

Peculiarities of Copper Local Depassivation in Perchlorate Solutions with Different pH in Presence of Alanine

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At the previous publications [1,2] was shown not simple role of amino-acids in copper anodic processes in alkaline solutions where metal is in passive state but under organic additive influence it can be more stable or can undergoes a local corrosion. The kinetic regularities of copper anodic processes in perchlorate solutions (pH=5,7-8,4) in the β -alanine presence were studied in the present work which is continuing this research. The peculiarities of used background electrolyte were the following: on one hand, ClO_4^- -ions form stable complexes with Cu^{+2} -ions in volume of solution, on the other hand they initiate copper pit in neutral and alkaline mediums [3].

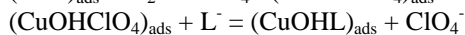
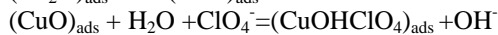
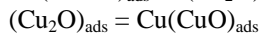
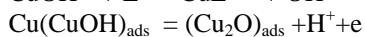
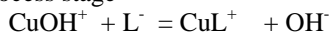
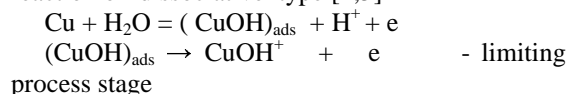
The experiments were carried out with using complex of physico-chemical methods (inversion (IVA) and cyclic (CVA) voltamperometry, chronoamperometry, microscopy). Concentration of β -alanine was changed from 1×10^{-4} to 1×10^{-1} mol/l.

Comparative analysis of copper anodic behavior in pure perchlorate solutions and in solutions with β -alanine additive has shown that in both systems copper exposed local activation (LA). In this case copper resistance to LA is increasing under influence of small amino-acids concentrations ($c = 10^{-4}$ - 10^{-2} mol/l). At the same time the depth and the number of metal local destruction are decreasing with parallel pit size's extension. But when β -alanine concentration is more over 10^{-2} mol/l pit corrosion is transferring to spot corrosion. The observing effects can be connected with competitive adsorption of perchlorate-ions and amino-acid ions under primary role of the amino-acid ions. When the alanine concentration is insufficient for displacement ClO_4^- -ions from reaction zone amino-acid is acting like inhibitor but when all ClO_4^- -ions are displacing from interface metal/electrolyte (under $c > 10^{-2}$ mol/l) amino-acid is becoming copper local corrosion activator. The analogy of copper surface destruction's type in alkaline and perchlorate solutions at the last case is the confirmation of this fact.

At the same time in difference from alkaline solutions only CuOH, Cu_2O and CuO compounds are responsible for copper passive state in perchlorate solutions. Moreover the specific for the investigated systems is being the appearance of the cathodic peak (under 0,190-0,240V (NHE) potential zone) which can be connected with Cu^{+2} -ions reduction to Cu^+ -ions. In presence of amino-acid in copper passive film CuO vanishes and thus passive layers become less stable than in background electrolyte. This phenomenon is confirmed by disappearance of the peak which is being responsible for conversion $\text{Cu}^{+2} \rightarrow \text{Cu}^+$ because Cu^{+2} -ions presenting in system are combining with alanine in stable complex (CuHL^{+2} , CuL^+ or CuL_2 [4], where L is ligand)

The concentration's dependence of LA potential (E_{LA}) and LA induction period (τ_{ind}) (the value of which is inversely proportion the

process pit initiation rate [5]) was analyzed in researched systems for identification of copper local activation mechanism. The received experimental data have shown the indifference of these values to β -alanine concentration. Consequently copper local depassivation process can be interpreted like nucleophilic substitution reaction of dissociative type [4,5]



where L^- - alanine anion.

Thus the results of this investigation have shown that β -alanine influence on LA copper in perchlorate solutions differentiates according to the additive concentration. Under small β -alanine concentration ($c = 10^{-4}$ - 10^{-2} mol/l) process LA is inhibited, under $c > 10^{-2}$ mol/l it is stimulated. This data are interpreted on basis modern theories competitive adsorption and nucleophilic substitution.

References

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