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Passivation and pitting corrosion of tin in gluconate solutions and the effect of halide ions

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The passivation and pitting corrosion of tin in sodium gluconate (SG) solutions was studied by using potentiodynamic and cyclic voltammetric techniques. Some samples were examined by X-ray and SEM. The effect of the concentration of gluconate ion, pH, potential scanning rate, successive cyclic voltammetry, switching potential and progressive additions of halide ions on the passivation and pitting corrosion of a tin anode was discussed. The data obtained show that low concentrations of SG have an inhibition effect on the pitting corrosion of tin in neutral media. The pitting corrosion of tin increases with increasing SG concentrations due to the formation of soluble tin–gluconate complex. The critical pitting potential depends on the gluconate ion concentration, pH and scan rate. Two cathodic peaks are observed in the cathodic polarization curve, corresponding to the reduction of the dissolved pitting corrosion products. The critical pitting potential shifts progressively to more negative values with increasing halide ion concentration. In all experiments, the aggressive action of halides decreased in the order $Cl^- > Br^- > I^-$.

1. Introduction

Tin is a moderately corrosion resistant metal, widely employed in the production of tin plate, soft solders, bronze and other alloys. The knowledge of its electrochemical behaviour is, therefore, of considerable interest. The corrosion behaviour of tin has been studied in aqueous solutions [1–12]. Sodium, calcium and zinc salts of gluconic acid have been reported to be successful inhibitors against the corrosion of iron and mild steel in near neutral media [13–17]. There is evidence for an anodic inhibition mechanism by calcium gluconate in sea water [13]. In zinc gluconate solution, a predominant role in inhibiting cathodic oxygen reduction has been attributed to the $Zn(OH)_2$ formed on the cathodic areas [14, 15]. Gluconates are used as scaling inhibitors in cooling water treatment [16]. Gluconic acid is used as a component in sequestering formulations for industrial cooling water control to prevent oxide accumulation and, consequently, underdeposit conditions, owing to its ability to form soluble iron complexes [18]. SG shows an inhibition effect on the dissolution of mild steel in the near neutral media (i.e., low SG concentration) and with increasing SG concentration the anodic dissolution increases. The increase in corrosion rate suggests the formation of a soluble gluconate complex [19, 20]. The present paper examines the inhibition effect of SG on tin pitting corrosion, the stability of the passive film towards pitting corrosion of tin in SG solutions and the influence of the presence of halide anions on the protective layer formed by SG solutions on the tin surface.

2. Experimental details

A rod of tin (99.999% Johnson Matthey GmbH) was used as working electrode; this had an apparent surface area of 0.25 cm^2. Before use the electrodes were polished successively with emery paper down to zero grade, degreased with acetone and then rinsed with doubly distilled water. The working electrode was placed in a five-compartment Pyrex glass electrolysis cell. A platinum sheet was used as a counter electrode. The potential was measured against a saturated calomel electrode (SCE). Experiments were carried out in SG solutions of various concentrations in the absence or presence of NaCl, NaBr or NaI. The required pH was achieved by dropwise addition of standard gluconic acid or NaOH solutions. A Lseibolo Wien pH meter was used to measure pH. All solutions were prepared from bidistilled water and AR chemicals, and purged with purified nitrogen. A new set of polished electrodes was used for each run. All experiments were carried out at room temperature (25 °C). The potentiodynamic and cyclic voltammograms were run on a potentiostat (Wenking model POS 73) which was PC-controlled. X-ray diffraction analysis was carried out using an X-ray diffractometer (Siemenes D500/501). The morphology of the tin surface after treatment was examined by scanning electron microscopy (CamScan, Cambridge).

3. Results and discussion

Figure 1 shows potentiodynamic polarization curves of Sn in various concentrations of SG in the potential ranging from −2000 to 3500 mV vs SCE at a scan rate

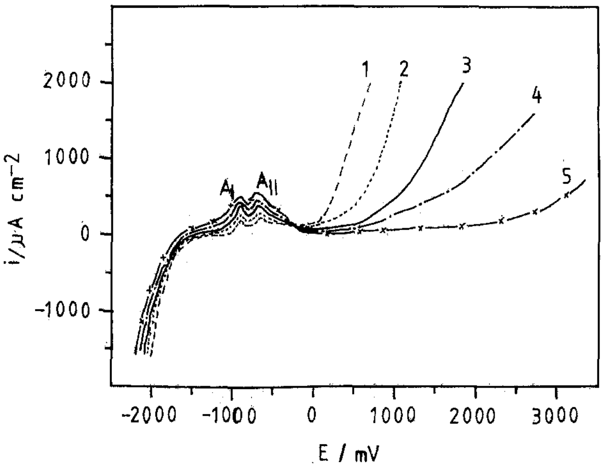

Fig. 1. Anodic potentiodynamic curves for tin in solutions of various concentrations of SG at scan rate 30 mV s^{-1}. Concentrations: (1) 1.0, (2) 0.5, (3) 0.3, (4) 0.1 and (5) 0.001 M.

30 mV s^{-1}. Each anodic curve exhibits two dissolution peaks and a permanent passive region prior to oxygen evolution. As may be expected from the literature and by comparing the measured potentials with the theoretical values for the most probable electrooxidation reactions for tin in aqueous media [5, 21, 22], the inhibition of the anodic dissolution at the first potential peak A_I can be assigned to the electroformation of $Sn(OH)_2$ and/or SnO. The second anodic inhibition process (A_{II}) corresponds to the formation of stannic hydroxide which may take place either by direct oxidation of the metal or by conversion of Sn(II) to Sn(IV). Further polarization (after the A_{II} peak) is accompanied by dehydration of both stannous and stannic hydroxides to give the metastable oxides SnO and SnO_2. The composition of the passive film found on the surface of Sn potentiodynamically polarized in 0.3 mol dm^{-3} SG from −2000 to 1500 mV at 30 mV s^{-1} was examined by X-ray diffraction. The X-ray diffraction data reveal the composite nature of the passive films and confirm the existence of SnO, SnO_2 and Sn in the samples examined. These data support the view that the passive film on tin in alkaline media is duplex in nature and consists of two oxides [5, 11, 23]. A low passivation current density, i_{pass}, in the passive region is in agreement with the assumption that the oxide film is nonporous.

Increase in sodium gluconate concentration causes a decrease in the current peaks A_I and A_{II} and shifts the corresponding potentials to more negative values. When the polarization reaches a certain critical potential, E_{pit}, the passive current suddenly rises steeply without any sign of oxygen evolution denoting breakdown of the passive layer and initiation of visible pitting corrosion. In low concentrations SG, the anodic dissolution is partly inhibited by adsorption of gluconate ions on the metal surface or on the oxide passive film, where the permanent passive region extends over a potential range of about 1.8 V. With increasing SG concentration, E_{pit} shifted in the negative direction (Fig. 1) corresponding to decreased resistance to pitting corrosion. One can speculate that by raising the SG content the stability constant of soluble Sn–G complex is increased and tin corrosion is essentially increased. The same effect, which corresponds to the complex formation, was observed in previous studies [19, 20]. Thus, the resistance of the passive film to pitting corrosion decreases with increasing SG concentration. Figure 2 shows E_{pit} vs log [SG]: a straight line is obtained according to the following equation:

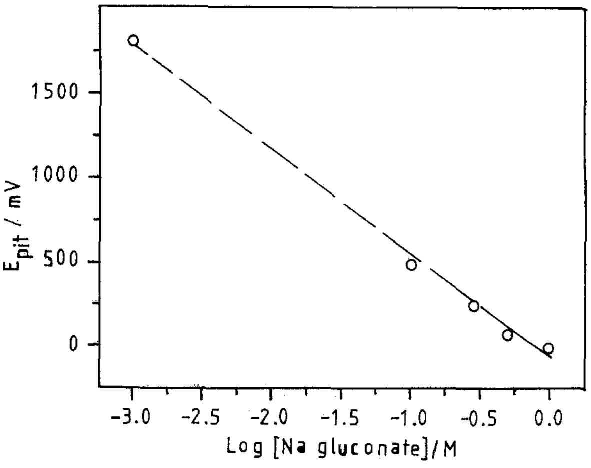

Fig. 2. The dependence of E_{pit} on SG concentration.

$$E_{pit} = a - b \log [\text{gluconate}]$$

where a and b are constants. The value of b was found to be +600 mV. This result shows that the pitting potential of tin in SG solutions depends on the gluconate ion concentration.

The effect of pH on the anodic polarization features for tin in 0.3 mol dm^{-3} SG at 30 mV s^{-1} is illustrated in Fig. 3. The two anodic peaks A_I and A_{II} as well as i_{pass} increase with increasing pH. A new peak, A_{III}, appears at pH > 7.5. This new anodic inhibition process is most probably caused by the formation of $Sn(OH)_3^+$ [10] which leads to precipitation of $Sn(OH)_4$ in the pores of the film. Upon further polarization, anionic activation occurs leading to pit formation on the tin. The pitting potential decreases linearly with increasing pH (Fig. 4). The relation between

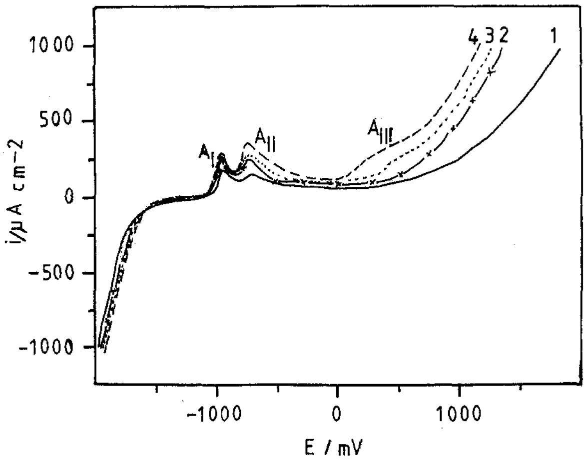

Fig. 3. Anodic potentiodynamic curves for tin in 0.3 mol dm^{-3} SG solutions at various pH values. pH: (1) 5.2, (2) 7.2, (3) 8.5 and (4) 10.2.

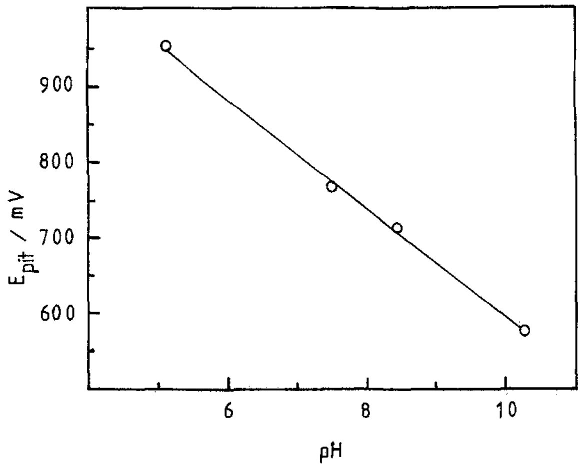

Fig. 4. Dependence of E_{pit} on pH.

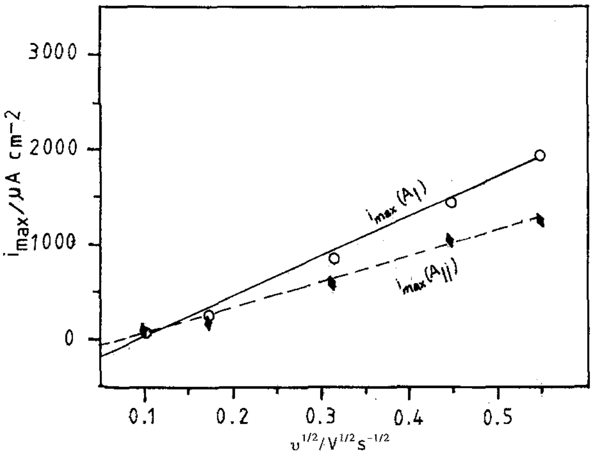

Fig. 6. Dependence of height of the anodic peaks A′ and A″ on $\nu^{0.5}$.

the pitting potential and the pH of the medium is

$$E_{pit} = a - b \text{ pH}$$

where a and b are constants. The value of b was found to be +76 mV. These results show that, with increasing pH, the stability of the passive film against pitting corrosion decreases. In acidic medium the Sn(II) ion is bound into a complex via a ligand carboxyl group, and the stability constants have relatively low values ($\log k_1 = 3.01$ and $\log k_2 = 2.28$) [24], but in alkaline medium coordination on the secondary alcohol group is followed by liberation of a proton. Formation of chalet rings is also possible in this case. Thus the stability constant values are higher [24]. Initiation of pitting corrosion can be attributed to adsorption of G ions at adsorption sites on the oxide covered surface. With increasing G concentration (i.e., increasing pH) and at the pitting potential, the G ions react with the passivating species (passive layer species) to form the Sn–G complex at some locations and promotes local anodic dissolution, thereby resulting in pit nucleation. Following this, pit propagation occurs rapidly due to an increase in G concentration resulting from its migration to the pits.

Figure 5 shows the potentiodynamic profiles recorded for tin in 0.3 mol dm^{-3} SG at 30 mV s^{-1} at different anodic end points (E_{sa}) when $-850 < E_{sa} < 300$ mV. On reversing the potential scan after peak A_I is formed, only one cathodic peak C_I is observed. On the other hand on stepwise increase of E_{sa}, a new cathodic peak C_{II} appears, at first as a hump (curve 5), and then as a sharp peak in the positive potential side of peak C_I. It is probable that the anodic layer is electroreduced in two consecutive steps to Sn(II) and to Sn in the potential range of peaks C_I and C_{II}, respectively. The cathodic current density of the C_I and C_{II} peaks increases and shifts in the negative direction with increasing E_{sa}. This can be explained by the increasing stability and protectiveness of the anodic layer as a result of dehydration. Polarization curves were also recorded at different scan rates in 0.3 mol dm^{-3} SG in the potential range −2000 to 2000 mV. Increase in the scan rate leads to an increase in the anodic current density throughout the anodic polarization curve and the potential of peaks A_I and A_{II} shifts to more positive values. Fig. 6 shows that the current peaks A_I and A_{II} vary linearly with the square root of the potential sweep rate and the two lines pass near to the origin. This indicates that the peaks are due to a dissolution process controlled by diffusion.

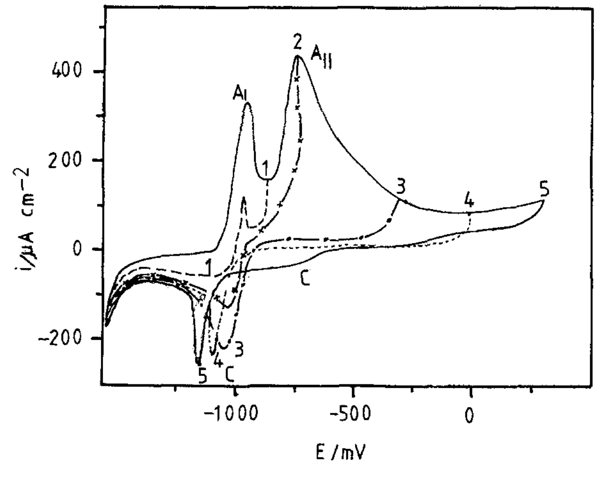

Fig. 5. Cycling voltammograms of tin in 0.3 mol dm^{-3} SG. Runs started from −2000 mV and reversed at various potentials. E_{sa}: (1) −0.85, (2) −0.72, (3) −0.32, (4) 0 and (5) 0.3 V.

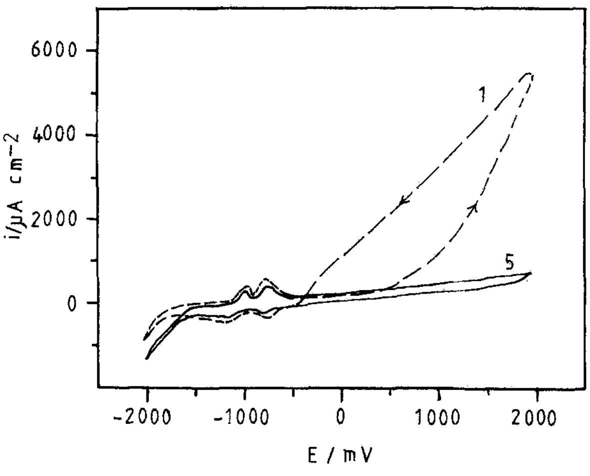

Fig. 7. Successive cycling voltammograms of tin electrode between −2000 and 2000 mV at 30 mV s^{-1}. The numbers on the curves denote the cycle number.

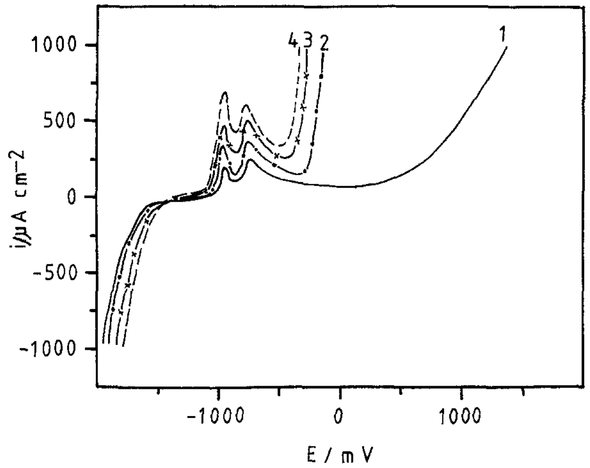

Fig. 8. Anodic potentiodynamic polarization of tin anode in 0.3 mol dm^{-3} SG at 30 mV s^{-1} in the presence of various concentrations of NaCl. [NaCl]: (1) 0, (2) 0.01, (3) 0.1 and (4) 0.4 M.

The cyclic voltammograms of Sn in 0.3 mol dm^{-3} SG at scan rate 30 mV s^{-1} was repeated in the range −2000 to 2000 mV for five cycles, as shown in Fig. 7. The results indicate that the amount of charge consumed in the anodic and cathodic peaks decreases as the number of cycles increases. This may be due to sluggish discharge process, caused by the increase in the resistance of the oxide film against the completion of the discharge (reduction) process. This means that some of the passive film remains unreduced.

The effect of halide ions (Cl^-, Br^- and I^-) on the passivation of an Sn anode in 0.3 mol dm^{-3} SG were investigated potentiodynamically at a scan rate of 30 mV s^{-1} between −2000 and 2000 mV. Figure 8 is an example. The increase in halide concentration increases both the anodic current peaks A_I and A_{II} with slight shift of the corresponding potentials in the active (negative) direction and increases the passivation current (i_{pass}), indicating that the presence of these ions decreases the inhibition and protection effect of Sn by SG solutions. The magnitude of the change in the current peaks and corresponding potential is in the following order $Cl^- > Br^- > I^-$. The effect of halogens can be attributed to their direct participation in dissolution processes and the formation of soluble complexes [25] of the type SnX_3^- and SnX_6^{2-}, and the adsorption of X^- on the surface, forming potentially active dissolution sites. SEM examination of Sn surfaces potentiodynamically polarized from −2000 to 2500 mV at a scan rate at 30 mV s^{-1} in SG solutions free from, and containing, Cl^- ions were carried out. In the presence of Cl^- the surface is covered with a high density of pits (Fig. 10). The effect of the halides on the pitting potential is in the order $Cl^- > Br^- > I^-$ (Fig. 9). This may be ascribed to the variation in the polarizabilities of these ions, which are in the order $I^- > Br^- > Cl^-$ [26]. The more polarizable anion forms the more stable complex. The aggressiveness of the halide ions as pitting agents may be attributed [27] to their competitive adsorption with the passivating species as OH^- and H_2O on the surface of the passive film. When the applied potential reaches E_{pit}, the aggressive ions penetrate the film and pitting proceeds. After E_{pit}, the halide adsorption is favoured and breakdown of passivity occurs. As both the potential and halide ion concentration increase, the protective characteristics of the film decrease.

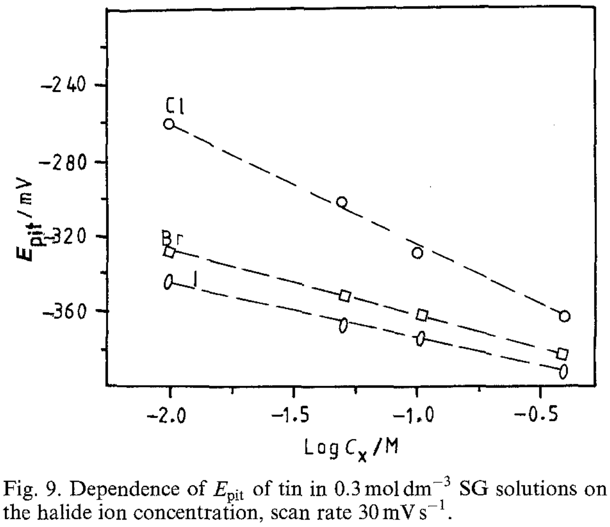

Fig. 9. Dependence of E_{pit} of tin in 0.3 mol dm^{-3} SG solutions on the halide ion concentration, scan rate 30 mV s^{-1}.

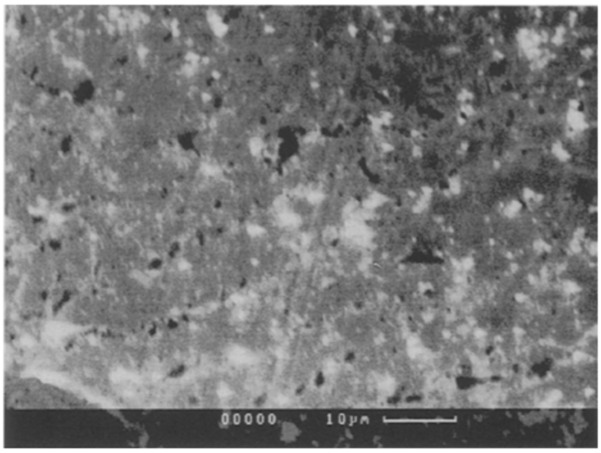

Fig. 10. Scanning electron micrograph of the surface of tin anode after scanning at 30 mV s^{-1} from −2000 to −500 mV in 0.3 mol dm^{-3} SG solution containing 0.4 mol dm^{-3} NaCl.

4. Conclusion

The potentiodynamic polarization measurements revealed that sodium gluconate has an inhibitive effect on the pitting corrosion of tin in near neutral media. In low concentration solutions the anodic reaction is inhibited by the adsorption of G on the oxide layer or on the metal surface. At higher G concentration, E_{pit} shifted in the negative direction, corresponding to decreased resistance to pitting corrosion. The corresponding increased pitting corrosion must arise from the formation of soluble Sn–G complex. It may be concluded that SG may be successfully applied as an inhibitor for tin in near neutral media. SG has the advantage of being harmless to the environment and non toxic. Increase in halide concentration increases the rate of metal dissolution, the pitting corrosion and the passivation currents, indicating that the presence of these anions decreases the inhibition effect of Sn at low SG concentration in near neutral media.

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