The Anodic Behavior of Tin in an Alkaline Solution

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(Received February 1, 1962)

In this paper, the anodic behavior of tin in an alkaline solution will be described.

Lowenheim¹⁾ demonstrated that tin is anodically polarized through two potential stages in an alkaline solution. In the first stage, the anodic film of tin dissolves into the alkaline solution to form stannite ions at a relatively less noble potential. In the second stage, the anode becomes passive and shows quite a noble potential. Wakked²⁾ observed the same two stages, and he also showed that the film in the first stage consists of stannous hydroxide.

In contrast with the results of these previous investigators, in the present experiment the author has found three clearly distinguishable potential stages in the anodic polarization curves. This paper presents not only the polarization curves but also the nature of the film in each stage. The rate-determining step in the anodic dissolution process is also discussed.

Experimental

The study of the anodic polarization curves was carried out in a 100 ml. beaker containing a sodium hydroxide solution. The anode was polarized against a platinum cathode, and the anodic potentials were measured against a Hg-HgO reference electrode. The cell was sealed from the atmosphere and was so constructed as to bubble nitrogen or oxygen gas into the electrolytic solution through finely sintered glass.

A circular tin plate was used as the anode. Before being used, this specimen was polished with different grades of emery paper, and then its surface was rubbed with degreased cotton which had been wet by hot water. Finally it was rinsed with ethyl alcohol. Immediately after this treatment, the specimen was placed between two methacrylic resin plates. One of the plates had a circular hole, 0.3 cm^2 in area; this sized area was, therefore, exposed to the electrolytic solution as an anodically polarized electrode.

Results and Discussion

The Anodic Polarization Curves.—The anodic polarization curves of tin in a 0.1 N sodium hydroxide solution are shown in Fig. 1. It may be seen that these curves show three stages of dissolution potentials.

In order to examine the current efficiency and potential variation with time, experiments on the anodic dissolution of tin were carried out for several hours, under constant current densities at the potentials selected within the potential ranges of each stage in Fig. 1. These results are shown in Figs. 2 and 3.

In addition to these experiments, reversible

Part of this paper was reported in *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 1488 (1959); **64**, 851 (1961).

1) F. A. Lowenheim, *Metal Finishing*, **49**, 60 (1951).

2) S. E. S. E. L. Wakked, *J. Chem. Soc.*, **1954**, 3103.

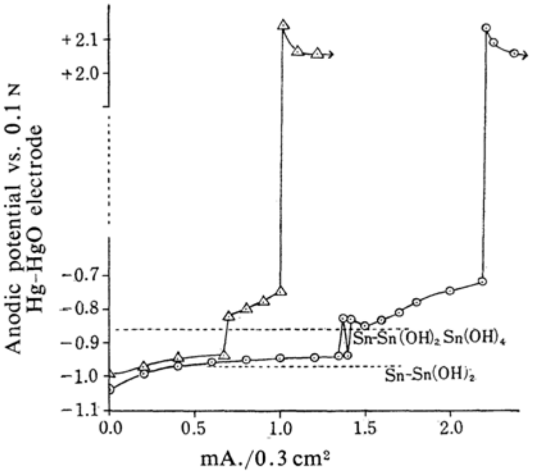

Fig. 1. Anodic polarization curves in 0.1 N sodium hydroxide solution at 25°C.
⊙ N_2 atmosphere △ O_2 atmosphere

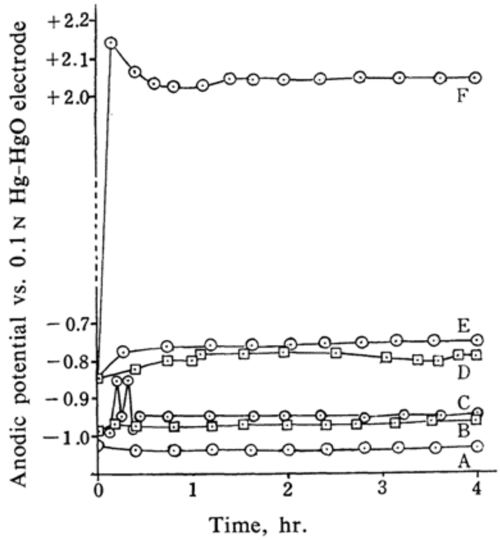

Fig. 2. Potential-time curves at constant current densities in nitrogen atmosphere.
A: 0 mA (simple immersion)
B: 0.6 mA, Curr. eff.=106.0%
C: 0.9 mA, Curr. eff.=103.2%
D: 1.5 mA, Curr. eff.=79.0%
E: 2.0 mA, Curr. eff.=77.6%
F: 2.2 mA, Curr. eff.=7.6%

potentials calculated from thermodynamic data[3] were taken into consideration. These values are given in Table I.

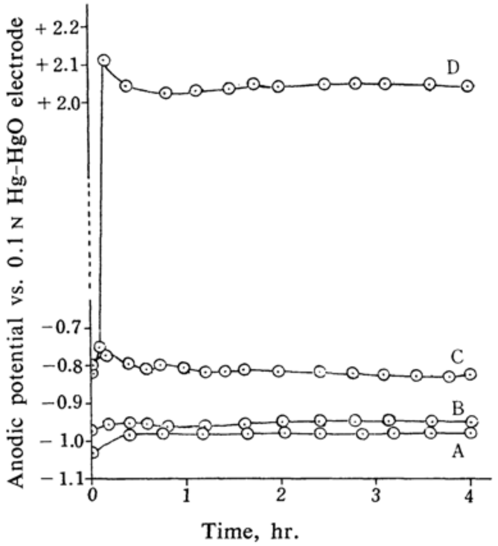

Fig. 3. Potential-time curves at constant current densities in oxygen atmosphere.
A: 0 mA (simple immersion)
B: 0.3 mA, Curr. eff.=162.3%
C: 0.9 mA, Curr. eff.=96.5%
D: 1.0 mA, Curr. eff.=10.0%

TABLE I. REVERSIBLE POTENTIALS OF HALF CELLS CALCULATED EROM FREE ENERGY

Half cell	Potential vs. Hg-HgO-0.1 N NaOH V.
Sn-$Sn(OH)_2$-0.1 N NaOH	−0.973
$Sn(OH)_2$-$Sn(OH)_4$-0.1 N NaOH	−0.873
Sn-$Sn(OH)_4$-0.1 N NaOH	−0.923
Sn-SnO-0.1 N NaOH	−1.036
SnO-SnO_2-0.1 N NaOH	−1.193

It will be seen from Fig. 1 that potentials in the former two stages nearly correspond to those listed in the first and the second lines, respectively, of Table I although the experimental values are slightly more noble than the table values. In the third stage, however, the anode indicates its passive state; here the potential becomes considerably more noble compared with any value listed in Table I. Since the first line of Table I shows the reversible potential value of the tin-stannous hydroxide system, the anodic film in the first stage seems to be stannous hydroxide. This was supported by the fact, shown in Fig. 2, that the current efficiencies in the first stage were nearly equal to 100%, if the current efficiencies were determined from the actual weight loss of anode and from the theoretical weight loss calculated by Faraday's law, assuming that tin was dissolved as a divalent species, i. e., stannous ion. In another experiment, the concentration of stannite ion and the total of tin in the electrolytic solution were determined after the electrolysis; the ratio between the two was found to be 0.9. This provides another evidence as to the nature of the anodic film mentioned above.

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[3] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions", Prentice-Hall Inc., New York (1952), p. 148.

In the second stage, the potential nearly corresponds to that of the stannous hydroxide-stannic hydroxide system, as can be seen from Table I. This result may allow us to suppose that the film consists of stannic hydroxide under which stannous hydroxide is present. However, it was found from the experiment represented by Fig. 2 that the film dissolved into both stannite and stannate ions, since the current efficiencies in that stage were about 70 to 80% and the ratio, defined as before, was about 0.64 in a nitrogen atmosphere. Moreover, the film did not have the characteristic white appearance of stannic hydroxide, but, rather, was black. The film in the second stage, therefore, can not be stannic hydroxide; it is more appropriate to consider that the film consists of some sorts of reaction products from stannic and stannous hydroxides. In order to ascertain this, another experiment was performed in which four kinds of half cells were constructed from freshly prepared components. The potentials of these cells are tabulated in Table II. The results indicate that the potential at the second stage in Fig. 1 approximately coincides with that of the third line in the table, although the former potential is slightly more noble than the latter, probably owing to ohmic polarization. This confirms the reasonableness of the consideration described above.

TABLE II. POTENTIALS OF HALF CELLS WHICH WERE FRESHLY PREPARED

Half cell	Potential vs. Hg-HgO-0.1 N NaOH V.
Sn-$Sn(OH)_2$-0.1 N NaOH	−0.980
Sn-$Sn(OH)_4$-0.1 N NaOH	−0.73∼−0.75
Sn-$Sn(OH)_2$ and $Sn(OH)_4$ mix. −0.1 N NaOH	−0.86∼−0.89

Some other knowledge of the nature of the film can be derived from Figs. 2 and 3. As can be seen from Fig. 2, the open circuit potential of tin in a nitrogen atmosphere is the same as that of the fourth line in Table I, so that a protective layer of stannous oxide, which is sparingly soluble, may be presumed to exist on the tin surface. In an oxygen atmosphere, however, the open circuit potential corresponds well to that of the first lines in both Tables I and II. This indicates that stannous hydroxide is present on the tin surface even as a result of simple immersion; thus, it can easily be supposed that stannous hydroxide is formed not only by electrochemical reaction but also by chemical reaction. The abnormally high current efficiency, over 100% in the oxygen atmosphere, as shown in Fig. 3, can be attributed to such a chemical process. It may also be found from Figs. 2 and 3 that a long duration of electrolysis at the first or the second stage does not give any passivity to the anode which might be caused by the growth of the film.

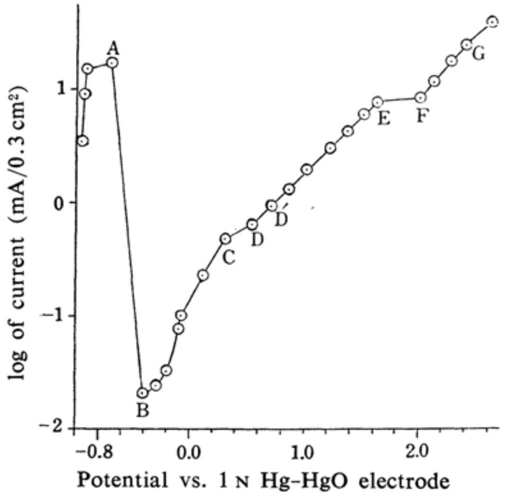

Fig. 4. Anodic polarization curve in 1.0 N sodium hydroxide solution.
A : Point just before passivation
B : Frade potential
C : Point adopted for investigation of decay curve
D : Reversible potential for oxygen evolution
D′: Oxygen evolution was actually observed.

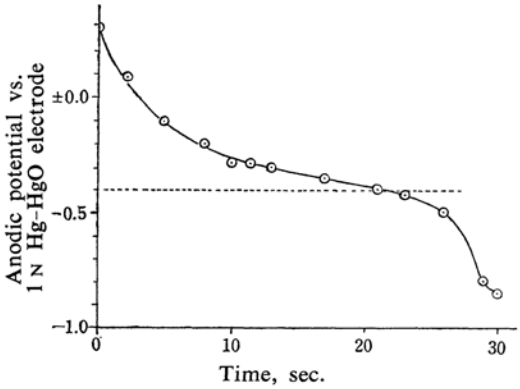

Fig. 5. Decay curve after cutting off the current at C in Fig. 4.

When the current density was increased beyond the second stage to reach the third stage, passivation occurred in which oxygen evolved at the anode. The process of this passivation can be more clearly observed in Fig. 4, in which the logarithm of current density is plotted against the anodic potential. The potential bordered on activation and passivation, which is generally known as the Frade potential, can be seen to be −0.400 V.

vs. the 1 N Hg–HgO reference electrode, which is indicated at B in Fig. 4. A decay curve of the potential after the current at C in Fig. 4 had been cut off was also drawn from the measured values, where a stagnation was observed at about −0.40 V., as is shown in Fig. 5. This potential coincides well with the potential at B in Fig. 4. As the anode was polarized beyond the Frade potential, three different stages were observed, the first of which was in BC before the oxygen evolution. If the anodic potential reached D′, oxygen was evolved and a bright yellow surface was observed until the potential was raised to E. Further polarization, however, altered the surface state considerably; the color of the film changed to dark black from bright yellow and a different Tafel line appeared. The yellow film in the D′E region was found to be relatively more soluble compared with the dark film in FG and dissolved to give a stannate ion with about a 10% current effiiciency. In the electroplating process of tin, the anode is generally controlled to maintain the yellow color in order to obtain the stannate ion, and so it can be seen that this state corresponds to that of the D′E region.

Relation between the Alkaline Concentration and the Limitting Current Density.—The same type of polarization curves as shown in various alkaline concentrations, so that the limiting current densities reaching the second or the third stage from the first or the second stage could be measured for various concentrations. The experiment was carried out under atmospheric conditions, and the electrolytic solution was not stirred. These results are shown in Fig. 6.

It has been seen from the previous experiments that the limiting current density is governed by the transference of the hydroxide ion from the bulk of the solution to an active site where the anode takes part in the reaction. In this case, it is not necessary to make consider the diffusion of the stannate or stannite ions from the active site to the bulk of the solution, because changes in the concentration of either ion did not appreciably alter the limiting current density. According to Fick's law, the current density I, which responds to the transference of the hydroxyl ions from the bulk of the solution to the surface of the film, is given by[4]:

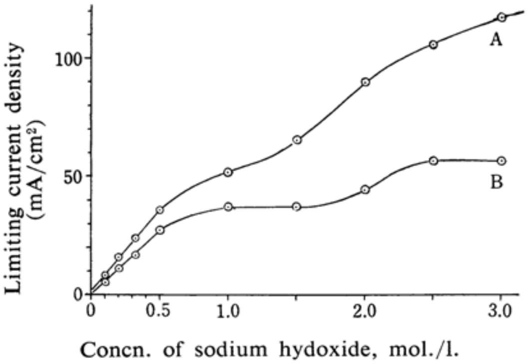

Fig. 6. Relation between alkaline concentration and limiting current density, I_L.

A I_L, from the second stage to the passive stage

B I_L, from the first stage to the second stage

$$I=\frac{D\cdot n\boldsymbol{F}}{(1-t_{\mathrm{OH}^-})\delta}(a-a_c) \tag{1}$$

where t_{OH^-} and D represent the transference number and the diffusion coefficient of the hydroxide ion respectively, δ is the thickness of the diffusion layer in the solution, a and a_c are the activities of the ion in the bulk of the solution and at the surface of the film respectively, and n is the valency of the ion.

In order for the anodic reaction to take place, the hydroxide ion must reach the active site by passing through the film. Although the mechanism concerning such an ionic transference is little known, Fick's law may also be adopted in this case; it so, the current density I in the film may be expressed by the following equation:

$$I=\frac{D'\cdot n\boldsymbol{F}}{(1-t'_{\mathrm{OH}^-})\delta'}(a_c-a_d) \tag{2}$$

where t'_{OH^-} and D' are the transference number and the diffusion coefficient of the hydroxide ion in the film respectively, δ' is the thickness of the film, and a_d is the activity of the hydroxide ion at the active site. Since the current densities I in both Eqs. 1 and 2 should be equal, Eq. 1 can be combined with Eq. 2, in which case the current density I may be rewritten as:

$$I=\frac{a-a_d}{(1-t_{\mathrm{OH}^-})\delta/D\cdot n\boldsymbol{F}+(1-t'_{\mathrm{OH}^-})\delta'/D'\cdot n\boldsymbol{F}} \tag{3}$$

When the current density is increased to the maximum value, which is represented by I_L, a_d should be almost epual to zero, and hence I_L is given by:

$$I_L=\frac{a}{(1-t_{\mathrm{OH}^-})\delta/D\cdot n\boldsymbol{F}+(1-t'_{\mathrm{OH}^-})\delta'/D'\cdot n\boldsymbol{F}} \tag{4}$$

It follows from this equation that the relation of the limiting current density to the concentration of the hydroxide ions would be a linear function provided that the denominator of Eq. 4 is constant. As can be seen from Fig. 6, this relation is actually satisfied in the region of 0～0.5 N sodium hydroxide. In the denominator of Eq. 4, it is considered that the first and the second terms correspond to resistances for the transference of hydroxide ions throughout the diffusion layers in solution and in film respectively. Therefore, if each term is known, it can be determined in which layer the rate-determining step exists. In the case of the limiting current density reaching the third stage from the second stage, the first term was calculated to be 0.44×10^{-2} up to a 0.5 N concentration at 30°C by introducing the following values:

$t_{\mathrm{OH}^-}=0.817$, $\boldsymbol{F}=96500$ coulombs,

$\delta=0.05$ cm.[4], $D=2.14\times10^{-5}\,\mathrm{cm}^2\cdot\mathrm{sec}^{-1}$

The sum of the first and the second terms in the denominator of Eq. 4 (i. e., a/I_{L}), could be obtained from the slope of the straight line in Fig. 6; it was 1.0×10^{-2} up to a 0.5 N concentration. Thus, the second term could be evaluated by subtracting the first term from a/I_{L}; it was found to be 0.56×10^{-2}. From these values, it may be stated that the diffusion layers in solution and in film both equally resist the transference of hydroxide ions up to a 0.5 N concentration.

As the concentration is increased beyond 0.5 N, however, the slope in Fig. 6 tends to become less steep, although still not proportional to the concentration, and the linear function no longer obtains. This indicates that the denominator of Eq. 4 begins to increase and shows no constant value. According to one table[5], any value in the first term is almost independent of the alkaline concentration. This means, therefore, that the second term tends to increase and is not constant. Since the increase of the second term means an increase of δ' and a decrease of D', it follows that thickening of the film should occur. Therefore, it can be concluded that the rate-determining step is the process in which hydroxide ions reach the active site by passing through the film.

The limiting current density reaching the second stage from the first stage can be treated in the same manner as above. Equation 4 may still be employed, because the electrode process still proceeds by replenishment of the hydroxide ions.

Since a linear function was obtained in the region of 0～0.5 N sodium hydroxide solutions, the first and the second terms of the denominator in Eq. 4 were calculated to be 0.44 and 1.19 respectively. This indicates that the rate of the transference of the hydroxide ion is practically determined by the rate of its passage through the film of stannous hydroxide; that is, the film of the first stage resists the transference of the hydroxide ion more intensely than the film of the second stage.

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[4] G. Kortum and J. O'M. Bockris, "Textbook of Electrochemistry", Elsevier Publishing Co., New York (1951), p. 402.

[5] National Research Council, "International Critical Table", Vol. VI, McGraw-Hill Book Co., New York (1929).