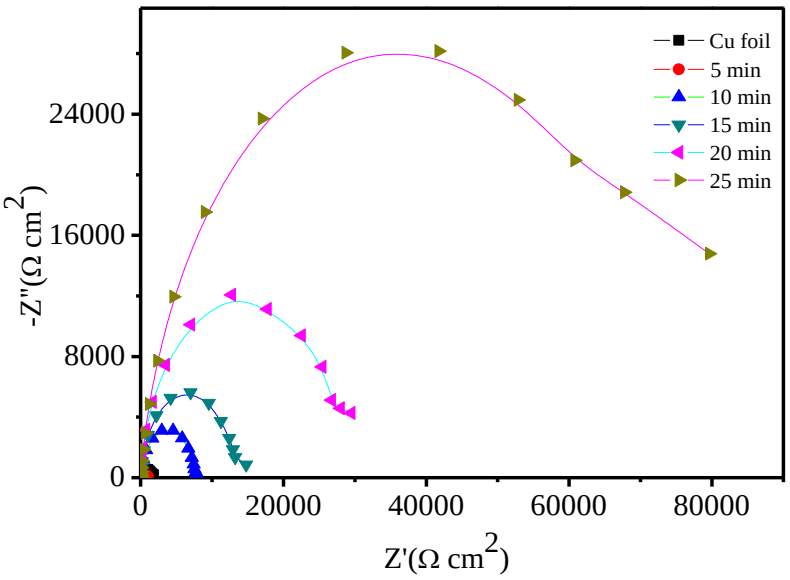

Figure 9. Nyquist curves in 3.5 % NaCl solution for Ni-plated Cu tabs treated at different times

Table 4. Fitted parameters associated with the impedance diagrams for Ni-plated Cu tabs treated for different times.

	Rs (Ωcm^2)	Rc (Ωcm^2)	Rct (Ωcm^2)	Qc/Fcm^{-2}	Qdl/Fcm^{-2}
Untreated	3.114	11.96	1630	5.164E-5	1.244E-4
5min	3.523	29.11	837	4.984E-5	1.581E-4
10min	4.549	6884.00	1016	1.224E-5	4.388E-4
15min	3.592	0.01	10230	1.034E-5	1.275E-5
20min	4.824	0.13	1855000	2.146E-5	3.852E-5
25min	4.923	34520.00	12020000	9.536E-6	3.124E-5

Fig.9 shows the EIS characteristics of Ni-P coatings treated for different times. The nyquist diagram shows an increasing arc with increasing time. The charge transfer resistance also shows a similar pattern, which increases from 837Ωcm^2 for sample treated for 5min to 12020000Ωcm^2 for sample treated for 25min. This is because the corrosion resistance of these samples increases with increasing thickness of Ni-P coatings, which is in turn increases with increasing treatment time.

At last, all samples were immersed in the electrolyte at 80 °C for 48h. The results show that none of these Ni-P coatings fall off or change in color, indicating that these samples have good electrolyte resistance.

4. CONCLUSIONS

In this study, Ni-P coatings have been successfully deposited on the Cu substrate by the electroless plating technique. The results show that treatment time and temperature have a significant

effect on the surface morphology and corrosion resistance of Ni-P coatings. These coatings are composed mainly of NaH_2PO_2, nickel phosphides, P, Ni, oxide/hydroxide, and Ni_2O_3. The Ni-P coating treated at 75 °C for 25min has the best corrosion resistance, and all Ni-P coatings have good electrolyte resistance.

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