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Corrosion behavior of copper in 3 % NaCl with addition of cynarae extract

Koroziono ponašanje bakra u 3% rastvoru NaCl sa dodatkom ekstrakta cynarae

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Abstract

In this work, corrosion behavior of cooper in corrosion media consisted of aerated aqueous electrolyte of 3% NaCl with addition of different amount of cynarae extract as green corrosion inhibitor, is presented. Techniques used in this study involved open circuit measurements, evaluation of charge transfer resistance and corrosion current density during exposure to corrosion environment. Also, electrochemical impedance spectroscopy measurements are presented. Potentiodymamic polarization curves were also used for the evaluation of the corrosion current density and corrosion potential of coper in corrosion media. Based on these results, it was concluded that the satisfactory results of corrosion inhibition exceeding 70 % were obtained with small amount of only $37 \cdot 10^{-2}$ of mas. % of cynarae extract, based on open circuit behavior which involved decrease of the open circuit potentials of copper in the presence of cynarae extract it was concluded that this extract served as cathodic inhibitor.

Keywords: *cooper; green inhibitors; cynarae extract; cathodic inhibitor*

Izvod

Koroziono ponašanje bakra u aerisanom vodenom rastvoru 3% NaCl bez i sa dodatkom različite količine ekstrakta cynarae (artičoka) je ispitano u cilju evaluacije inhibicije korozije bakra i mogućnosti primene ekstrakta cynarae kao zelenog inhibitora korozije. Za evaluaciju efikasnosti zaštite korišćene su uobičajene eksperimntalne tehnike praćenja potencija otvorenog kola, otpornosti prenosa naelektrisanja i struje korozije u vremenu kao i spektroskopija elektrohemijske impedancije. Ustanovljeno je da veoma male količine ovog inhibitora od svega $37 \cdot 10^{-2}$ mas. % pružaju zadovoljavajuću zaštitu od korozije u 3% NaCl. Na osnovu smanjenja potencijala otvorenog kola bakra u prisustvu ekstrakta cynarae, ustanovljeno je da je inhibitor katodnog tipa.

Ključne reči: *bakar, zeleni inhibitori, ekstrakt cynarae, katodni inhibitor*

Introduction

Owing to its properties such as: excellent electrical and thermal conductivity, good mechanical properties and acceptable corrosion resistance, copper is widespread use in many industrial applications. Copper and its alloys are quite resistant to corrosion in atmospheric conditions and in mild corrosion environments. However, in aggressive corrosion media at lower pH or in neutral conditions where oxygen is present, copper is prone to corrosion with rate increasing significantly with increasing the amount of dissolved oxygen. Since the presence of oxide layer is not expected in such aggressive environments, the use of inhibitors is favorable. Numerous corrosion inhibitors for copper for various environments are intensively investigated and their protective mechanisms are postulated [1-3]. They involve both inorganic and organic compounds although the number or organic

inhibitors prevails. These compounds involves azoles, amines and amino-acids [1,3-5]. Following the environmental concerns and bearing in mind that lot of commercial copper inhibitors are toxic, lot of attention is paid in investigation of so-called green inhibitors involving both usage of green chemical and plant extracts [2,6–9]. To the best of our knowledge, the application of cynarae extract is not investigated before, the aim of this work is to present preliminary results of our studies involving application of cynarae extract as inhibitor of copper corrosion in aerated 3% NaCl electrolyte.

Experimental

Copper (99.99 % purity) square shaped plats (A=1,0 cm^2) were used as electrodes. Before experiments copper electrodes were mechanically polished with fine emery papers, degreased in acetone and rinsed with distilled water. Copper corrosion was investigated in aerated 3% aqueous electrolyte without and with addition of different amount of commercial cynare extract solution ranging from 1 to 7 ml with 7,5 mas.% of extract in solution.
Corrosion experiments were performed at ambient temperature in standard three compartment electrochemical cell with copper as working electrode, platinum wire as counter and saturated calomel electrodes as counter (SCE), with all potentials given in respect to SCE. Open circuit potentials charge transfer resistances and corrosion current were recorded in time. Potentiodynamic polarization curves of copper and coper with chosen amount of 5ml of cynare extract were recorded at 1 mV s^{-1}, while electrochemical impedance spectroscopy (EIS) measurements were performed at opencircuit potentials in the frequency range from 0.1 to 10^5 Hz with 5 mV of amplitude. All experiments were done using Gamry, Interface 1010 potentiostat/galvanostat

Results and discussion

Aiming to discover the type of potential corrosion inhibition of copper with cynarae extract, specimens were exposed to 3 % NaCl without and with addition of different volume ranging from 1 ml to 7.5 ml of cynarae extract and open circuit potentials were monitored over time of exposure as presented in Fig.1. with mean values of the open circuit potentials over time given in Insert of the figure. As it can be seen from Fig.1, soon after exposure of copper to corrosion media, open circuit potential of copper dropped from -180 mV to more negative values of : -199, -211, -214, -217 and -216 mV with addition of different amount of inhibitor as marked on the figure. During the time of exposure to corrosion media open circuit potentials decreased slowly except for lowest added amount of the extract. As it can be seen from Fig.1., the values of the open circuit potentials and their mean values were decreasing as the amount of inhibitor increased except for the lowest amount, as expected for cathodic type of corrosion inhibitors.

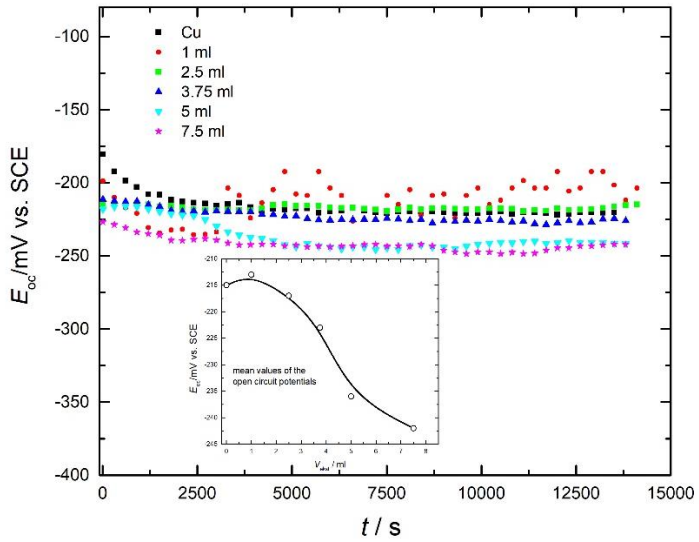

Figure 1. *Open circut potential, Eoc over time for copper in 3 % NaCl witout and with addition of cynare extract, as marked on the figure. Insert: Mean values of the open circuit potential.*

For estimation of an inhibitor efficiency, values of either charge transfer resistances (i.e. polarization resistances) or corrosion current are often used, following the well-known equations:

$$\eta = \frac{R_{p,0}^{-1} - R_p^{-1}}{R_{p,0}^{-1}} \cdot 100\% \quad (1)$$

$$\eta = \frac{I_{cor,0} - I_{cor}}{I_{cor,0}} \cdot 100\% \quad (2)$$

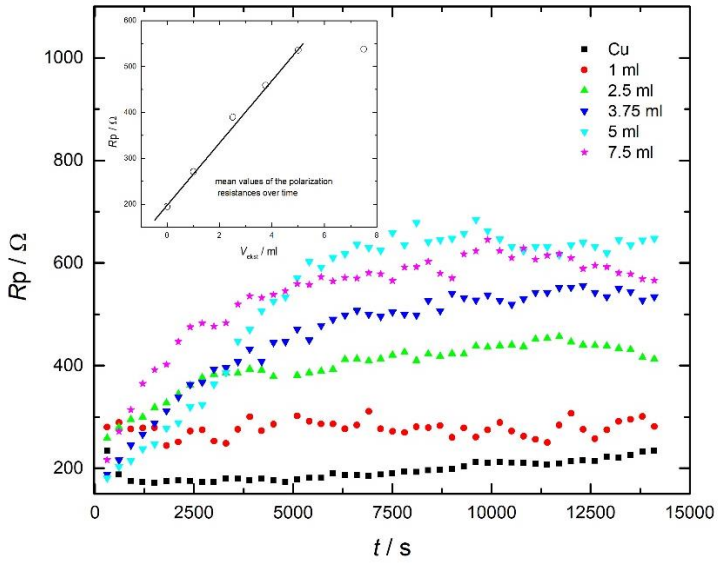

Figure 2. *Time dependances of polarization resistance for copper in 3 % NaCl witout and with addition of cynare extract, as marked on the figure. Insert: Dependance of the mean value of polarization resistance on volume of the extract.*

where η, refers to corrosion inhibition efficiency, while $R_{p,0}$ and R_p, are charge transfer resistances without and with inhibitor respectively and $I_{cor,0}$ and I_{cor} are related corrosion curents.
Fig.2., displays the dependance of the charge transfer resistance, for copper in 3 % NaCl without and with addition of different amounts of cynarae extract as marked on figure, while insert of the same

figure gives dependances of its mean values over time of the exposure. As it can be seen from Fig.2. that addition of the cynarae extract resulted in increase of the charge transfer resistances i.e. polarization resistance over increase of the amount of the added extract, indicating corrosion protection. The corrosion current provided by the software tended to decrease over time comparing to the values of copper in the environment without cynarae extract, with stabile and constant value after around 2500 s of exposure. The values of the inhibitor efficiency are collected and given in Table 1. As it can be seen from Table 1, acceptable efficiency is achieved, bearing in mind low amount of the inhibitor.

Table 1. Corrosion efficiency determined from polarization resistance and corrosion current

10^{-2} mas. % of extract	η_{Rp} / %	η_{Icor} / %
7.5	12	5
18.7	49	52
28.1	58	65
37	65	68
56.2	66	71

Results of SEI measurements in complex and frequency diagrams are given together in Fig.3., without analysis in the terms of electrical equivalent circuit.

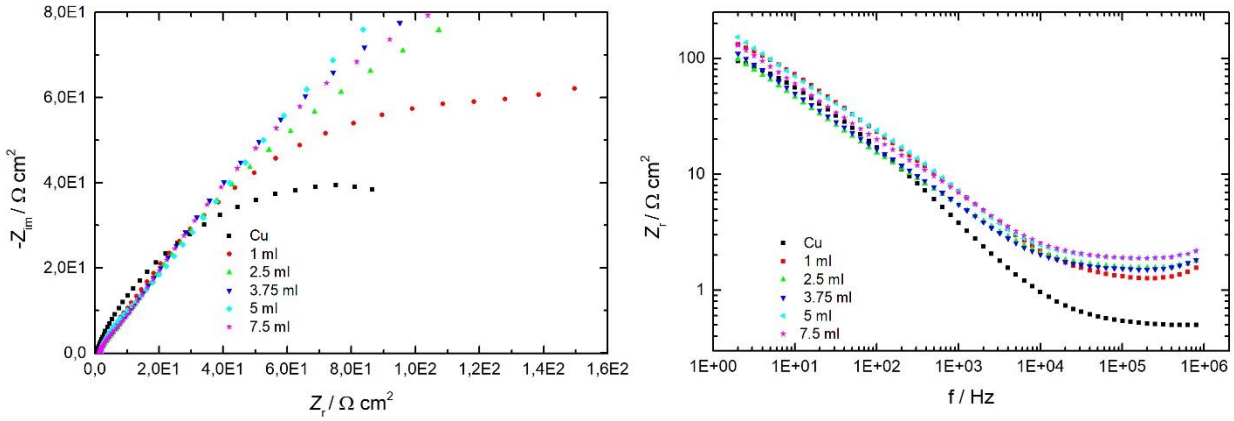

Figure 1. *SEI spectra in: complex plane (left) and Bode plane (right) of copper in 3 % NaCl witout and with addition of cynare extract, as marked on the figure.*

Data on Fig.3. clearly indicated that after 2h of exposure to corrosion environment corrosion of copper started while the protective nature of cynarae extract is observable in increase of the overall impedance, on the other hand diffusion component of the impedance is also observable which is related to the diffusion control of the cathodic corrosion half-reaction.

Potentiodynamic anodic curves of copper in 3% NaCl without and with 5 ml ($37 \cdot 10^{-2}$ mas.%) of cynarae extract were recorded in order to obtain corrosion current density, as presented in Fig.4.

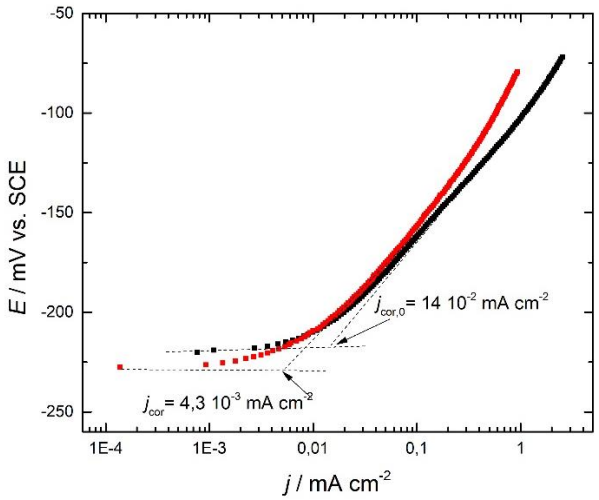

Figure 4. *Potentiodiynamic anodic polarization curves, at 1 mV s^{-2} of copper in 3% NaCl without and with addition of 37·10^{-2} mas. % of* cynare extract.

As it can bee seen in Fig.4. anodic reaction of copper dissolution is in both electrolytes under activation control with Tafel slope of 60 mV dek^{-1}, while corrosion potentials of unprotected and protected copper are -215 and -230 mV with corrosion current densities of 14·10^{-2} and 4.3·10^{-3} mA cm^{-2} respectively. Based on these data, cathodic inhibition type of cynarae extract is confirmed. The calculated inhibition efficiency of 69 % is estimated, which is in accordance with the data from Table 1.

Conclusion

Cynarae extract was used to study corrosion inhibition of copper in aerated 3 % NaCl. It was observed that cynarae extract offered cathodic type of inhibition in very low amount which was confirmed by lowering the corrosion current, increase of polarization resistance and overall impedance and polarization measurements. Corrosion inhibition efficiency of 69 % was observed for only 37·10^{-2} mas. % of the solid substance giving this extract interesting for further studies.

Acknowledgements

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References

1. M. M. Antonijevic and M. B. Petrovic Mihajlovic, Copper Corrosion Inhibitors. Period 2008-2014. A Review, *Int. J. Electrochem. Sci.*, **10(2)**, 1027–1053, 2015.
2. A. Fateh, M. Aliofkhazraei, and A. R. Rezvanian, Review of corrosive environments for copper and its corrosion inhibitors, *Arab. J. Chem.*, **13(1)**, 481–544, 2020.
3. G. Vastag, E. Szöcs, A. Shaban, and E. Kálmán, New inhibitors for copper corrosion, *Pure Appl. Chem.*, **73(12)**,1861–1869, 2001.
4. C. Shi, Y. Wang, Y. Yu, J. Li, D. Zhang, and L. Gao, The role of cuprous ions on the click-assembled triazole films against copper corrosion, *Corros. Sci.*, **145**, 100–108, 2018.
5. G. L. F. Mendonça, S. N. Costa, V. N. Freire, P. N. S. Casciano, A. N. Correia, and P. de Lima-Neto, Understanding the corrosion inhibition of carbon steel and copper in sulphuric acid medium by amino acids using electrochemical techniques allied to molecular modelling methods, *Corros. Sci.*, **115**, 41–55, 2017.

6. M. B. Valcarce and M. Vázquez, Phosphate ions used as green inhibitor against copper corrosion in tap water, *Corros. Sci.*, **52(4)**, 1413–1420, 2010.
7. G. Tansuğ , A new corrosion inhibitor for copper protection, *Corros. Sci.*, **84**, 21–29, 2014.
8. Y. Qiang, S. Zhang, L. Guo, X. Zheng, B. Xiang, and S. Chen, Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid, *Corros. Sci.*, **119**, 68–78, 2017.
9. G. Vastag, A. Shaban, M. Vraneš, A. Tot, S. Belić, and S. Gadžurić, Influence of the N-3 alkyl chain length on improving inhibition properties of imidazolium-based ionic liquids on copper corrosion, *J. Mol. Liq.*, **264**, 526–533, 2018.