

CORROSION AND PASSIVATION OF TIN ANODE IN Na_2CO_3 SOLUTIONS AND THE EFFECT OF HALIDE IONS

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The corrosion and passivation of tin anode in Na_2CO_3 (0.01 to 1.0 M) was investigated using potentiodynamic and cyclic voltammetry techniques and complemented by X-ray and scanning electron microscopy. The polarization curves exhibit two anodic peaks assigned to the electroformation of Sn(II) and Sn(IV) species, respectively, prior to permanent passive region. The anodic dissolution reactions are controlled by diffusion. X-Ray diffraction showed that the permanent passive layer is duplex and consists of SnO and SnO_2 . A multiplicity of cathodic peaks is related to the electroreduction of the anodically formed compounds. Addition of Cl^- , Br^- or I^- ions into the carbonate solutions enhances the anodic dissolution of tin to some extent depending upon the sodium carbonate concentration. In the passive region, addition of the halide ions causes pitting corrosion at a critical pitting potential. The pitting potential decreases with increasing both the halide ion concentration and the scanning rate but increases with increasing the sodium carbonate concentration. SEM examination confirms the occurrence of pitting corrosion.

The electrochemical studies of tin are closely related to its wide applications in industry. Reviews of the literature on the anodic behaviour of tin electrode in alkaline media showed that most of the work has been done in NaOH solutions¹⁻⁸. Very little work has been carried out in carbonate solutions⁹. In alkaline media, potentiodynamic polarization is characterized by the appearance of two anodic peaks assigned to the formation of Sn(II) and Sn(IV) species, respectively, prior to permanent passive region. The structure of the passive layer as revealed by ESCA and X-ray diffraction techniques consists of SnO and SnO_2 (ref.⁸).

The anodic behaviour of tin in alkali containing halide ions has been also studied^{10,11}. The effect of the aggressive halide ions depends upon the type and concentration of the halide ions used as well as on the pH of the medium.

The present work records the results for experiments clarifying the anodic dissolution and passivation of tin in Na_2CO_3 solutions and the influence of the presence of Cl^- ,

Br^- or I^- ions in the carbonate solutions using potentiodynamic and cyclic voltammetry techniques and complemented by X-ray and SEM.

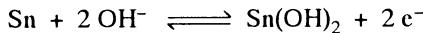
EXPERIMENTAL

The working electrode was made of tin rods (99.999% Johnson Matthey Chemicals Ltd) axially embedded in Araldite holders to obtain exposed circular area of 0.5 cm^2 . Before being used the electrodes were polished successively with emery papers down to 000 grade, degreased with acetone and then rinsed with doubly distilled water. The working electrode was assembled in a five-compartment pyrex glass electrolysis cell. A Pt wire was used as a counter electrode. The potential was measured against a saturated calomel electrode as a reference (SCE) via a salt bridge. Experiments were carried out in Na_2CO_3 solution in absence and in presence of NaCl , NaBr or NaI as a pitting corrodant agents. All solutions were prepared from doubly distilled water and A.R. chemicals and purged with purified nitrogen for 1 h previous to each run. Freshly prepared solution and new polished set of electrodes were used for each run. Runs were carried out at $25 \pm 1^\circ\text{C}$.

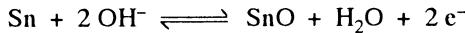
Current density/potential (i/E) profiles at required scan rates (v) between the cathodic (E_{sc}) and the anodic (E_{sa}) switching potentials were recorded by using potentiostatic type Wenking Model POS 73 and X-Y recorder (Series 2000, omnigraphic). SEM observation were made with a Jeol Model JSM 50 A. X-Ray diffraction analysis of the passive layer was carried out using a Philips diffractometer (30 KV, 20 mA) with Fe filter and Co-radiation.

RESULTS AND DISCUSSION

Typical potentiodynamic i/E curves of Sn in various concentrations of Na_2CO_3 solutions (0.01 to 1.0 M) are given in Fig. 1. The curves were swept from $E_{sc} = -2.0 \text{ V}$ to $E_{sa} = 2.0 \text{ V}$ at scan rate $v = 0.03 \text{ V s}^{-1}$. On positive going scan, the cathodic current density decreases continually reaching E_{corr} at zero current density. Each anodic curve exhibits two dissolution peaks I and II, permanent passive and transpassive (peak III) regions prior to oxygen evolution reaction. This behaviour is similar to that observed previously for Sn in alkaline media. Pugh et al.⁹ suggested that for Sn in Na_2CO_3 solutions, the following two reactions:

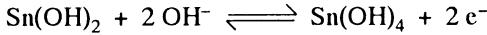


and

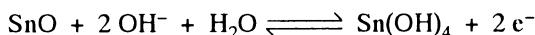


most closely correspond in potential to peak I. Therefore, at the completion of process I, the surface is visualized to be blocked partly by solid $\text{Sn}(\text{OH})_2$ and/or SnO phases and partly due to inactive sites created as a result of CO_3^{2-} adsorption.

In a similar manner, the potential range of peak II may be correlated with the following reactions⁹:



and



It may therefore be concluded that the more general reactions occur within peak II region are the electrooxidation of $\text{Sn}(\text{OH})_2$ and SnO to $\text{Sn}(\text{OH})_4$. In addition, other chemical reactions may take place, some involving chemical dissolution of the hydroxides and oxides to give $\text{Sn}(\text{OH})_4^{2-}$ and $\text{Sn}(\text{OH})_6^{2-}$ complexes, others involving dehydration of both $\text{Sn}(\text{OH})_2$ and $\text{Sn}(\text{OH})_4$ to give the thermodynamically more stable SnO and SnO_2 , respectively, particularly at high anodic potentials².

The permanent passive region extends over a potential range of about 1.0 V. The passive current density, i_{pass} , which flows through this region may correspond to film repairing of chemically dissolved materials. The composition of the passive film found on the surface of Sn potentiodynamically polarized in 0.8 M Na_2CO_3 from $E_{\text{sc}} = -2.0$ to $E_{\text{sa}} = 0.8$ at 0.03 V s⁻¹ was examined by X-ray diffraction. The patterns of X-ray diffraction indicate the existence of both SnO and SnO_2 in the samples examined. These data support the view that the passive film of tin anode in alkaline media is duplex in nature and consists of the two oxides^{3,8}. The transpassive region (peak III) can not be assigned to any particularly anodic oxidation reaction. Several authors^{9,10} attributed the observation of the transpassive region in alkaline media to a solid phase transformation.

Inspection of the data of Fig. 1 reveals that the increase in Na_2CO_3 concentration causes an increase in the heights of peaks I, II and III as well as the value of i_{pass} and shifts corresponding potentials to more negative values. This behaviour can be ex-

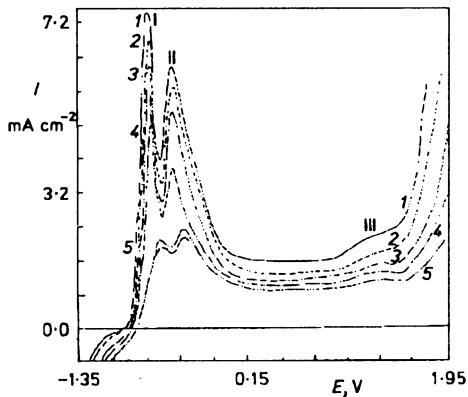


FIG. 1

Potentiodynamic anodic polarization curves of Sn at 0.03 V s⁻¹ in various concentrations of Na_2CO_3 , 1 1.0, 2 0.8, 3 0.4, 4 0.1, 5 0.01 mol dm⁻³

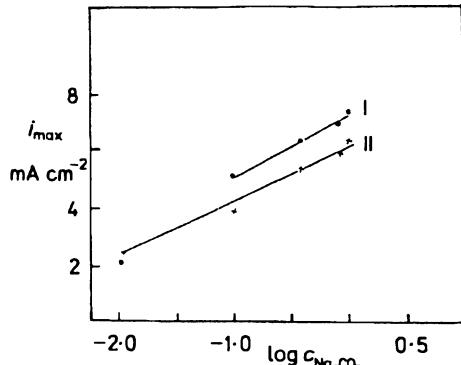


FIG. 2

Dependence of i_{max} of peaks I and II on Na_2CO_3 concentration c (in mol dm⁻³) at 0.03 V s⁻¹

plained in terms of increasing solubilities of Sn(II) and Sn(IV) hydroxides and oxides with increasing OH^- concentration¹². The relations between the peak current density, i_{\max} of peaks I and II vs $\log c_{\text{Na}_2\text{CO}_3}$, is given in Fig. 2. Reasonable linear dependences are shown.

Potentiodynamic polarization curves were also recorded at different scan rates. The data reveal that an increase in the scan rate results in an increase in the anodic current density flowing through the whole range of the anodic polarization curve and enabling the corresponding peak potentials. Plots of peak current density, i_{\max} , of peaks I and II vs $v^{1/2}$ is illustrated in Fig. 3. Linear relationships are obtained and the two lines pass through the origin. These results indicate that the processes I and II are under diffusion control.

Figure 4 shows typical cyclic voltammograms of Sn in 0.8 M Na_2CO_3 at 0.03 V s⁻¹ when $E_{\text{sc}} = -2.0$ V and E_{sa} is stepwise increased from -0.8 V to oxygen evolution potential. Inspection of the results indicates that at $E_{\text{sa}} = -0.8$ V, only one cathodic peak IV is observed. However, on stepwise increasing E_{sa} , a new cathodic peak V tends to appear at first as a hump at the positive potential side of peak IV. The multiplicity of the two cathodic peaks IV and V becomes clearer when E_{sa} becomes closer to oxygen evolution potential. It is probable that the duplex structured anodic layer is electroreduced into two consecutive steps to Sn(II) and to Sn at the potential range of peaks V and IV, respectively. The height of peaks V and IV increases and their potentials shift to more negative direction as E_{sa} increases. It seems that the increase in E_{sa} , increases the stability and protectiveness of the overall anodic layer presumably as a result of dehydration process. The negative shift in cathodic peak potentials confirms the suggestion that dehydration reactions occur with increasing the anodic potential values.

Successive cyclic voltammograms of Sn in 0.8 M Na_2CO_3 were recorded at 0.03 V s⁻¹ between $E_{\text{sc}} = -2.0$ to $E_{\text{sa}} = 1.65$ V. The data are shown in Fig. 5. The results infer that

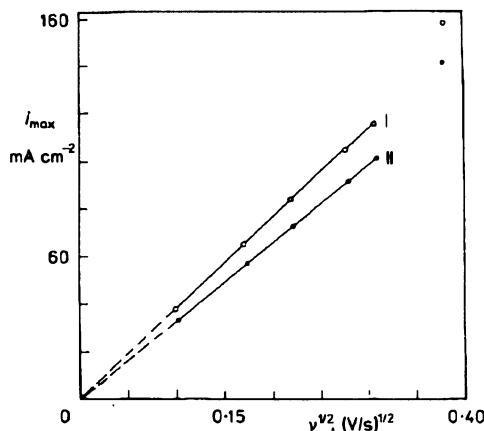


FIG. 3
Dependence of i_{\max} of peaks I and II on $v^{1/2}$ in 0.8 M Na_2CO_3

the amount of charge consumed through the complementary peaks I and IV, and II and V decreases as the number of cycles increase. These results may be due to incomplete reduction of the anodic layer during cathodic sweep. In this case certain amount of the passive film remains unreduced on the electrode surface although the evolution of hydrogen was observed before the end of cathodic sweep.

The effect of adding increasing amounts of Cl^- , Br^- and I^- ions on the corrosion and passivation of Sn anode in 0.01 and 0.8 M Na_2CO_3 were recorded potentiodynamically between $E_{\text{sc}} = -2.0$ V and $E_{\text{sa}} = 2.0$ V. Some results are given in Fig. 6. The presence of the halide ions increases the heights of peak I and II proportionally to c_{X^-} (where $\text{X}^- = \text{Cl}^-$, Br^- or I^-). The data show that peak I is the most affected. The addition of I^- causes the largest effect, Cl^- comes next and the lowest change is due to Br^- . Such effects of the halogens decrease with increasing the concentration of Na_2CO_3 . The stimulation influence of the halogens on the active dissolution of Sn in sodium carbonate solution can be attributed to their direct participation in dissolution processes and formation of

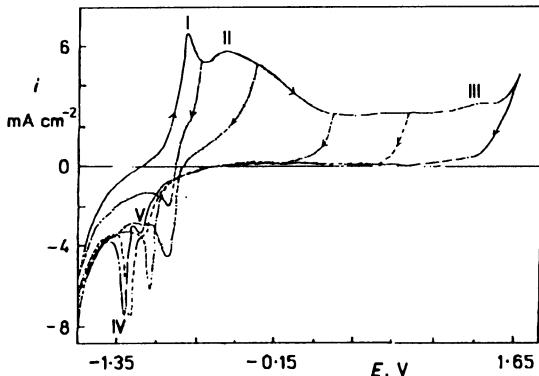


FIG. 4
Influence of increasing E_{sa} stepwise on cyclic voltammograms of Sn in 0.8 M Na_2CO_3 at 0.03 V s^{-1}

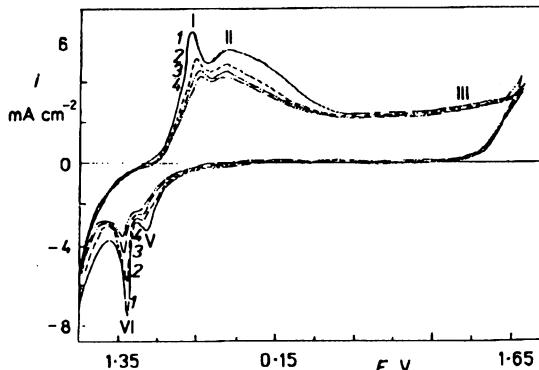


FIG. 5
Influence of successive cycling on cyclic voltammograms (curves 1 - 4) of Sn in 0.8 M Na_2CO_3 at 0.03 V s^{-1} between $E_{\text{sc}} = -2.0$ V and $E_{\text{sa}} = 1.65$ V

soluble complexes¹² of the type SnX_2^- and SnX_6^{2-} . In terms of adsorption model, both OH^- and X^- are likely to become adsorbed on the metal surface forming a potentially active dissolution sites in addition to the inhibited sites occupied by CO_3^{2-} ions. It seems that the subsequent anodic dissolution processes depend to some extent on the relative abundance of OH^- and X^- in the solution.

On the other hand, the presence of the halide ions causes drastic changes in the permanent passive region. The passive current density, i_{pass} , remains nearly constant and then increases abruptly when a critical potential value, E_b , is exceeded denoting film breakdown and pitting corrosion. SEM examination of Sn surfaces potentiodynamically polarized from $E_{\text{sc}} = -2.0$ V to $E_{\text{sa}} = 0.8$ V at 0.03 V s⁻¹ in Na_2CO_3 solutions free from and containing different concentrations of Cl^- was carried out. In presence of Cl^- the data showed the surface to be covered with a high density of pits (as an example Fig. 7). However, in Cl^- free solution the data gave no evidence of pitting.

In the presence of low concentrations of the halide ions, the increased currents are characterized by current oscillations. The oscillatory phenomenon indicates competition between pitting attack, resulting in an increase in the current density and repassivation of the pits resulting in a decrease in the current density. It is observed that the oscillations tend to disappear with increasing halide ion concentration. This means that the presence of a sufficient amount of halide ions is necessary to maintain an actively corroding pits. Similar results have been reported previously^{10,11}.

The increase in X^- concentrations shifts E_b towards more negative values (Fig. 8) according to the following equation:

$$E_b = a - b \log c_{\text{X}^-},$$

where a and b are constants whose values depend on the type of the halide ion, the concentration of the sodium carbonate solution and the scan rate. A closelook at Fig. 8,

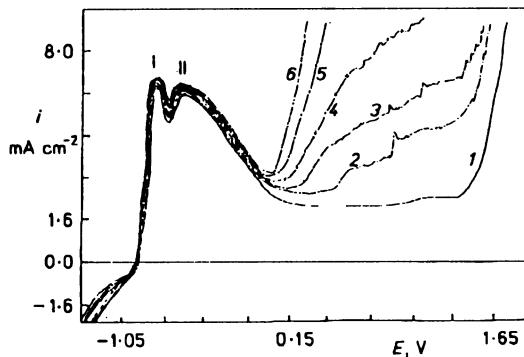


FIG. 6
Potentiodynamic polarization curves of Sn anode in 0.8 M Na_2CO_3 at 0.03 V s⁻¹ between $E_{\text{sc}} = -2.0$ V and $E_{\text{sa}} = 2.0$ V in the presence of various concentrations of NaCl . 1 0.00 , 2 0.01 , 3 0.05 , 4 0.1 , 5 0.2 , 6 0.4 mol dm⁻³

reveals that the aggressiveness of the halides decreases in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. Otherwise as Na_2CO_3 concentration increases, E_b becomes more noble corresponding to increase resistance to pitting. Similarly, a decrease in v results in a marked increase in E_b .

Several authors including Uhlig and co-workers¹³⁻¹⁵, Kolotyrkin¹⁶ and Hoar and Jacob¹⁷ attributed the aggressiveness of the halide ions as a pitting agents to their competitive adsorption on the film surface. In this case, the aggressive ions as well as the passivating species as OH^- and H_2O dipoles are adsorbed simultaneously. Above a critical pitting potential E_b , halide adsorption is favoured and breakdown of passivity occurs. On the other hand, Hoar et al.¹⁸ suggested that the adsorbed aggressive ion can inter and contaminate the passive film. As both the potential and halide ion concentration increase, the protective characteristics of the film decrease. This process implies the depletion of the passivating species and enrichment of the aggressive ions in the film. When the electrostatic field across the film/solution interface reaches a critical value corresponding to E_b , the aggressive ions penetrate the film. Rapid cation aggress occurs and pitting can proceed. Although Br^- and I^- are more polarizable¹⁹ and hence more adsorbable than Cl^- , the latter is the most effective. The ionic radius appears to be an important parameter since the ionic radii decrease in the order²⁰ $\text{I}^- > \text{Br}^- > \text{Cl}^-$, it is reasonable to assume that the smaller Cl^- can penetrate the film more easily.



FIG. 7

Scanning electron micrograph of surface of Sn anode after potentiodynamically treated in 0.1 M Na_2CO_3 containing 0.1 M NaCl , $\times 3500$

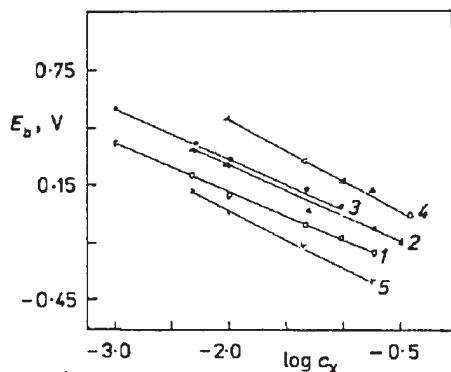


FIG. 8

Dependence of E_b on halide ion concentration c (in mol dm^{-3}): 1 0.01 M $\text{Na}_2\text{CO}_3 + \text{Cl}^-$ at 0.03 V s^{-1} ; 2 0.01 M $\text{Na}_2\text{CO}_3 + \text{Br}^-$ at 0.03 V s^{-1} ; 3 0.01 M $\text{Na}_2\text{CO}_3 + \text{I}^-$ at 0.03 V s^{-1} ; 4 0.8 M $\text{Na}_2\text{CO}_3 + \text{Cl}^-$ at 0.03 V s^{-1} ; 5 0.01 M $\text{Na}_2\text{CO}_3 + \text{Cl}^-$ at 0.10 V s^{-1}

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