



EFFECT OF MEAN DIAMETER SIZE OF DISPERSE PHASE ON MORPHOLOGY AND CORROSION RESISTANCE OF PHENOL – FORMALDEHYDE RESIN/Zn COATINGS

*Alina CIUBOTARIU¹, Lidia BENE¹, Pierre PONTIAUX²

¹"Dunarea de Jos" University of Galati,

Faculty of Environmental and Materials Engineering, Competences Center Interfaces – Tribocorrosion and Electrochemical Systems, 47, Domneasca Street, 80008, GALATI, Romania

²Ecole Centrale Paris, Laboratoire Genie de Procédés Matériaux Grand Voie des Vignes, 92290, Chatenay Malabry, France

*Corresponding author

email: Alina.Ciubotariu@ugal.ro

ABSTRACT

The present work has the purpose of obtaining composite coatings using phenol – formaldehyde (PF) resin electrodeposited with zinc. The phenol – formaldehyde resin/Zn coatings were electrodeposited from a suspension of PF resin particles with two dimensions for mean diameter size of particles (0.1 – 5.0 μm and 6 – 10 μm) in aqueous zinc sulphate electrolyte. Suspension was prepared by adding 10 g/L PF resin particles into solution. The thickness and morphology of the coatings were investigated by SEM method. By adding PF resin in zinc electrolyte for electrodepositing we obtained a very good distribution of PF resin particles on zinc surface. The electrochemical behavior of the layers in the corrosive solution was investigated by electrochemical methods. As electrochemical test solution 0.5M sodium chloride was used in a three electrode open cell. It was observed that by adding PF resin particles in zinc electrolyte for electrodeposition were obtained composite layers more resistant to corrosive attack of 0.5M NaCl than pure zinc obtained from electrodeposition at the same parameters for electrodeposition. Corrosion rate for pure zinc coatings was 72.05 $\mu\text{m}/\text{year}$ versus 15.34 $\mu\text{m}/\text{year}$ for coatings with mean diameter size of particles 0.1 – 5.0 μm , respectively 10.11 $\mu\text{m}/\text{year}$ for coatings with mean diameter size of particles 6 – 10 μm . Values of polarization resistance obtained with both electrochemical methods (potentiodynamic polarization and electrochemical impedance spectroscopy) were in a very good agreement.

KEYWORDS: phenol - formaldehyde resin particles, electrodeposition, coatings, coatings morphology, polarisation resistance

1. Introduction

The deterioration of metal and steel structures due to the atmospheric corrosion is one of the most serious problems in modern world, which leads to a loss of hundreds of billions of dollars each year [1]. Hence, it has become the main objective of material researchers to protect metal and steel against corrosion. In the latest years, composite coatings are regarded as one of the most effective materials to protect metal and steel against atmospheric corrosion.

Composite materials are material systems that consist of a discrete constituent (the reinforcement)

distributed in a continuous phase (the matrix) and that derive their distinguishing characteristics from the properties and behaviour of their constituents, from the geometry and arrangement of the constituents, and from the properties of the boundaries (interfaces) between the constituents.

Composites are classified either on the basis of the nature of the continuous (matrix) phase (polymer – matrix, metal – matrix, ceramic – matrix and intermetallic – matrix composites) or on the basis of the nature of the reinforcing phase (particle reinforced, fibre reinforced, dispersion strengthened, laminated etc.). The properties of the composite can

be tailored and new combinations of properties can be achieved [2].

Relevant work refers to some particles such as B₄C, CeO₂, graphite, TiO₂, ZrO₂, Al₂O₃, V₂O₅, SiO₂ – zinc reinforced system [3 – 10] while investigations regarding polymeric particles as disperse phase are relatively limited. To improve adherence and anti-corrosion behaviour of zinc, the existing few reports refer to composite zinc-coated steel, containing polymethylmethacrylate (PMMA), polystyrene (PS) or stabilized polymeric micelle (SPM; core-shell structures consisting of block co-polymers of polyethers) particles [11 – 13]. Recently it was reported that ultrahigh molecular weight polyethylene (UHMWPE) could be deposited in cobalt matrix [14].

Electrochemical deposition is a good method to obtain coatings with the advantage of low synthesis temperature, low costs and high purity in the product. This method also enables rigid control of film thickness, uniformity and deposition rate. Zinc electrodeposition is an industrial process and is widely used to coat on steel for enhancing its service life. The reason for the pre-eminence of zinc in the world of electrodeposition can be attributed to its relative readiness to deposition and better corrosion resistance [15 – 18].

The present work focuses on electrodeposition of PF resin particles (Novolac) with zinc from zinc sulphate plating bath. The thickness and surface morphology of the coatings were analyzed by SEM method. The corrosion resistance of composites coatings was estimated and compared to conventional zinc coating which used potentiodynamic polarization and impedance techniques.

2. Experimental part

Pure zinc and PF resin/Zn coatings were obtained on DC04 steel support from the bath solutions with the following composition: 310 g/L ZnSO₄ · 7H₂O; 75 g/L Na₂SO₄ · 10H₂O; 30 g/L Al₂(SO₄)₃ · 18H₂O. Zinc sulphate electrolyte has cathodic polarization bigger than zinc chloride electrolyte so that we used sulphate electrolyte for electrodeposition. Sodium sulphate increased the conductivity and ability for disperse and aluminium sulphate was used like buffering agent which stabilized the acidity of electrolyte. Concomitantly we obtain more shining layers.

The pH of the solution was 3.8. Deposition was carried out at current density of 3.0 A/dm², deposition time of 60 minutes and stirring rate of 800 rpm. Electrodeposition experiments were performed at room temperature.

The zinc metal plate with high purity and steel plates were employed as anode, respectively cathode. Before electrodeposition, steel plates were

mechanically polished, degreased with alkaline solution and washed with distilled water.

The PF resin/Zn coatings were electrodeposited from a suspension of PF resin particles type Novolac with commercial name Resital 6358/1 synthesized by Hüttenes - Albertus Germany in aqueous zinc sulphate electrolyte by adding 10 g/L PF resin particles with mean diameter size of 0.1 – 5.0 µm and 6.0 – 10.0 µm into bath solution.

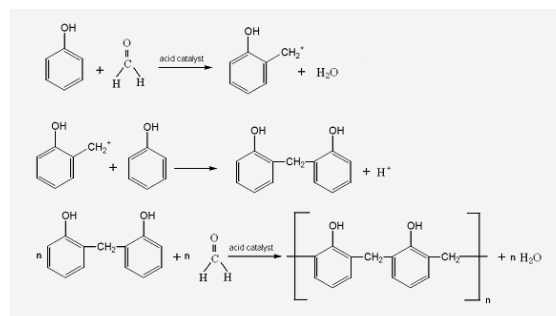


Fig. 1. Schematic illustrating the formation of the PF resin type structures

Phenol – formaldehyde resin is a thermo reactive polymer which become plastic with increased the temperature and lose his plasticity and become insoluble. PF resins type Novolac can be obtained from phenol and formaldehyde in acid medium (Figure 1).

Properties of phenol - formaldehyde resin used as disperse phase for electrodeposition are presented in Table 1.

Table 1. Properties of PF resin Resital 6358/1

Properties	Values
Molecular weight	3392 – 3816 g/mol
Melting point	70 – 80 °C
Viscosity at 120 °C	35 – 45Pa.s
Free phenol	< 1%
Water content	< 0.5 %
Not esterified	

The thickness and the morphology of deposits were examined by scanning electron microscopy (SEM) used a microscope type JEOL, JSM-T220 A.

For potentiodynamic polarization measurements it was used a three-electrode open cell with platinum electrode as counter, a mercury – mercurous sulphate electrode Hg/Hg₂SO₄/saturated K₂SO₄ as reference electrode (E = + 658 mV/NHE) and coatings as working electrode. Initial potential (I.P.) was -1.9V (Hg/Hg₂SO₄), final potential (F.P.) was - 1.2V (Hg/Hg₂SO₄) and a scan rate of 1.66mV/s.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed in the frequency range between 65 kHz – 0.1 Hz, with an AC sine wave amplitude of 10 mV, frequency per decade: 10 Hz and delay before integration 1s. The electrochemical corrosion tests were recorded after 30 min of immersion in corrosive medium 0.5M NaCl.

3. Results and discussions

3.1. SEM analysis

The thicknesses of pure zinc and PF resin/Zn coatings determined with scanning electron microscope are presented in Figure 2.

It could be observed that higher thickness is for pure zinc coatings and, by increasing the mean diameter size of resin particles the layers thickness increased. This can be explained, probably, because by adding disperse phase the morphology and uniformity of composite coating increase. A higher thickness for coatings with bigger mean diameter size of particles is possible because these particles do not uniform and compact coatings as much as resin with smaller mean diameter size.

Figures 3 - 5 compare morphological aspects of pure zinc coatings and PF resin/Zn coatings obtained with different mean diameter size of disperse phase under SEM method.

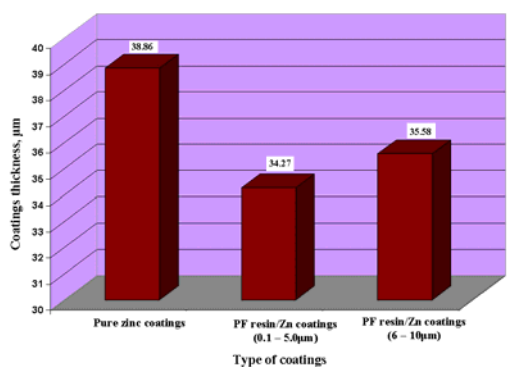


Fig. 2. Comparative thickness of coatings

As it can be seen from the micrographs there is an obvious and well distinguishable grain refinement in the presence of the polymer particles. So that the addition of PF resin particles in electrolyte bath significantly changes the morphology of the zinc deposits as compared to those obtained from solutions without disperse phase. The zinc coatings are made up of regular crystals. The polymer particles codeposit disorder the regular crystal structure of zinc coatings and zinc crystals becomes finely crystalline.

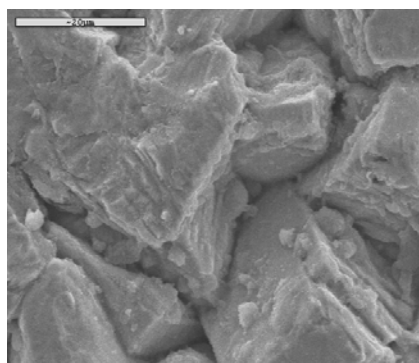


Fig. 3. SEM surface morphology of pure zinc coatings (x 2000)

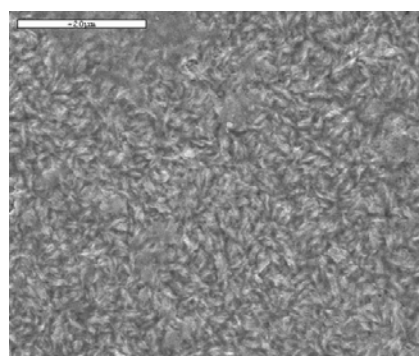


Fig. 4. SEM surface morphology of PF resin/Zn coatings with mean diameter size of PF resin 0.1 – 5.0 μm , (x 2000)

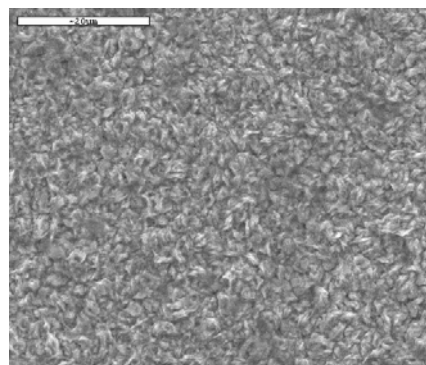


Fig. 5. SEM surface morphology of PF resin/Zn coatings with mean diameter size of PF resin 6 – 10 μm (x 2000)

The pure zinc coatings have a rather regular surface, whereas the composite coating surfaces have finer grains structure with particles of disperse phase uniformly distributed on the surfaces.

The polymer particles could be an inhibition effect of growing crystallite size of zinc.

3.1. Electrochemical measurements

The electrochemical investigation of each sample began with monitoring of the open circuit potential change immediately after the immersion into the testing solution till reaching a relatively stable stationary value (Figure 6).

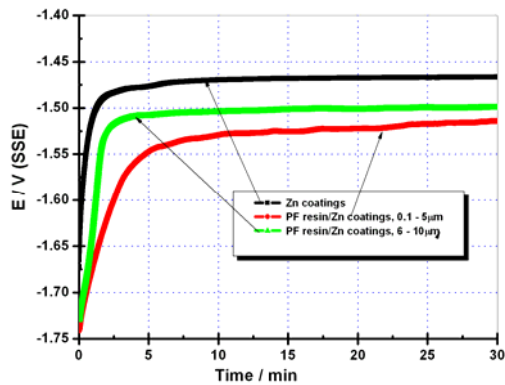


Fig. 6. Variation of the coatings potential function of time in 0.5M NaCl

From the dependence of potential function time it can be concluded that the tested samples are stable after 10 - 15 minutes from immersion in test solution.

The polarisation curves for coatings in 0.5M NaCl after 30 minutes from immersion are presented in Figure 7.

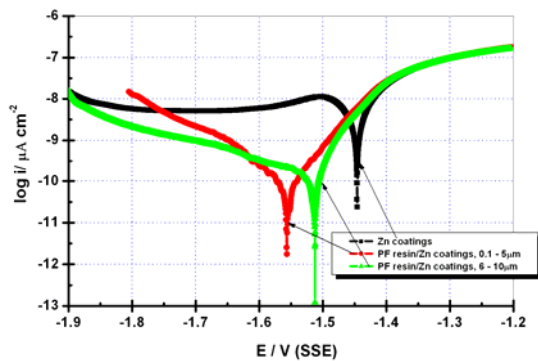


Fig. 7. Potentiodynamic polarisation data for coatings immersed in 0.5 M NaCl solution obtained after 30 minutes from immersion time (log scale)

Quantitative information on corrosion currents density and polarisation resistance can be extracted from the slope of the curves, using the Stern-Geary equation [19].

$$i_{corr} = \frac{1}{2.303R_p} \left(\frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c} \right) \quad (1)$$

Tafel parameters derived from Figure 7 using Tafel extrapolations are presented in Table 2.

Corrosion rates (CR) were calculated by equation (2):

$$CR(\mu\text{m}/\text{year}) = \frac{0.051 \cdot i_{corr} \cdot (E_q \cdot \text{wt.})}{d} \quad (2)$$

where: i_{corr} – corrosion current density calculated from Stern – Geary equation; $(E_q \cdot \text{wt.})$ is the equivalent weight and d is the density of the zinc metal in g/cm^3 .

The corrosion potential is shifted to more negative values for PF resin/Zn coatings than corrosion potential for pure zinc coatings.

From experimental data it was observed that polarisation resistance has a small value for pure zinc coatings ($34.54 \Omega \cdot \text{cm}^2$), a bigger value for PF resin/Zn composite coatings with mean diameter size of particles $0.1 - 5 \mu\text{m}$ ($238.75 \Omega \cdot \text{cm}^2$) and the biggest value for PF resin/Zn composite coatings with mean diameter size of particles $6 - 10 \mu\text{m}$ ($336.32 \Omega \cdot \text{cm}^2$). The values of corrosion rate calculated with formula (2) were: for pure zinc coatings $72.05 \mu\text{m}/\text{year}$ and for composite coatings $15.34 \mu\text{m}/\text{year}$, respectively $10.11 \mu\text{m}/\text{year}$.

Those parameters presented before indicated a good corrosion resistance of PF resin/Zn coatings in 0.5 M NaCl.

Figure 8 shows the Nyquist plots of zinc and PF resin/Zn composite coatings measured in 0.5M NaCl solution after 30 min from immersion in corrosive environment.

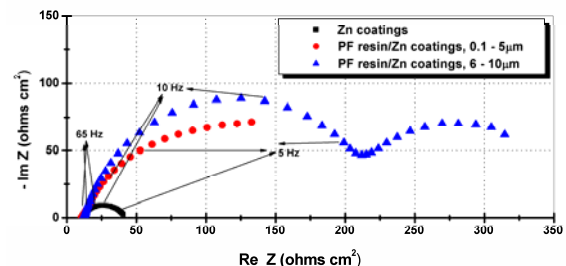


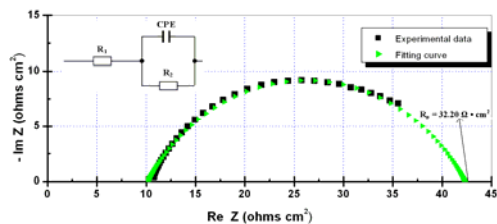
Fig. 8. Nyquist plots for pure zinc and PF resin/Zn coatings in 0.5M NaCl after 30 min from immersion

The fitting data of Nyquist plots for coatings are presented in Figure 9 (a - c).

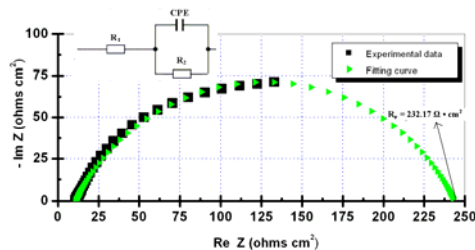
Table 2. Tafel parameters of pure zinc and composite coatings calculated from polarization potentiodynamic curves obtained after 30 min from immersion in solutions

Type of coatings	E_{corr} , V; vs SSE	i_{corr} , $\mu\text{ A/cm}^2$	β_a , mV/dec	β_c , mV/dec	R_p , $\Omega\cdot\text{cm}^2$	CR, $\mu\text{m/year}$
Zinc	- 1.45	152.75	28.76	21.04	34.54	72.05
PF resin/Zn coatings (mean diameter size of particles 0.1 – 5 μm)	- 1.53	32.52	38.02	33.77	238.75	15.34
PF resin/Zn coatings (mean diameter size of particles 6 – 10 μm)	- 1.51	21.44	20.98	79.60	336.32	10.11

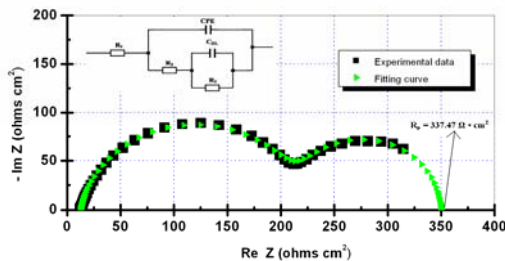
Two equivalent electrical circuits were proposed to account for the experimental impedance spectra. Those circuits allow obtaining an excellent agreement between experimental and simulated impedance plots.



(a)



(b)



(c)

Fig. 9. Nyquist plot of impedance spectrum of experimental data and fitting curve for: (a) pure zinc coatings; (b) Zn/PF resin coatings (0.1 – 5.0 μm); (c) Zn/PF resin coatings (6 – 10 μm) in 0.5M NaCl solution after 30 min of immersion

The fitting values confirmed that the incorporation of polymer particles enhances the corrosion resistance of composite coating samples. The polarization resistance obtained from fitting curve indicates a small value for pure zinc coating ($32.20 \Omega\cdot\text{cm}^2$) versus polarization resistance of composite coatings ($232.17 \Omega\cdot\text{cm}^2$, respectively $337.47 \Omega\cdot\text{cm}^2$).

It was observed that a good polarization resistance has PF resin/Zn composite coatings with mean diameter size of polymer particles 6 – 10 μm ; the value of polarization resistance for this type of coatings is about ten times bigger than the polarization resistance of pure zinc coatings.

Electrochemical measurements concluded that by adding PF resin particles in zinc electrolyte solution from electrodeposition it was obtained PF resin/Zn coatings more resistant to corrosive attack in 0.5M NaCl solution than pure zinc obtained by electrodeposition using the same parameters.

4. Conclusions

PF resin/Zn coatings was successfully deposited from solution containing 10 g/L PF resin particles with mean diameter size of particles 0.1 – 5.0 μm and 6.0 – 10.0 μm .

The coatings thickness for composite coatings is less than the thickness of pure zinc coatings because the resin particles increase the uniformity of the layers and decrease the grain size of zinc crystals.

PF resin particles affect the electrodepositing process of zinc coatings by changing the morphology of the surfaces of composite coatings versus pure zinc obtained at the same electrodeposition parameters.

From electrochemical measurements it was observed that by adding PF resin particles in zinc electrolyte it was obtained PF resin/Zn coatings more resistant to corrosive attack in 0.5M NaCl solution than pure zinc coatings.



The results confirm that the disperse phase introduced in electrolyte bath has an obvious corrosion inhibition effect on the resulted composite surfaces.

References

- [1]. H.Y. Li, J.Y. Duan, D.D. We - *Comparison on corrosion behaviour of arc sprayed and zinc-rich coatings*, Surface & Coatings Technology, 235, (2013), pp. 259 – 266.
- [2]. R. Asthana, A. Kumar, N. B. Dahotre, Materials Processing and Manufacturing Science, Edited by Butterworth-Heinemann, London, (2006).
- [3]. C. M. Praveen Kumar, T. V. Venkatesha, K.G. Chandrappa - *Effect of surfactants on co-deposition of B₄C nanoparticles in Zn matrix by electrodeposition and its corrosion behavior*, Surface and Coatings Technology, 206, (2012), pp. 2249–2257.
- [4]. S. Ranganatha, T.V. Venkatesha, K. Vathsala, M.K. Punith Kumar - *Electrochemical studies on Zn/nano-CeO₂ electrodeposited composite coatings*, Surface and Coatings Technology, 208, (2012), pp. 64–72.
- [5]. H. B. Muralidhara, Y. Arthoba Nayaka, J. Balasubramanyam, K. Yogesh Kumar, H. Hanumanthappa, M.S. Veena - *Electrodeposition of Zn-Graphite nanoparticles composite and their characterization*, Journal of Chemical and Pharmaceutical Research, 4, (2012), pp. 440–449.
- [6]. T. Frade, V. Bouzon, A. Gomes, M. I. da Silva Pereira - *Pulsed-reverse current electrodeposition of Zn and Zn-TiO₂ nanocomposite films*, Surface and Coatings Technology, 204, (2010), pp. 3592–3598.
- [7]. B. M. Praveen, T. V. Venkatesha - *Electrodeposition and properties of Zn-nanosized TiO₂ composite coatings*, Applied Surface Science, 254, (2008), pp. 2418–2424.
- [8]. K. Vathsala, T. V. Venkatesha - *Zn-ZrO₂ nanocomposite coatings: Electrodeposition and evaluation of corrosion resistance*, Applied Surface Science, 257, (2011), pp. 8929–8936.
- [9]. O. Sancakoglu, O. Culha, M. Toparli, B. Agaday, E. Celik - *Co-deposited Zn-submicron sized Al₂O₃ composite coatings: production, characterization and micromechanical properties*, Materials And Design, 32, (2011), pp. 4054–4061.
- [10]. S. Bindiya, S. Basavanna, Y. Arthoba Naik - *Electrodeposition and corrosion properties of Zn-V₂O₅ composite coatings*, Journal of Materials Engineering and Performance, 21, (2012), pp. 1879–1884.
- [11]. M. Azizi, W. Schneider, W. Plieth - *Electrolytic co-deposition of silicate and mica particles with zinc*, Journal Solid State Electrochemistry, 9, (2005), pp. 429–437.
- [12]. D. Vasilakopoulos, M. Bouroushian - *Electrochemical codeposition of PMMA particles with zinc*, Surface and Coatings Technology, 205, (2010), pp. 110–117.
- [13]. O. Kammona, K. Kotti, C. Kiparissides, J. P. Celis - *Synthesis of polymeric and hybrid nanoparticles for electroplating applications*, Journal Electrochimica Acta, 54, (2009), pp. 2450–2457.
- [14]. D. Koleva, N. Boshkov, G. Raichevski, L. Veleva - *Electrochemical corrosion behaviour and surface morphology of electrodeposited zinc, zinc-cobalt and their composite coatings*, Transactions of the Institute of Metal Finishing, 83, (2005), pp. 188–193.
- [15]. L. Benea, M. Mardare-Prlea - *Electrodeposition of UHMWPE particles with cobalt for biomedical applications*, Digest Journal of Nanomaterials and Biostructures, 6, (2011), pp. 1025 – 1034.
- [16]. J. Morales, L. Sanchez, S. Bijani, L. Martinez, M. Gabas, J. R. Ramos-Barrado - *Electrodeposition of Cu₂O: An excellent method for obtaining films of controlled morphology and good performance in Li-ion batteries*, Electrochemical and Solid State Letters, 8, (2005), pp. A159 – A162.
- [17]. V. Georgieva, M. Ristov - *Electrodeposited cuprous oxide on indium tin oxide for solar applications*, Solar Energy Materials and Solar Cells, 73, (2002), pp. 67–73.
- [18]. Z. Quan, S. Ohguchi, M. Kawase, H. Tanimura, N. Sonoyama - *Preparation of nanocrystalline LiMn₂O₄ thin film by electrodeposition method and its electrochemical performance for lithium battery*, Journal of Power Sources, 244, (2013), pp. 375–381.
- [19]. J. Xue, Q. Shen, W. Liang, X. Liu, L. Bian, B. Xu - *Preparation and formation mechanism of smooth and uniform Cu₂O thin films by electrodeposition method*, Surface and Coatings Technology, 216, (2013), pp. 166–171.
- [20]. M. Stern, A. Geary - *Electrochemical polarization I. A theoretical analysis of the shape of polarization curves*, Journal Electrochemical Society, 104, (1957), pp. 56–63.