

Electrochemistry and vibrational spectroscopy in investigation of protective coatings for bronze artworks

Angelja K. Surca¹, Mohor Mihelčič²

¹ *National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia*
angelja.k.surca@ki.si, mohor.mihelcic@ki.si

Abstract – Herein are discussed the possibilities of how to exploit vibrational spectroscopic and electrochemical techniques in the studies of protective coatings for bronze artworks. Protective coatings for bronze 85,555 are prepared on the basis of polyurethanes or fluoropolymers. Reflection-absorption infrared spectroscopy under near grazing conditions is described as a powerful tool for studying the bronze surfaces when exposed to various conditions (solutions, strippers, temperature). Electrochemical techniques, especially the potentiodynamic polarization technique, are very powerful in the evaluation of protective coatings. The combination of electrochemical and spectroscopic techniques enables the tracking of changes in the protective coating that occur with an increase in the anodic potential. This is an accelerated test and similar changes are expected to occur in the protective coatings with time, i.e., exposure to atmospheric conditions (rain, humidity ...). Various solutions were also tested as strippers to evaluate the removability of the coatings.

I. INTRODUCTION

Investigating protective coatings for bronze artworks is not straightforward. Such coatings have to comply with conservation ethics and regulation to both (i) act as adequate protection and (ii) be removable from the artwork [1,2]. Moreover, the coatings should be transparent and allow easy application to the object. Since bronze monuments are often outdoors, the coatings must not be soluble in water-rain, they should withstand pollutants and particles from the atmosphere and as well as temperature changes. With the eyes of a classic protective coating researcher, such requirements seem contradictory, since a classic corrosion protective coating should adhere perfectly to the substrate and be dense and impermeable to atmospheric moisture and other species. Finally, it is difficult to compete with the existing wax and Incralac coatings [2-4] currently used to protect bronze artworks; both serve a purpose although they need

to be renewed regularly. Organic coatings on the basis of benzotriazole derivatives are also studied [4-6].

In recent decades, some attempts have been made to investigate also other polymer coatings for protection of bronze [1,2,7-13]. Specifically, the knowledge gained about the molecular design of polymers in the last two decades has pushed the investigation of polyurethanes [1,7], fluoropolymers [2,8,9] and siloxanes [10-13] a little further. For example, by adding inorganic building blocks to organic networks to improve the protective characteristics of coatings [14-18]. Concurrently with the investigations of such polymer coatings, also the techniques, usually applied in the investigation of corrosion protective coatings were transferred to the field of artworks protection.

Herein, we aimed to present some techniques that can be applied in investigation of polymer protective coatings for bronze artworks. Among the electrochemical techniques, potentiodynamic polarization technique [4,6-9] is the easiest to use, while the electrochemical impedance spectroscopy [3,7,9] requires more skills. Near Grazing Incidence Angle (NGIA) reflection-absorption infrared (RA IR) spectroscopy is appropriate for surface investigations and adsorption studies. Moreover, it can be coupled with electrochemical techniques to study the degradation of protective coatings. Examples of such investigations are described on polyurethane-based coatings that have been studied for application to bronze surfaces.⁷

II. EXPERIMENTAL

A. Preparation of materials

Bronze discs with thickness of 5 mm were cut from 85,555 bronze rod with a diameter of 3 cm (Casa Del Bronzo Srl foundry, Brescia, Italy).

A custom-made stripper was prepared from benzyl alcohol, tetraethylene glycol and Triton X100. A commercial Hempel stripper was also tested, consisting of 1,3-dioksolane and dimethoxymethane in isopropanol and methanol alcohols and oil.

The basis of commercial Incralac (Art. 56171,

Bresciani) is the acrylic resin Paraloid B-44 with the addition of benzotriazole corrosion inhibitor. 2.4 g of Inccralac was diluted in 1.6 g toluene and spin-coated onto bronze disc.

Polyurethane-based coatings were prepared according to preparation procedure in Fig. 1. The resin used was Duroftal VPI 2803/78 BAC purchased at Allnex company [7]. A hexamethylene diisocyanate (HDI)-based polyisocyanate hardener produced by Covestro was applied to start the reaction of polymerization. The additive trisilanol-heptaisooctyl-POSS was used with the aim to improve the protective efficiency of the coatings [14-18].

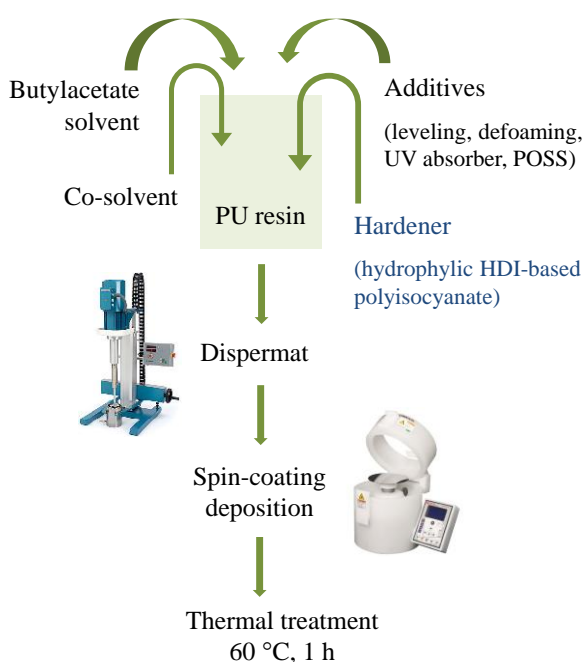


Fig. 1. Schematic presentation of the preparation procedure of polyurethane-based coatings.

B. Instrumental

Reflection-absorption infrared (RA IR) spectroscopic measurements were performed on a Bruker IR spectrometer IFS 66/S. Near Grazing Incidence Angle (NGIA) conditions were achieved using specular reflectance accessory (Specac). All spectra are shown as measured, without background correction or any other manipulation.

Potentiodynamic polarization curves were measured on an Autolab potentiostat-galvanostat PGSTAT 302N. A flat cell K0235 obtained from Princeton Applied Research was filled with a 0.5 M NaCl electrolyte.

III. NEAR GRAZING INCIDENCE ANGLE (NGIA) REFLECTION-ABSORPTION INFRARED (RA IR) SPECTROSCOPY

Reflection-absorption IR spectroscopy under near grazing conditions is commonly used to investigate thin films on reflecting substrates. The underlying theoretical background is thoroughly described and can be found elsewhere [19,20]. Herein, the practical applicability of this technique is considered, and a schematic presentation of the measurement is depicted in Fig. 2.

Bronze is a reflective substrate, which makes it suitable for IR RA measurements. It is possible to either follow changes of the bronze surface itself or changes in protective coatings on bronze. The measurement is performed under near grazing conditions relative to the bronze surface, for example 80° (Fig. 2). The incidence beam is P-polarized, which means that only those vibrations, whose dipole moment vibrates perpendicular to the bronze surface appear in the spectra [19,20]. Bands in RA IR spectra appear as so-called longitudinal optical (LO) modes, the wavenumbers of which are somewhat shifted relative to the transversal optical (TO) modes (which usually appear in transmittance IR spectra). These shifts can be negligible for organic compounds, but can reach more than 100 cm^{-1} for inorganic materials. Assigning LO modes is therefore not straightforward but requires calculations and experience.

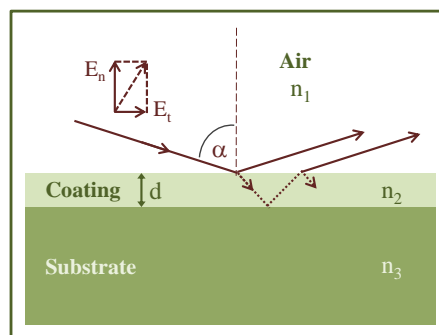


Fig. 2. Schematic presentation of beams during RA IR measurements under near grazing conditions.

An example of IR RA measurements [7] is the examination of what changes occur on the surface of bronze discs if they are soaked for 1 day in various solutions (Fig. 3). These solutions were tested as possible candidates for the removal of polymer protective coatings. The results in Fig. 3 clearly reveal that neither the custom-made stripper nor Hempel stripper made any changes to the surface of the bronze disc. However, water caused hydroxylation of the surface, which is recognizable by the appearance of bands at 3340 and 1080 cm^{-1} [21]. In addition, the formation of CuO_2 became recognizable by the formation of a low-intensity

band at 621 cm^{-1} . This value is close to the wavenumbers assigned to LO of CuO_2 in the literature, ranging from 640 cm^{-1} [22] to $627\text{-}619\text{ cm}^{-1}$ [23] and 617 cm^{-1} [24].

The soaking of bronze in 0.1 M NaOH , however, led to an even greater change in the surface of bronze compared to water. The presence of carbonates is notable from the bands at 1496 , 1375 and 883 cm^{-1} , originating either from the alkaline solution or the atmosphere. Hydroxylation is less prominent compared to soaking in water, but the low-intensity bands at 3320 and 1062 cm^{-1} can be observed. The shoulder at 645 cm^{-1} may indicate the presence of CuO_2 [22-24], while the bands at 1682 and 687 are close to the water bands. Consistently with the NGIA RA IR technique, the bands at lower wavenumbers are pronounced relative to the bands at higher wavenumbers.

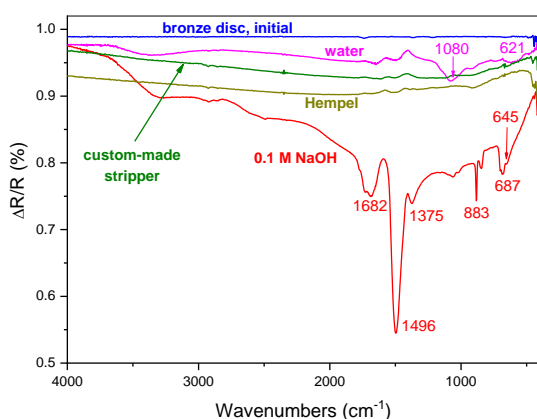


Fig. 3. RA IR measurements of a bronze surface under near grazing conditions after exposure to different solutions for 1 day.

The conclusion of the RA IR measurements can be that custom-made and commercial Hempel strippers do not alter the surface of the bronze and, therefore, can be tested as a solution for removing protective coatings on bronze.

RA IR technique can also be used to study the thermal behavior of bronze, i.e., to determine the temperature at which oxidation of bronze occurs [8]. In this study (Fig. 4), bronze was consecutively exposed to increasing temperatures for 30 min. At 150 °C , a band at 648 cm^{-1} appeared that could be assigned – as already mentioned – to the CuO_2 compound [7,22-24]. The intensity of this band increased significantly if thermal treatment continued at higher temperatures. On the other hand, thermal treatment of protective coatings at lower temperatures, for example 60 or 80 °C , did not change the structure of the bronze disc.

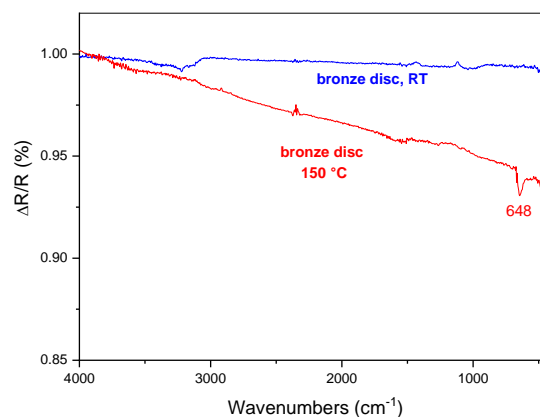


Fig. 4. RA IR measurements of the bronze surface under near grazing conditions during thermal treatment. RT – room temperature.

IV. POTENTIODYNAMIC POLARIZATION TECHNIQUE

The potentiodynamic polarization technique is a reasonably fast measurement. It is a relative technique that enables the comparison of protective coatings when measurements are made under the same conditions. It has already been applied in investigation of protective coatings for bronze [4,6-9].

The electrochemical cell consists of three electrodes, of which the working electrode (WE) is the protective coating on bronze (Fig. 5A). The counter electrode is a platinum grid that conduits the current from the WE. $\text{Ag/AgCl/KCl}_{\text{sat}}$ is used as a reference electrode. The coating is first exposed to an open circuit potential (30 min), followed by linear sweep voltammetry with a very slow scan rate, for example, 1 mV/s or even less. The starting potential of this sweep is set $200\text{-}300\text{ mV}$ below the open circuit potential (OCP), at which cathodic and anodic currents (j_c and j_a) are equal. The sweep then continues towards more positive potentials. The resulting current (j) vs. potential (E) measurement is presented as $\log(j)$ vs. E . Such presentation, when calculated per 1 cm^2 area, clearly indicates the current density at OCP (j_0) which is a measure of protective efficiency of the coating. As well, the lowering of cathodic and anodic current with regard to the response of the bronze is a measure of the good protection offered by the coating. The lower the j_0 and cathodic, anodic currents, the more effective is the protective coating.

This technique is widely used in the field of corrosion protection but not in the field of cultural heritage. The reason also lies in the special requirements for protective coatings of artworks, for instance, the water solubility of protective coatings for indoor bronze objects.

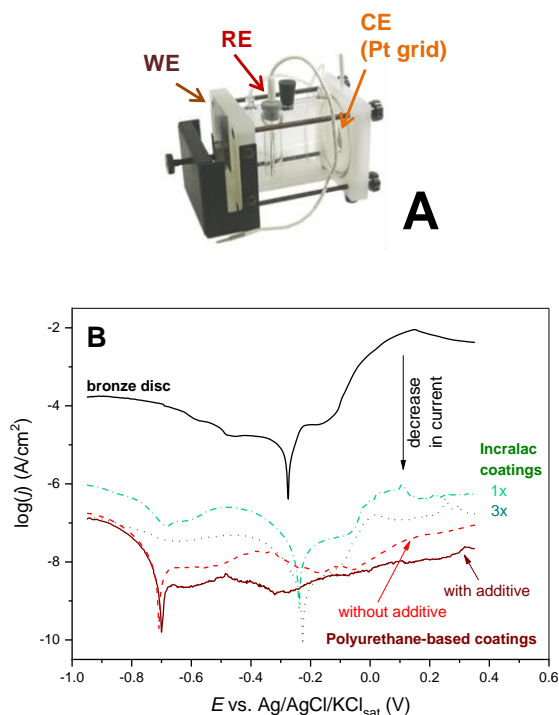


Fig. 5. A) Flat cell used for potentiodynamic polarization measurements. B) Potentiodynamic polarization curves of polyurethane- and Incralac-based coatings with regard to the response of the uncoated bronze disc.

An example of potentiodynamic polarization measurements [7] is shown in Fig. 5B. The cathodic current of bronze is of the order of magnitude 10^{-4} A/cm². The protective coatings diminished the cathodic current to the range of 10^{-7} – 10^{-6} A/cm². The anodic current of the coatings further revealed that the polyurethane-based coating with added silsesquioxane achieved the best efficiency, followed by the polyurethane-based coating without additive. Incralac coatings are somewhat less efficient, but their efficiency depends on the thickness. A coating prepared with 3x depositions performs better.

V. EX-SITU RA IR SPECTROELECTROCHEMISTRY

The third approach that can provide important insight into the behavior of protective coatings is ex-situ RA IR spectroelectrochemistry [7-9]. This technique is a combination of electrochemical and spectroscopic measurements. The protective coating on the bronze is first electrochemically treated at increasing potentials and after each step (potential increase) the RA IR spectrum is measured under grazing conditions. Treatment in the

electrochemical cell is carried out using the chronocoulometric technique, i.e. holding of the sample (WE) at a constant potential.

Ex-situ RA IR spectroelectrochemical measurements of polyurethane-based coatings did not reveal mayor differences in RA IR spectra at the first glance [7]. However, the direct comparison of the initial spectrum of this coating with the spectrum of the most polarized one showed the hydration (Fig. 6). It is evident from the increase in the intensity of the broad band between 3600 – 3000 cm⁻¹. A slight decrease in the intensity of the polyurethane bands was observed for the coating with the silsesquioxane additive, indicating slight dissolution of this coating. A somewhat more pronounced decrease in the intensity of polyurethane bands was noted for the polyurethane-based coating without additive. This shows that the coatings without additive were much more prone to dissolution during the ex-situ experiment. Such a finding confirmed the beneficial influence of the silsesquioxane additive. It might be good to point out again that the spectra are shown as they were measured. We did not do any background correction or any other manipulations in order not to affect the intensity and positions of the bands.

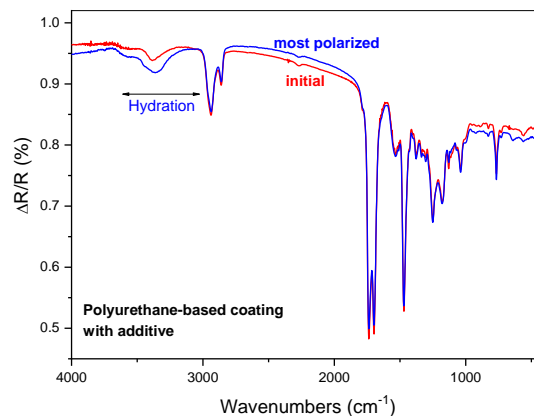


Fig. 6. Ex-situ RA IR measurements of a polyurethane-based coating with silsesquioxane additive. The spectra of coating in the initial state and in the most polarized state (0.8 V vs. Ag/AgCl/KCl_{sat}) are shown.

The gradual removal of the coating in 0.1 M NaCl electrolyte is not surprising. Due to the ethic in the protection of artworks, the coatings need to be removable. For this reason, they have been designed in such a way, to allow removal with strippers. Fig. 7 depicts the bronze disc with drops of custom-made stripper and water. After the drops have been wiped off, it can be seen that the stripper has removed the coating but water has not. Anyway, prolonged exposure of the

coating to the electrolyte, as well as manipulation of the coating during transfer from the electrochemical cell to the sample compartment of the IR spectrometer and back, resulted in gradual dissolution of the coating.

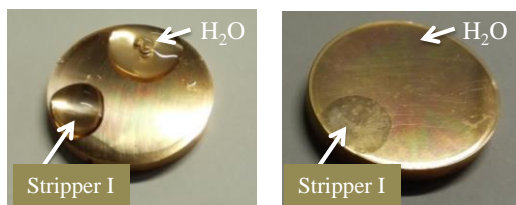


Fig. 7. Testing the removal of a polyurethane-based coating using a custom-made stripper and water.

VI. CONCLUSIONS

Our purpose in this report was to describe the electrochemical and spectroscopic techniques that can be used in research on protective coatings for bronze. RA IR measurements under near grazing conditions are very valuable in investigation of surfaces. It can give answers whether some oxides, hydroxides or other species formed/adsorbed on the bronze surfaces.

The potentiodynamic polarization technique can provide quick comparisons of different protective coatings. However, the measurement must be made under the same conditions.

Spectroelectrochemistry is a combination of electrochemical and spectroscopic techniques. Such measurements reveal the changes in protective coatings that would develop upon their prolonged exposure to atmospheric conditions.

VII. ACKNOWLEDGEMENTS

The study of polymer protective coatings for bronze artworks received funding from the European Union's Horizon 2020 research and innovation programme, No. 646063 Grant agreement (NANOMaterials for the RESToration of works of ART). Special thanks to Gabriella Di Carlo and Marino Lavorgna for assisting us with commercial Incralac and bronze products. The use of electrochemical and vibrational spectroscopic techniques in investigation of protective coatings has been investigated and upgraded throughout various projects such as L2-5484 and J1-4401 and programme P2-0393, funded by the Slovenian Research Agency.

VIII. CITATIONS AND REFERENCES

[1] T.J. Shedlosky, A. Huovinen, D. Webster, G. Bierwagen, "Development and evaluation of removable protective coatings on bronze", Proc. Met. 2004, National Museum of Australia Canberra

- ACT, Canberra, 2004, pp. 400-413.
- [2] G. Bierwagen, T.J. Shedlosky, K. Stanek, "Development and testing a new generation of protective coatings for outdoor bronze sculpture", Prog. Org. Coatings, 2003, vol. 48, pp. 289-296.
- [3] N.A. Swartz, T.L. Clare, "Understanding the differences in film formation mechanisms of two comparable solvent based and water-borne coatings on bronze substrates by electrochemical impedance spectroscopy", Electrochim. Acta, 2012, vol. 62, pp. 199-206.
- [4] T. Kosec, A. Legat, I. Milošev, "The comparison of organic protective layers on bronze and copper", Prog. Org. Coatings, 2010, vol. 69, pp. 199-206.
- [5] K. Rahmouni, H. Takenouti, N. Jajjaji, A. Srhiri, L. Robbiola, "Protection of ancient and historic bronzes by triazole derivatives", Electrochim. Acta, 2009, vol. 54, pp. 5206-5215.
- [6] G. Brunoro, A. Frignani, A. Colledan, C. Chiavari, "Organic films for protection of copper and bronze against acid rain corrosion", Corros. Sci., 2003, vol. 45, pp. 2219-2231.
- [7] M. Mihelčič, M. Gaberšček, G. Di Carlo, C. Giuliani, M. Salzano de Luna, M. Lavorgna, A.K. Surca, "Influence of silsesquioxane addition on polyurethane-based protective coatings for bronze surfaces", Appl. Surf. Sci., 2019, vol. 467-468, pp. 912-925.
- [8] M. Mihelčič, L. Slemenik Perše, E. Šest, I. Jerman, C. Giuliani, G. Di Carlo, M. Lavorgna, A.K. Surca, "Development of solvent- and water-borne fluoropolymer protective coatings for patina-gree bronze discs", Prog. Org. Coatings, 2018, vol. 125, pp. 266-278.
- [9] M. Mihelčič, M. Gaberšček, M. Salzano de Luna, M. Lavorgna, C. Giuliani, G. Di Carlo, A.K. Surca, Mater. Design, 2019, vol. 178, pp. 107860.
- [10] E. Bescher, J.D. Mackenzie, "Sol-gel coatings for the protection of brass and bronze", J. Sol-Gel Sci. Technol., 2003, vol. 26, pp. 1223-1226.
- [11] F. Zucchi, "Sol-gel coatings for the preservation of metallic heritage artefacts". In: "Conservation of cultural heritage metallic artefacts, Woodhead Publishing Limited, Oxford, 2013, pp. 540-551.
- [12] C. Chiavari, A. Balbo, E. Bernardi, C. Martini, F. Zanotto, I. Vassura, M.C. Bignozzi, C. Monticelli, "Organosilane coatings applied on bronze: influence of UV radiation and thermal cycles on the protectiveness", Prog. Org. Coatings, 2015, vol. 82, pp. 91-100.
- [13] E. Kiele, J. Senvaitiene, A. Griguceviciene, R. Ramanauskas, R. Raudonis, A. Kareiva, "Application of sol-gel method for the conservation of copper alloys", Microchem. J., 2016, vol. 124, pp. 623-628.
- [14] G. Kickelbick, "Concepts for the incorporation of

- inorganic building blocks into organic polymers on a nanoscale”, *Prog. Polym. Sci.*, 2003, vol. 28, pp. 83-114.
- [15] A.K. Nanda, D.A. Wicks, S.A. Madbouly, J.U. Otaigbe, “Nanostructured polyurethane/POSS hybrid aqueous dispersions prepared by homogeneous solution polymerization”, *Macromolecules*, 2006, vol. 39, pp. 7037-7043.
- [16] H. Honarkar, M. Barmar, M. Barikani, P. Shokrollahi, “Synthesis and characterization of polyhedral oligomeric silsesquioxane-based waterborne polyurethane nanocomposites”, *Korean J. Chem. Eng.*, 2016, vol. 33, pp. 319-329.
- [17] Q. Zhang, X. Huang, X. Wang, X. Jia, K. Xi, “Rheological study of the gelation of cross-linking polyhedral oligomeric silsesquioxanes (POSS)/PU composites”, *Polymer (United Kingdom)*, 2014, vol. 55, pp. 1282-1291.
- [18] J.P. Lewicki, K. Pielichowski, M. Jancia, E. Hebda, R.L.F. Albo, R.S. Maxwell, “Degradative and morphological characterization of POSS modified nanohybrid polyurethane elastomers”, *Polym. Degrad. Stab.*, 2014, vol. 104, pp. 50-56.
- [19] P. Grosse, “Conventional and unconventional infrared spectrometry and their quantitative interpretation”, *Vibr. Spectrosc.*, 1990, vol. 1, pp. 187-198.
- [20] A.K. Surca, M. Rodošek, A. Kreta, M. Mihelčič, M. Gaberšček, “In situ and ex situ electrochemical measurements: Spectroelectrochemistry and atomic force microscopy”. In: M.H. Delville, A. Taubert (Eds.), “Hybrid organic-inorganic interfaces: Towards advanced functional materials”, 2018, pp. 793-838.
- [21] Y.X. Zhang, M. Huang, F. Li, Z.Q. Wen, “Controlled synthesis of hierarchical CuO nanostructures for electrochemical capacitor electrodes”, *Int. J. Electrochem. Sci.*, 2013, vol. 8, pp. 8645-8661.
- [22] G.W. Poling, “Infrared reflection studies of metal surfaces”, *J. Colloid Interface Sci.*, 1970, vol. 34, pp. 365-374.
- [23] M.R. Johan, M.S.M. Suan, N.L. Hawari, H.A. Ching, “Annealing effects on the properties of copper oxide thin films prepared by chemical deposition”, *Int. J. Electrochem. Sci.*, 2011, vol. 6, pp. 6094-6104.
- [24] N. Serin, T. Serin, S. Horzum, Y. Celik, “Annealing effects on the properties of copper oxide thin films prepared by chemical deposition”, *Semicond. Sci. Technol.*, 2005, vol. 20, pp. 398-401.