ELECTROCHEMICAL BEHAVIOR OF COPPER IN CHLORIDE MEDIUM IN THE PRESENCE OF WALNUT SHELL MACERATE

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Abstract

The use of plant extracts to inhibit the corrosion of copper and its alloys has been the subject of numerous scientific studies. This paper presents the results of research the electrochemical behavior of copper during oxidation in a 0.5 mol/dm³ NaCl solution in the absence and presence of walnut shell macerate in different concentrations. The electrochemical behavior of copper was investigated by method of open circuit potential measurement and cyclic voltammetry method. The results of measuring the open circuit potential show that the values obtained in the presence of walnut shell macerate are more positive in relation to the value recorded without the addition of walnut shell macerate. Three current peaks that correspond to copper chloride and copper oxide formation appear on the anode polarization curve obtained without the presence of walnut shell macerate. The value of current peaks decreases with increasing concentration of walnut shell macerate in the electrolyte. Lower current values in the presence of walnut shell macerate indicate that walnut shell macerate has got an inhibitory effect on processes resulting with these current peaks.

***Keywords**: copper, electrochemical behavior, chloride medium, walnut shell macerate*

1. INTRODUCTION

Due to its properties, copper is one of the most important metals used in industry. First of all it has good electrical and thermal conductivity, good mechanical workability and partly noble properties. It has found wide application in the electronic industry, in the production of wires, sheets, pipes for households, in the computer and microelectronic industry, as well as in the production of a large number of alloys [1]. Copper corrosion and its inhibition in different environments, especially those containing chloride ions, have been subject of numerous scientific studies [2-4] The possibility of protecting copper from corrosion is attracting the attention of numerous researchers, so that a large number of possible inhibitors have been tested to date. Inhibitors are substances that are added in various concentrations to a given solution that contains aggressive ions. They can have organic or inorganic origin. However, many inhibitors have shown negative effects like damaging the environment, so the discovery and development of new environmental friendly inhibitors and the study of the mechanism of their action is the subject of many actual scientific studies [5, 6].

Plant extracts as potential corrosion inhibitors have become the subject of numerous scientific studies in recent years. Extracts of various parts of plants, such as seeds, bark and flowers can be used as metal corrosion inhibitors.

2. EXPERIMENTAL

The experiments were performed on a system consisting of:
- electrochemical cell with three electrodes (working, reference and auxiliary),
- hardware (PC, AD/DA converter PCI-20428W manufactured by Burr-Brown and analog interface developed at the Technical Faculty in Bor) [7],
- measurement and control software (LabVIEW platform and specially developed application for electrochemical measurements) [7].

Experimental investigation of the electrochemical behavior of copper in 0.5 mol/dm³ NaCl without and with the addition of walnut shell macerate (in further text: w.s.m) were performed by measuring the open circuit potential in relation to the saturated calomel electrode (SCE) during 60 seconds, and recording anode polarization curves in the potential range of -0.4 V vs. SCE up to 1 V vs. SCE with a scan rate of 20 mV/s.

The substances used for the preparation of working solutions are NaCl p.a purity, manufactured by d.d. "Zorka Pharma" Šabac, chopped walnut shells and distilled water. The macerate was prepared as follows: 100 g of chopped walnut shells were added to 1000 mL of distilled water and heated to 60 ˚C. The mixture was stirred four hours on a magnetic stirrer at a mixing speed of 400 min^{-1}. After four hours, the obtained macerate was filtered on a Bihner apparatus and stored in the refrigerator.

3. RESULTS AND DISCUSSION

The results of measuring the open circuit potential for pure copper in 0.5 mol/dm³ NaCl with and without the presence of w.s.m. during 60 seconds are shown in Figure 1.

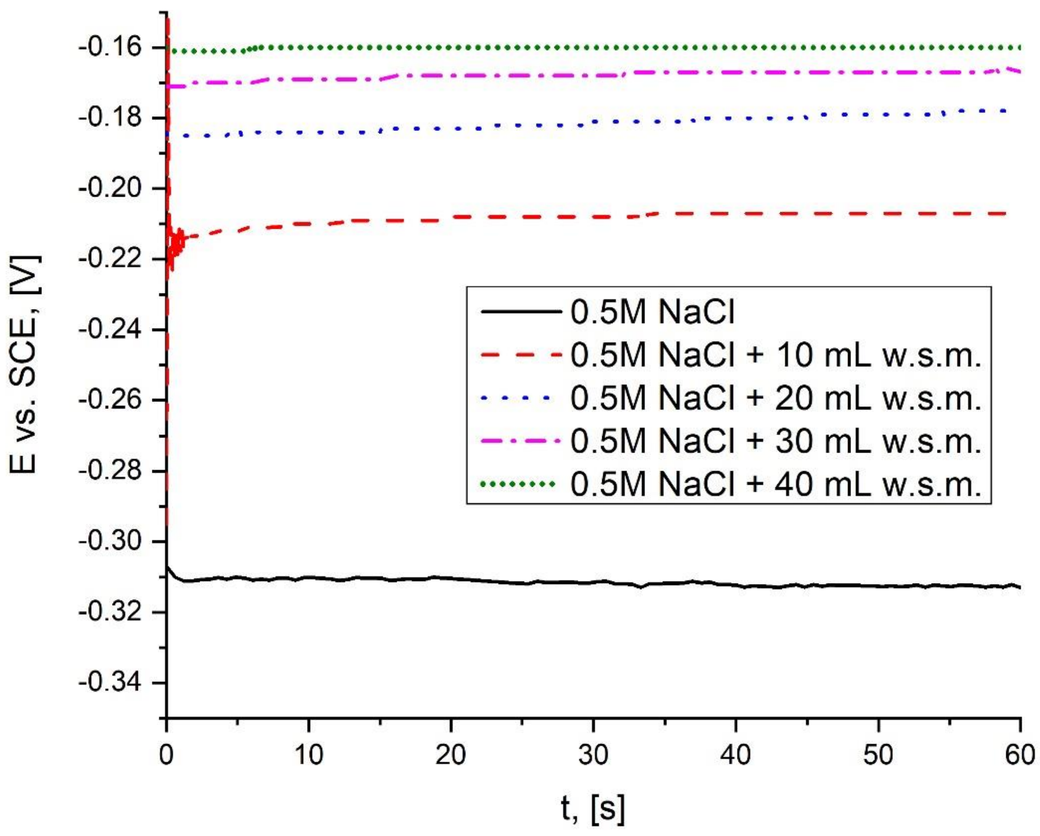

Figure 1. Open circuit potential of copper in 0.5 mol/dm³ NaCl, with and without the addition of walnut shell macerate; (w.s.m. - walnut shell macerate)

Based on the measurement of the open circuit potential, it can be noticed that the open circuit potential for copper in pure 0.5 mol/dm³ NaCl is the most negative with the value of -0.313 V vs. SCE. With the addition of 10 mL w.s.m. the open circuit potential is -0.207 V vs. SCE, after stabilization. With the addition of 20 mL w.s.m., the open circuit potential is -0.178 V vs. SCE. With the addition of 30 mL and 40 mL w.s.m. the open circuit potential stabilizes very quickly. Finally, with the addition of 30 mL w.s.m. the open circuit potential is -0.166 V vs. SCE, while with the addition of 40 mL the open circuit potential is -0.160 V vs. SCE.

Figure 2 shows the anodic polarization curves for pure copper without and in the presence of w.s.m. in different concentrations.

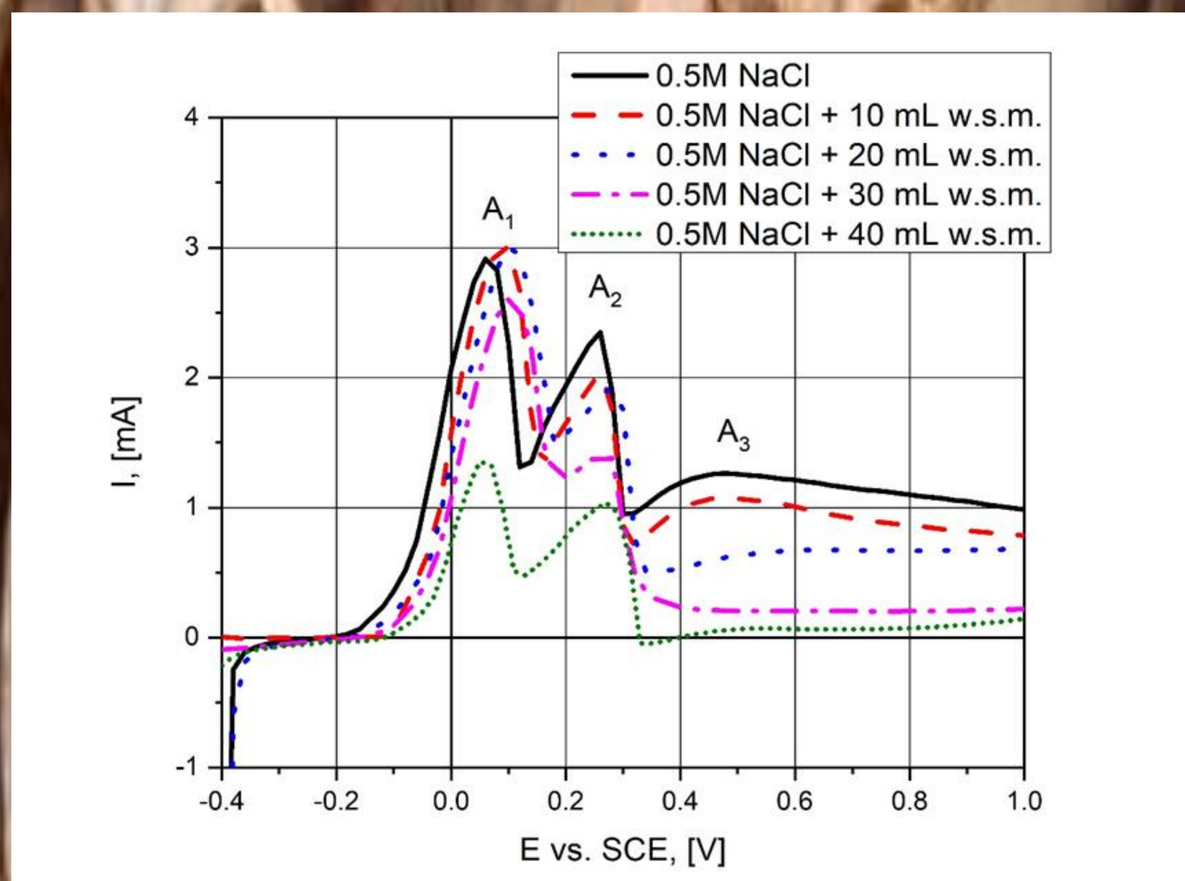

Figure 2. Anodic polarization curves for copper in 0.5 mol/dm³ NaCl, with and without the addition of walnut shell macerate; (w.s.m. - walnut shell macerate); scan rate 20 mV/s

Three current peaks were observed on the anode polarization curve recorded for copper in 0.5 mol/dm³ NaCl. Current peak A_1 appears at 0.06 V vs. SCE, current peak A_2 at 0.26 V vs. SCE, and the current peak A_3 at 0.46 V vs. SCE.

The current peaks A_1 and A_2 correspond to the formation of copper chloride by the following mechanism [8,9]:

$$Cu + Cl^- = CuCl_{ads} + e^- \quad (1)$$

$$CuCl_{ads} + Cl^- = CuCl_2^- \quad (2)$$

$$Cu + CuCl_2^- = 2CuCl + e^- \quad (3)$$

The current peak A_3 corresponds to the formation of Cu_2O oxide according to the equation [10]:

$$2CuCl + 2OH^- = Cu_2O + H_2O + 2Cl^- \quad (4)$$

With the addition of 10 mL and 20 mL w.s.m., the current values for peak A_1 are higher than the current without the addition of w.s.m, while with the addition of 30 mL and 40 mL w.s.m., the current values are lower than the current obtained in pure NaCl solution. In the potential range where current peaks A_2 and A_3 occur, the current values are lower at all w.s.m. concentrations than the current values in pure NaCl solution. Also current peaks obtained in the presence of w.s.m. appear at more positive potentials. The results obtained by the cyclic voltammetry method show that w.s.m. acts as an anodic inhibitor of copper corrosion.

4. CONCLUSION

Increasing concern for the environment has led to stricter regulations regarding the use of chemicals that can have a detrimental effect on the environment, which has resulted with the reduction or complete suspension of the use of a number of highly effective copper corrosion inhibitors. Recently, the focus of research has been put on the inhibitory effect of so called green inhibitors.

Green inhibitors can be of animal or plant origin. They are biodegradable, cheap and do not harm the environment. The inhibitory effect of some plant extracts is achieved thanks to the presence of tannins, vitamins and natural polymers in their composition. The possibility of using walnut shell macerate to protect copper from corrosion was investigated in this paper.

Based on the performed experiments, the following conclusions can be made:

- According to the obtained results of measuring the open circuit potential for copper in 0.5 mol/dm³ NaCl without and with the addition of walnut shell macerate, it can be concluded that the open circuit potential values are more positive in the presence of the macerate than the open circuit potential without macerate addition.

- Investigation of the electrochemical behavior of copper by the method of cyclic voltammetry in 0.5 mol/dm³ NaCl showed that three current peaks appear on the anode polarization curve. The current peaks A_1 and A_2 correspond to the formation of copper chloride, while the current peak A_3 corresponds to the formation of copper oxide on the surface. In the presence of walnut macerate, the inhibitory effect of macerate is achieved in the area of potential A_1 with the addition of more than 20 mL, while in the area of potentials A_2 and A_3, walnut macerate has an inhibitory effect at all tested concentrations of walnut macerate.

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