The Anodic Oxidation of Metals at Very Low Current Density. Part VI.* Tin.

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The anodic oxidation of tin at very low current density is examined in solutions of different pH values. It is shown that in weakly alkaline electrolytes the tin anode becomes passive. The initial stage in this process is the formation of a layer 1—2 molecules thick of stannous hydroxide on the electrode surface which is further oxidised to stannic hydroxide before evolution of oxygen. In strongly alkaline, neutral, and acid solutions no passivation occurs at such very low current densities. In nitric acid solutions two types of passivity, chemical and electrochemical, are found to take place.

IN continuation of previous work (El Wakkad and Emara, *J.*, 1952, 461; 1953, 3504, 3508), the anodic oxidation of tin at very low current density has been investigated. No previous work on tin from the present standpoint has been published but other methods of investigation have yielded some indirect although somewhat conflicting information; thus Schon (*Z. anal. Chem.*, 1871, **10**, 291) showed that tin becomes passive in nitric acid when in contact with platinum. Foerster and Dolch (*Z. Elektrochem.*, 1909, **16**, 559) found that tin anodes passed into sodium hydroxide solutions as bivalent ions until a definite concentration was attained and then the potential changed almost instantaneously to a more positive value and the dissolved tin was oxidised to the quadrivalent state and oxygen was liberated at the anode, which had become passive. Valessi (*Boll. Soc. Eustachiana*, 1933, **31**; *Chem. Zentr.*, 1933, II, 2318), on the other hand, found that tin anodes in sodium hydroxide solutions dissolved directly as sodium stannite and sodium stannate. Newbery (*J.*, 1916, 1066) found that tin showed no passivity in acid electrolytes but readily became passive in alkaline solutions, and Rothmund (*Z. physikal. Chem.*, 1924, **110**, 384) and Steinherz (*Z. Elektrochem.*, 1924, **30**, 279) found that tin could be made passive in sulphuric, hydrochloric, hydriodic, hydrobromic, and hydrofluoric but not in nitric, iodic, perchloric, and acetic acids. Knowlton (*J. Phys. Chem.*, 1928, **32**, 1572) considered the passivation of tin in nitric acid to be due to formation of oxide film and not to that of stannic nitrate. Kerr (*J. Soc. Chem. Ind.*, 1938, **57**, 405) studied the anodic films formed on tin in sodium hydroxide solution. He found that at lower temperatures a brown film was formed, whereas at higher temperatures a yellow film was obtained. Analysis of the brown film gave SnO_2, 80·9; SnO, 9·3; H_2O, 9·8%, and that of the yellow film gave SnO_2, 68·5; SnO, 12·4; H_2O, 19·1%. Bianchi (*Chimica e l'Industria*, 1947, **29**, 295) studied the anodic passivation of tin in alkaline solutions and three different types of films were noticed on the passive metal; this colour varied from dark to light brown depending on the current density used.

The results of investigations on the nature of films formed on metallic tin, when exposed to or heated in air or oxygen, seem to indicate that on the surface of the metal stannous oxide is first formed, then stannic oxide (Steinheil, *Ann. Physik*, 1934, **19**, 465).

In the present study it is shown that in weakly alkaline electrolytes tin anodes at very low current densities become passive. The initial stage in this process is the formation of a layer 1—2 molecules thick of $Sn(OH)_2$ on the electrode surface, and this is further oxidised to $Sn(OH)_4$ before evolution of oxygen. In strongly alkaline, neutral, and acid solutions no passivation occurs at such very low current densities. In nitric acid solutions two types of passivity take place, chemical and electrochemical.

EXPERIMENTAL

The electrical circuit and the electrolytic cell used were as previously described (El Wakkad and Emara, *J.*, 1952, 461). The tin anodes were prepared by electrodeposition from a bath prepared by dissolving 2·8 g. of $SnCl_2,2H_2O$ in 40 ml. of 2N-sodium hydroxide. Deposition

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* Part V, preceding paper.

was carried out at a current of 15 mA/electrode for 20 min. at 80° on a platinum foil of 1 cm.² apparent area. The deposited tin was in a spongy form, so direct measurement on the variation of its potential when polarising it anodically at very low current density was possible. The tin electrode was washed several times with conductivity water, and then with the solution in which it was to be studied before it was introduced into its compartment in the electrolytic cell. Each experiment was carried out with a freshly prepared electrode from a fresh bath. The anode was placed in such a position with respect to the cathode as to ensure uniform distribution of the polarising current at the anode surface. The cathode was a platinum spiral about 10 cm. long and 0·1 cm. in diameter.

Measurements have been carried out mainly in 0·1M-sodium borate (pH 9·2) with use of a polarising current of 20 μA/electrode, in 0·1M-sodium carbonate solution (pH 11·5) with a polarising current of 200 μA/electrode, in 0·1N-sodium hydroxide (pH 13), in the phosphate–citric acid neutral buffer solution of pH 7, in 0·1M-sodium sulphate solution of pH 7, and in 0·1N-hydrochloric acid (pH 1). In the last four solutions the polarising currents used were 200—400 μA per electrode. The behaviour of the tin anode in 0·1N-nitric acid was also studied by use of a polarising current of 400 μA/electrode. The solution in the cell was boiled before use and cooled in an atmosphere of pure nitrogen to remove dissolved oxygen. The detailed experimental procedure for obtaining the anodic, the cathodic, and the decay curves was essentially as described before (El Wakkad and Emara, *loc. cit.*). In the case of nitric acid solution two procedures were adopted in obtaining the anodic curves; the first was the usual one, and in the second the tin electrode was immersed under cathodic current, *i.e.*, the current was switched cathodically on the electrode before dipping it in the solution. The polarising current was then reversed to start the anodic polarisation.
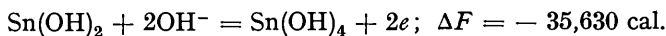
RESULTS AND DISCUSSION

Curve *A*, Fig. 1, is the characteristic anodic polarisation curve of tin at 25° with a polarising current of 200 μA in 0·1M-sodium carbonate. Curve *A*, Fig. 2, is the same anodic polarisation curve in sodium borate solution of pH 9·2 for a polarising current of 20 μA. From these curves, which show the variation of the potential of the tin anode with the quantity of electricity passed, it can be seen that, at first, there is a rapid initial build-up of potential, ascribed, by analogy with the cases previously studied (El Wakkad and Emara, *locc. cit.*), to the charging of the double layer which is followed by two well-defined arrests before oxygen evolution. Measurements from a large number of polarisation curves gave an average value for the double-layer capacity of ∼1600 μF/electrode for the tin anode under investigation in the carbonate solution of pH 11·5. In the borate solution of pH 9·2, the average value was ∼6700 μF/electrode.

The standard condition was taken to be the borate solution since in this solution the oxides of tin possess minimum solubilities. The first arrest after the charging of the double layer appears to start at −0·74 v in sodium carbonate solution and at −0·61 v in the borate solution. The second arrest appears to start at −0·62 and −0·53 v in the two solutions respectively.

In the following table are shown the starting potentials of these two arrests in the two electrolytes as compared with the equilibrium potentials of the systems Sn–Sn(OH)$_2$ and Sn(OH)$_2$–Sn(OH)$_4$ at the corresponding pH values. These equilibrium potentials were obtained as follows : The free energies of stannous hydroxide, stannic hydroxide, and hydroxyl ions being taken as −115,200, −226,000, and −37,585 cal., respectively (Latimer, "The Oxidation States of Elements and their Potentials in Aqueous Solutions," New York, 1938, p. 137), the free-energy changes of the reactions

$$Sn + 2OH^- = Sn(OH)_2 + 2e; \quad \Delta F = -40,030 \text{ cal.}$$

and
$$Sn(OH)_2 + 2OH^- = Sn(OH)_4 + 2e; \quad \Delta F = -35,630 \text{ cal.}$$

give $E_B°$ (the potential value at the extreme alkaline range of pH) as −0·87 v and −0·77 v for the two systems, respectively.

By applying the ordinary equation for the variation of the potential of these systems with pH. the values shown in cols. 4 and 5 in the following table were obtained. The

very close agreement between the first and the second arrests and the equilibrium values for the two systems leaves little doubt that these two steps in the anodic polarisation in such solutions correspond to the consecutive formation of stannous hydroxide or oxide and stannic hydroxide or oxide on the tin anode before evolution of oxygen.

Solution	Starting potential of the first arrest, v	Starting potential of the second arrest, v	Equilibrium potential of the system $Sn-Sn(OH)_2$, v	Equilibrium potential of the system $Sn(OH)_2-Sn(OH)_4$, v
0·1M-Carbonate	−0·74	−0·62	−0·72	−0·62
0·1M-Borate ...	−0·61	−0·53	−0·58	−0·48

The quantity of electricity passed from the beginning to the end of the first step in the borate solution was found to be about 30,000 μc/electrode. This is sufficient for the liber-
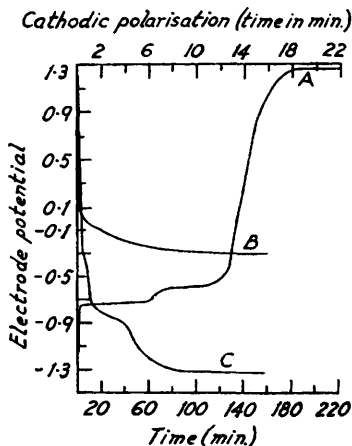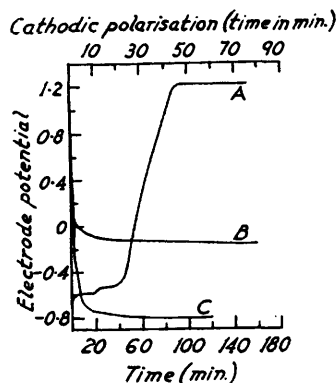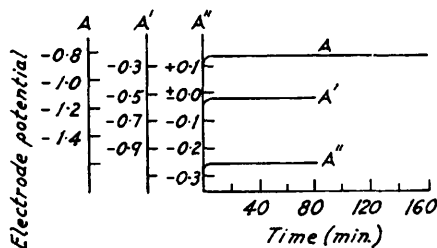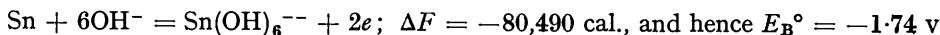
FIG. 1.

FIG. 2.

FIG. 3.

ation of about $9·42 \times 10^{16}$ atoms of oxygen. The diameter of the tin atom being taken as $3·04 \times 10^{-8}$ cm. (from specific gravity), there would be about $1·08 \times 10^{15}$ atoms of tin per true sq. cm. at the tin surface. A rather rough estimate for the ratio of the real to the apparent area of the tin anode under investigation can be obtained from the value of the capacity of the double layer at the anode under the standard conditions and comparison of this with the capacity of the real area which is estimated from previous studies as 100 μF/true sq. cm. (El Wakkad and Emara, *locc. cit.*). This gives the value of 67 : 1 for the ratio real : apparent area of our tin anode, and hence there would be about $7·24 \times 10^{16}$ atoms of tin on the whole surface of our electrode. This shows that the quantity of electricity passed in the first step corresponds to the formation of a stannous hydroxide film 1—2 molecules thick.

The quantity of electricity passed in the second step is of the same order as that of the first step, suggesting the conversion of stannous hydroxide or oxide into stannic hydroxide or oxide.
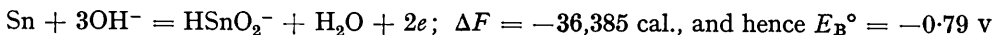
In 0·1N-sodium hydroxide solution, curve A, Fig. 3, the result indicates anodic dissolution at $-0·84$ v. This is in very close agreement with the potential of the system $Sn-Sn(OH)_2$ at the corresponding pH value, *viz.*, $-0·81$ v, which suggests that the anodically formed stannous hydroxide is freely soluble in the alkaline hydroxide.

Calculation of the standard potentials of the systems $Sn-Sn(OH)_6^{--}$ and $Sn-HSnO_2^-$ gives the following interesting results :

The free energies of $Sn(OH)_6^{--}$, $HSnO_2^-$, water, and hydroxyl ion being taken as $-306,000$, $-92,450$, $-56,690$, and $-37,575$ cal., respectively (Latimer, *op. cit.*), the free-energy changes of the reactions are

$$Sn + 6OH^- = Sn(OH)_6^{--} + 2e; \quad \Delta F = -80,490 \text{ cal., and hence } E_B° = -1·74 \text{ v}$$

and

$$Sn + 3OH^- = HSnO_2^- + H_2O + 2e; \quad \Delta F = -36,385 \text{ cal., and hence } E_B° = -0·79 \text{ v}$$

This suggests that, although in alkaline solutions the stannous hydroxide is expected to be freely soluble (curve A, Fig. 3) to form the stannite, yet as the standard potential of the

FIG. 4.

FIG. 5.
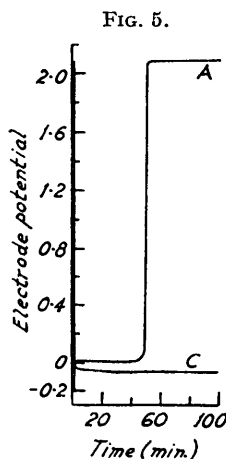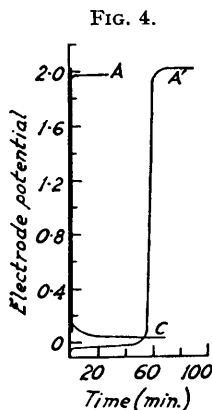
system tin–stannite is more positive than the corresponding potential of tin–stannate, one must expect that the former in such alkaline solutions is unstable, decomposing to the stannate.

For solutions of pH 7 (curve A', Fig. 3), the results indicate anodic dissolution of tin at $-0·45$ v, which is in very close agreement with the potential of the system $Sn-Sn(OH)_2$ at the corresponding pH value. In 0·1N-hydrochloric acid (curve A'', Fig. 3), the results also indicate anodic dissolution of tin at about its reversible potential.

The passivation of tin in 0·1N-nitric acid solution is of great interest. Curves A and A', Fig. 4, show the characteristic anodic polarisation curves of tin in such a solution with a current of 400 μA/electrode. Curve A was obtained by the usual procedure, but curve A' was obtained by the modified procedure in which the current was switched on cathodically before the tin electrode was dipped into the nitric acid solution. From curve A, Fig. 4, it can be seen that the potential of the electrode jumped directly from the hydrogen- to the oxygen-evolution values as soon as the anodic polarisation started. This indicates that in the usual procedure the tin electrode became passive as soon as it was dipped in the nitric acid solution; the cathodic treatment was not able to activate the electrode, and thus when the polarising current was reversed to start the anodic polarisation the potential of the anode jumped directly to the oxygen-evolution value. Further evidence for this view comes from the fact that the constant potential registered when the electrode was polarised cathodically before starting the anodic polarisation under these conditions coincided with the potential of the system $Sn-Sn(OH)_2$ at the corresponding pH value.

With the modified procedure, although the constant potential registered when the elec-

trode was polarised cathodically was found to coincide also with the Sn–Sn(OH)$_2$ potential at the corresponding pH value, yet when the polarising current was reversed anodically, the potential of the electrode did not jump directly to the oxygen-evolution value, but a well-defined step appeared, indicating oxide formation. This step started at a potential approaching that of the system Sn(OH)$_2$–Sn(OH)$_4$, where it remained for a comparatively long time, after which the potential changed to the oxygen-evolution value. These results indicate two types of passivity : chemical passivity by the action of nitric acid, and electrochemical passivity by the anodic current. When the tin electrode was dipped in the nitric acid solution it became passive by chemical means; the cathodic polarisation of the electrode was then unable to reduce the oxide formed, since the rate of reduction was less than the rate of oxidation. When the polarising current was reversed anodically, the potential of the electrode jumped directly to the oxygen-evolution value. On the other hand when the current was switched on to the electrode cathodically before dipping it in the nitric acid solution, the chemical passivity was greatly reduced and a definite step appeared on the anodic polarisation.

One must expect that, if this is the case, when a higher polarising current is switched on to the electrode cathodically before dipping it in the nitric acid solution, the chemical passivity will be still greatly reduced and the quantity of electricity passed during the anodic polarisation for the oxide formation will be greatly increased. Curve *A*, Fig. 5, shows the result obtained when a polarising current of 1·5 mA/electrode was switched on to the tin electrode cathodically before it was dipped in the nitric acid solution. From this curve it is clear that the tin-cathode potential is then more negative than in the other two cases. When the polarising current of 1·5 mA/electrode was reversed to start the anodic polarisation, a well-defined step appeared, starting at the potential of the system Sn–Sn(OH)$_2$, and changed rather quickly with such comparatively high polarising current to that of Sn(OH)$_2$–Sn(OH)$_4$ before rising to the oxygen-evolution value. The quantity of electricity passed in the step of oxide formation is comparatively greater than in the previous cases, confirming our view.

The anodic decay (curves *B*, Figs. 1 and 2) reveals that, on interruption of the polarising current when the anode is at the oxygen-evolution potential, the potential dropped to a value somewhat more positive than the corresponding value of the sytem Sn(OH)$_2$–Sn(OH)$_4$, and then changed—although very slowly—towards the potential of the above system. This is reached after a period varying between 18 and 24 hr.

The cathodic curves (curves *C*, Figs. 1 and 2) reveal the reduction of stannic and stannous hydroxides before hydrogen evolution. In the case of sodium carbonate solution, curve *C*, Fig. 1, the two reduction steps are quite clear and started at the reversible potentials of the systems Sn(OH)$_4$–Sn(OH)$_2$ and Sn(OH)$_2$–Sn. In the borax solution, curve *C*, Fig. 2, the reduction steps were less clear.

The cathodic curves obtained for the nitric acid solution, curves *C*, Figs. 4 and 5, show that the potential of the electrode dropped directly to the value of the system Sn(OH)$_2$–Sn(OH)$_4$, where it remained constant.

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