

INFLUENCE OF ANIONS ON THE MECHANISM OF ANODIC DISSOLUTION OF, AND CATHODIC REDUCTION OF OXYGEN ON COPPER AND BRASS—A ROTATING RING DISC STUDY

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The effect of anions like chloride, sulphate and nitrate on the anodic dissolution of copper and brass on the one hand and cathodic reduction of oxygen on the other was examined using a rotating ring disc electrode. In the case of chloride solution the copper dissolves essentially as monovalent ion in the initial stages with subsequent formation of a film consisting of basic cupric chloride leading to passivation. The anodic dissolution is independent of pH in the sulphate and chloride (in the active region) solutions.

The anions considerably change the potential domains of preferential and simultaneous dissolution of brass.

While the diffusion effects are observed on copper in chloride solution only near about the passivation region, they are predominant in the case of brass at low potentials.

The oxygen reduction on copper and brass indicates the presence of two steps, the one corresponding to formation of H_2O_2 and the other to the formation of OH^- . The rate of oxygen reduction also depends on the nature of the anions and also on the presence of NH_4^+ ion. Thus the rate of oxygen reduction is the highest in ammonium sulphate solutions. Generally the reduction is faster in sulphate than in chloride solution. The ring disc study indicates that in the cases of ammonium sulphate solution the H_2O_2 is formed as an intermediate whereas in sodium chloride solution H_2O_2 is formed in parallel step as a stable product.

Keywords : Anions; Anodic Dissolution; Cathodic Reduction; Rotating Ring Disc

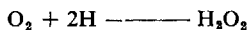
Discussion

L. I. KRISHTALIK (*Institute of Electrochemistry, Academy of Sciences of USSR, Moscow*): 1. You have explained the hysteresis by anions adsorption. What is the reason for pH influence on it? 2. Have you any explanation for specific influence of the NH_4^+ ion on the selectivity of brass dissolution?

K. BALAKRISHNAN: 1. It is known that anion adsorption is more on oxide covered surface than an oxide free surface. It is likely that the anions are not so much adsorbed in solution of low pH where oxide film is present to a less extent. 2. Though the relative dissolution is exhibited in all the cases over different potential region, this starts at a comparatively more negative potential in the case of solutions containing NH_4^+ ion. However, the selective dissolution also changes to simultaneous dissolution at comparatively more negative potentials. This effect is due to the complexing property of NH_4^+ ion.

V. S. BAGOTSKY (*The Institute of Electrochemistry of the Academy of Sciences of USSR, Moscow*): What is the meaning of the negative slope of the I_d/I_r vs. $\omega^{1/2}$ dependence?

K. BALAKRISHNAN: We have no specific explanation for it. However, it can be pointed out that Bockris *et al.* (*J. electroanal. Chem.*, **15**, 173, 1967) have reported negative slopes for oxygen reduction on Pt and Au in acid solutions. They have suggested that in the case of Pt the rate of hydrogen discharge becomes small in comparison to oxygen reduction as



and in the case of Au the oxygen reaction takes place under diffusion control on oxide patches whereas H_2O_2 is formed at bare electrodes.

R. NARAYAN (*Indian Institute of Technology, Madras*): 1. Did you take into consideration the fact that Cu will preferably go into solution as Cu^+ in chloride media? 2. The n should not be called as a rate for the $E-i$ curve, unless areas are specified. The true areas of the solid Cu & Brass cannot be the same. Further the number of atoms on surface of brass has got to be smaller than that on copper and several other factors like grain boundaries, activities will have to be considered? 3. What is the difference in solubility of O_2 in the presence of various anions. The difference cannot be large to account for the diffusion observed? 4. Did you try to detect H_2O_2 chemically?

K. BALAKRISHNAN: 1. In the potential range where copper dissolves as Cu^+ , this has been taken into account. At higher potentials Cu^{2+} has been taken into account. 2. Under cathodic conditions and for comparison purposes geometric area has been taken as same. 3. It cannot be accounted by mere changes in oxygen solubility. 4. H_2O_2 was detected and estimated electrochemically at the ring electrode.