

Electrochemical behaviour of tin in alkaline solutions

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The polarisation characteristics of tin electrode in NaOH solutions have been investigated by cyclic voltammetric and linear polarisation techniques. In cyclic voltammetry, the effect of sweep rate and concentration on the primary and secondary passivation processes has been studied. A sweep rate-concentration diagram was obtained from the charge vs sweep rate curves which establishes the condition under which the primary or secondary passivation process predominates. Linear polarisation studies explain the nature of the primary anodic dissolution process.

Key words: Tin in NaOH, linear polarisation studies, cyclic voltammetry

INTRODUCTION

The electrochemical behaviour of tin in NaOH solutions using different experimental techniques has been explored by many workers [1-2] with a view to throw light on the mechanism of electrode reactions. This paper provides additional information to the literature on the electrochemical behaviour of tin in alkaline solutions.

EXPERIMENTAL

The experimental set up used and the electrode pretreatment details are described elsewhere [3]. D.C. linear polarisation studies were carried out using Princeton Applied Research Corporation Model 350A corrosion measurement console.

RESULTS AND DISCUSSION

Typical cyclic voltammogram for tin in 0.05M NaOH solution traced at 60 mV s^{-1} is shown in Fig. 1. The nature of the anodic and cathodic peaks are found to change with concentration of the electrolyte and sweep rates. Anodic peaks A_1 and A_2 are due to the primary and secondary passivation. CA_1 and CA_2 are the anodic peaks, C_1 and C_2 are the cathodic peaks formed during the reverse sweep. Figure 2 shows the variation of charges consumed for the primary passivation process $Q(A_1)$ and secondary passivation process $Q(A_2)$. The meeting point of the two curves indicates that for each concentration at a particular sweep rate the charge $Q(A_1)$ becomes equal to $Q(A_2)$.

A derivative curve Fig. 3 was obtained by making use of these points. Though both primary and secondary passivation occur in the region marked as "A", the charge

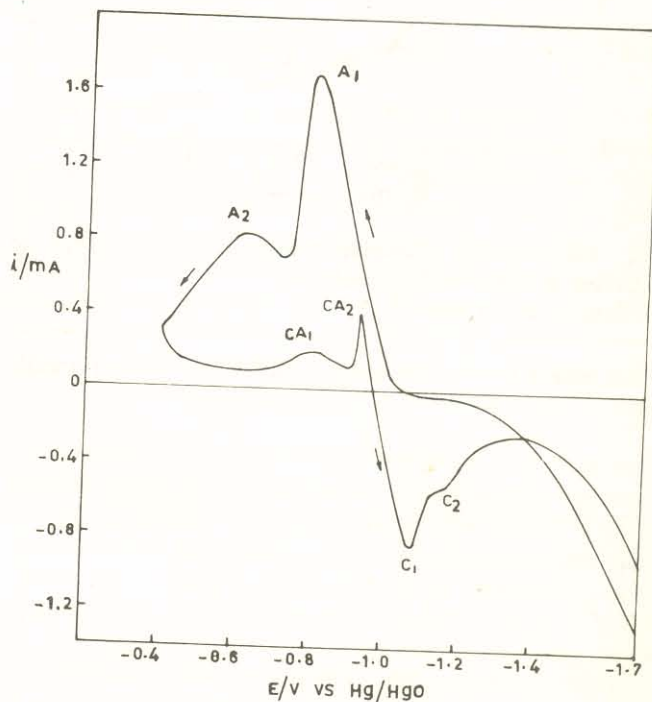


Fig. 1: TPS of tin electrode in 0.05M NaOH solution Scan rate 60 mV s^{-1}

consumed for the formation of secondary passivation is greater than that for the primary passivation. Under the condition stipulated in this area, the formation of a porous nature of Sn(OH)_2 film on the electrode surface favours direct oxidation of the metal to Sn(OH)_4 to SnO_2 . In the region marked as 'B', the charge consumed under the primary passivation is greater than that for the secondary passivation. This can be explained by considering the formation of nonporous thick Sn(OH)_2 film on the metal

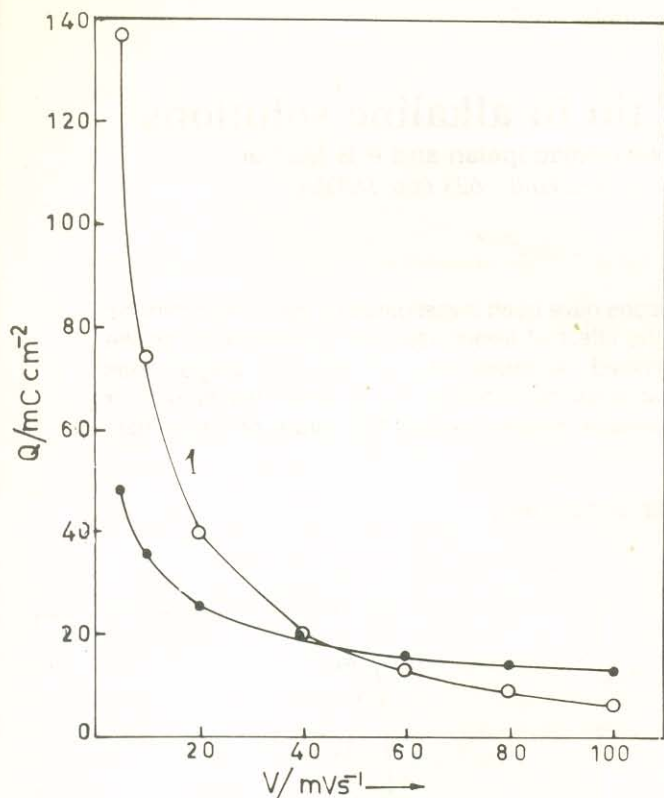


Fig. 2: Dependence of anodic charge $Q(A_1)$ and $Q(A_2)$ on sweep rate in 0.05M NaOH solutions
 ○—○ $Q(A_2)$ ●—● $Q(A_1)$

surface which lowers the magnitude of the second anodic peak.

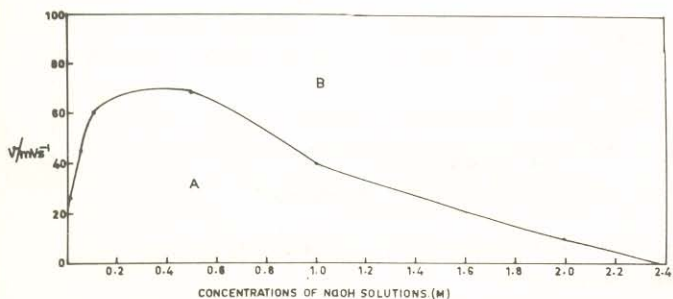


Fig. 3: Dependence of charge on sweep rate at different alkali concentrations.

●—● $Q(A_1) = Q(A_2)$

The R_p values obtained from the linear polarisation measurements were plotted against the sweep rates as

shown in Fig. 4. This shows that the R_p values decrease with increase of sweep rate in a given concentration and increase with decrease in the concentration of NaOH. The high R_p values obtained at lower alkali concentration, say 2M, may be due to the presence of passive film on the electrode surface. The dissolution of the film and the diffusion of the dissolved species away from the electrode surface increase with increase in the concentrations of alkali, causing gradual drop in the R_p values. From this, it can be concluded that at higher concentrations the anodic process is largely due to the influence of diffusion controlled process.

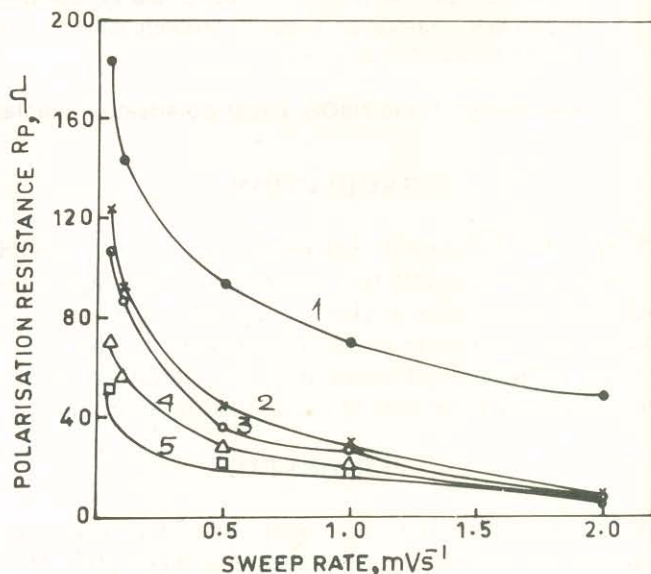


Fig. 4: Polarisation resistance vs sweep rate obtained for Sn in different alkali concentrations
 (1) 2M NaOH (2) 4M NaOH (3) 6M NaOH (4) 8M NaOH (5) 10M NaOH

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