Peculiarities of electrochemical behavior of copper in ionic liquid $BMImNTf_2$

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Ionic liquids (IL) are widely used in electrochemistry due to their excellent properties such as good ionic conductivity, wide electrochemical potential window, high viscosity, high thermal stability, wide liquid range and tunable solvent properties. Electropolishing is widely used in the metal finishing industry because of its simplicity, also it can be applied to objects of a complex shape. The process of polishing includes removing of surface roughness resulting from defects in the crystalline structure and presence of surface oxides of a metal. Therefore the problem of removing of oxides from the metal surface is very important [1].

In the current work, copper samples having natural oxide coating were studied. They were prepared by oxidation of a copper sample by air at room temperature. This coating consists of CuO and Cu_2O layers. The behavior of oxide layers was investigated by the method of electrochemical etching in IL and it was shown in Fig. 1.

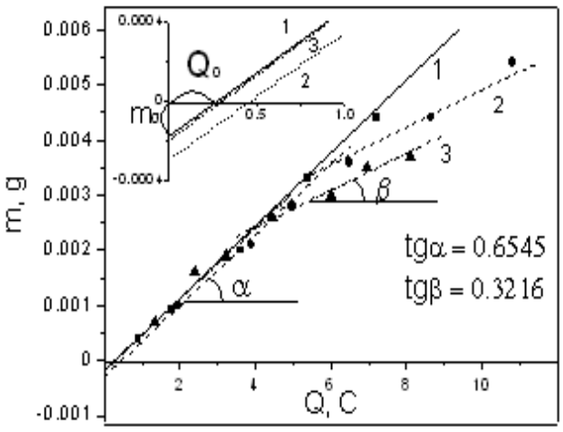

Fig. 1. The change of the weight of the copper sample (m) vs. the quantity of electricity (Q) consumed for the polishing of Cu in the $BMImNTf_2$ medium at i=8 mA/cm^2, T=25°C: (1) the copper sample pretreated by HCl, (2) the copper sample with natural oxide coating,(3) the preliminarily oxidized copper sample. Q_0 is the quantity of electricity spent for oxidation of O^{2-}

Figure 1 shows the m – Q dependence, wich consists of two linear plots and does not pass through the origin of coordinates. The presence of CuO and Cu_2O on the surface of copper samples was confirmed. In the initial section (Fig.1) the quantity of electricity is spent for oxidation of O^{2-} species that are present in the oxide coating. The first linear plot has a slope of 0.6545 mg/C. This corresponds to the electrochemical equivalent of copper equal to 0.6588 mg/C and is consistent with the half-reaction $Cu^{+} - 1e \rightarrow Cu^{2+}$. The second linear plot, which has a slope of 0.3216 mg/C is consistent with the half-reaction $Cu^{0} - 2e \rightarrow Cu^{2+}$ which is characterized by the electrochemical equivalent of copper equal to 0.3294 mg/C. The thickness of each oxide layer was calculated.

It was suggested that the mechanism of etching of copper in IL consisted in consecutive removing of CuO and Cu_2O and dissolution of Cu. A similar dependence was obtained for the copper sample pretreated by HCl (Fig. 1).

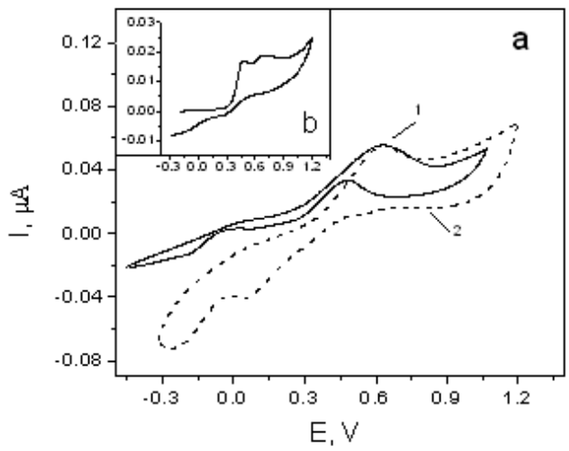

Fig. 2 CVA curves for Cu in the $BMImNTf_2$ medium. The potential scan rate is 10 mV/s. The reference electrode is an Ag wire. The 10^{th} scan cycle: (1) the copper sample with natural oxide coating, (2) the copper sample pretreated by HCl (a). The 1^{st} scan cycle for the copper sample with natural oxide coating (b)

The suggested mechanism was proved by the data of the cyclic voltammograms (Fig. 2). An irreversible peak current in the first scan cycle (Fig. 2b) is observed at E = 0.65 V, which is indicative of the irreversible oxygen oxidation. After repeating ten cycles, the CVA curves for all samples coincides with each other (Fig. 2a). The same result was obtained in the electrochemical study of the copper sample that has been preliminarily oxidized at 700°C for 15 seconds in air (Fig. 1).

REFERENCES

1. O. Lebedeva, G. Junguroval, D. Kultin, L. Kustov, A. Zakharov, K. Kalmikov, E. Chernikova and Vladimir Krasovskiy, *J. Green Chem*., **13**, 1004-1008 (2011).