

THE ANODIC DISSOLUTION OF TIN IN ACIDIC CHLORIDE SOLUTIONS

J. W. JOHNSON and E. C. LIU

Department of Chemical Engineering and Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Mo. (U.S.A.)

(Received July 3, 1973)

SUMMARY

The anodic dissolution of Sn in acidic chloride solutions (pH = -2.0 to 2.9) was studied at 25°C. The apparent valence of the dissolving ions varied from about 0.4 to 2.4, and was a function of both electrolyte and c.d. The complexing of Sn²⁺ by Cl⁻ had an important influence, with SnCl₃⁻ apparently being the dominant product. A reaction sequence is proposed involving the stepwise oxidation of Sn, accompanied by reaction with Cl⁻.

INTRODUCTION

In the absence of complexing and oxidizing agents, Sn exhibits good stability toward aqueous solutions whose pH's range from moderately acidic to slightly basic. This stability is attributed both to a protective oxide film and to a high hydrogen overpotential. Chloride ions are known for their ability to complex with Sn and make the metal susceptible to corrosion either by lowering the anode potential or by breaking down the protective film (or a combination of both). An extensive study of these effects in nearly neutral solutions has been reported by Hoar¹. The purpose of this study was to determine the anodic behavior of Sn in acidic chloride solutions. In such solutions, passivation by oxide-film formation should be at a minimum, which allows one to examine the anodic dissolution process.

EXPERIMENTAL

Cylindrical Sn specimens were cut from rods cast from bars of 99.999% minimum purity*. They were wet-polished on grinding paper down to grit 600, rinsed with distilled water, dried in a desiccator, and mounted in a Teflon holder to complete the anode assembly². All solutions were made from analytical grade chemicals and distilled water. The electrolyses were carried out in the usual H-cell (300 ml capacity) at 25 ± 0.1°C with a Pt cathode. The reference electrode was Hg/Hg₂Cl₂

* Electronic Space Products, Inc., Los Angeles, Calif. 90035, 5 N grade.

TABLE I
 APPARENT VALENCE OF Sn IONS, REST-POTENTIALS AND TAFEL SLOPES FOR THE ANODIC DISSOLUTION OF Sn AT 25°C

Electrolyte		Current density, i (mA/cm^2)							Rest potential* (V (SHE))	Tafel slope (V)		
HCl	KCl	pH	pCl ⁻	i	3	10	20	30			60	100
10.00	—	-2.0	-2.0	0.39	0.81	1.48	—	1.89	1.84	1.94	-0.481	0.024
6.00	—	-1.3	-1.3	0.39	0.82	1.49	—	1.94	1.83	1.92	-0.423	—
3.00	—	-0.6	-0.6	1.77	1.77	1.91	1.99	1.99	1.96	1.97	-0.351	0.027
2.00	—	-0.31	-0.31	1.69	1.77	1.88	1.97	1.96	1.94	1.95	-0.326	—
1.00	—	0.1	0.1	1.79	1.82	1.82	—	1.91	1.93	1.98	-0.309	0.027
0.10	—	1.1	1.1	1.82	1.79	1.82	—	1.94	2.05	1.99	-0.247	—
0.100	0.900	1.2	0.20	—	2.01	—	—	2.00	—	1.96	-0.310	0.027
0.100	1.900	1.0	-0.08	—	2.01	—	—	1.99	—	1.96	-0.320	0.030
0.100	2.900	0.9	-0.25	—	—	—	—	—	—	—	-0.330	0.027
0.010	0.990	2.2	0.22	—	2.07	—	—	2.05	—	—	-0.323	0.028
0.001	0.999	2.9	0.22	—	1.99	—	—	2.04	—	2.08	-0.320	0.028
				—	2.36	—	—	2.30	—	1.95	-0.320	0.028
				—	2.36	—	—	2.36	—	1.97	—	—

* Corrected for junction potentials using equivalent conductance data.

(1 N KCl) and was connected to the anode *via* a Luggin capillary and salt bridge of the same electrolyte as that used in the electrolysis cell. All potentials reported are relative to the standard hydrogen electrode (SHE) at 25°C and have been corrected for junction potentials. Pre-purified nitrogen was bubbled through the electrolyte to provide stirring and an inert atmosphere.

The amounts of Sn dissolved were determined by a direct weight-loss method. The anodic polarization behavior was determined both galvanostatically and potentiostatically (Fig. 1). Reasonably steady states (less than 10% change/h) were obtained in all cases except as noted.

RESULTS

Valence measurements

The results of the valence measurements are shown in Table I. The individual values were reproducible to $\pm 3\%$. In the more acidic electrolytes ($\text{pH} \leq 0.2$), a black film was present on the anode surface which spalled off at high c.d.'s. An examination of the spalled film showed it to contain small metal particles, as reported previously by Straumanis³. For these solutions, the apparent valencies were lowest at the lower c.d.'s and approached the expected value of two as the current was increased. In 10 N HCl, there was substantial self-dissolution of the Sn as evidenced by H₂ evolution at local cathodic sites, and also pitting during anodic dissolution. No pitting or gas evolution was noted in the other solutions.

In the solutions of higher pH (1.2, 2.2, and 2.9), the apparent valencies were *ca.* 2 or slightly greater. In 0.1 N HCl + 0.9 N KCl, the anode surface retained its metallic appearance at low c.d.'s. In the other solutions, a black film was initially formed that slowly turned gray. X-ray diffraction analyses of the films yielded lines associated primarily with SnO and 2 SnO · H₂O. No gas (O₂) evolution was noted, even at the high c.d.'s, and no Cl₂ was detected in the anolyte after the electrolyses.

When apparent valencies significantly greater than 2+ were obtained, small quantities of Sn(IV) were detected in the anolyte along with Sn(II). For all the other cases, only Sn(II) was found.

Polarization measurements

The rest "open-circuit" potentials of the Sn electrode in various solutions are also shown in Table I. Steady values were obtained in about 20 min and remained quite stable for several hours. With the exception of 10 N HCl, there was only very slight evidence of self-dissolution (corrosion) during these periods, and this was primarily confined to a small amount of etching that revealed the underlying grain structure. Evidently, though, a small amount occurred continuously, as evidenced by the low valencies at 1 and 3 mA/cm². There were linear Tafel sections in the potential region slightly more positive than the rest-potentials. No passivation was found for the electrolytes $\text{pH} \leq 1.2$, though limiting (potential independent) currents were found that showed no simple concentration dependence. The commencement of this latter type of behavior appeared to be potential dependent.

With the electrolytes $\text{pH} = 2.2$ and 2.9, significantly lower currents with increasing potential were obtained above a critical potential. An inspection of the data from the previous section shows that this is only "quasi" passivation and that Sn

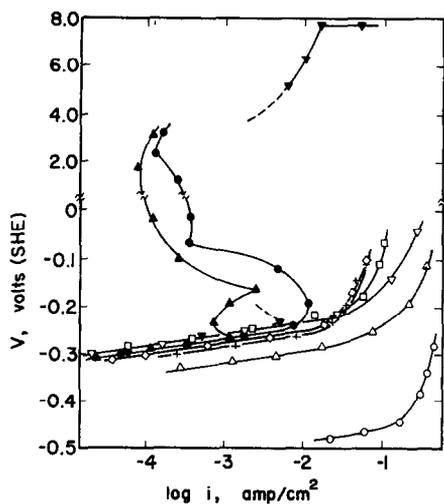


Fig. 1. Anodic polarization curves for the Sn electrode in acidic chloride solutions at 25°C. (○, 10 *N* HCl; △, 3 *N* HCl; ▽, 1 *N* HCl; □, 0.1 *N* HCl+0.9 *N* KCl; ◇, 0.1 *N* HCl+1.9 *N* KCl; +, 0.1 *N* HCl+2.9 *N* KCl; ●, 0.01 *N* HCl+0.99 *N* KCl; ▲, 0.001 *N* HCl+0.999 *N* KCl; ▼, 0.001 *N* HCl+0.999 *N* KCl [galvanostatic].)

dissolution is the predominant reaction at this and even higher c.d.'s. The critical currents are apparently pH dependent, as they appeared in solutions in which the Cl^- concentration was held constant. The quasi-passivation commenced at potentials of -0.25 to -0.20 V.

Cyclic voltagrams for the Sn electrode in 1 *N* HCl and 0.001 *N* HCl+0.999 *N* KCl are shown in Fig. 2. The polarizations began at the rest-potentials in the anodic direction. The anodic currents flow smoothly with increasing potential in both cases with no evidence of passivation or unusual polarization phenomena during the short periods of the potential cycle. The peaks in the cathodic currents are typical of diffusion limited reactions, as would be the case here where Sn ions for deposition are available primarily from the preceding anodic portion of the cycle.

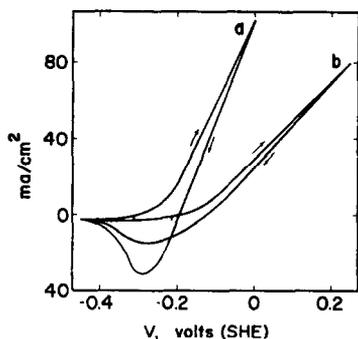


Fig. 2. Cyclic voltagrams (20 mV/s) for the Sn electrode in acidic chloride solutions at 25°C. (a-1 *N* HCl, b-0.001 *N* HCl+0.999 *N* KCl.)

DISCUSSION

The apparent valencies of the Sn ions determined from coulombic data lie both above and below the expected value of 2+. The lower values occur in the electrolytes of lower pH and at the lower c.d.'s. They are consistent with anodic dissolution that is accompanied by self-dissolution (local corrosion). In the extreme case, (10 N HCl, $i=0$), spontaneous dissolution was quite rapid. This process is undoubtedly assisted both by the increased H^+ concentration and the ability of Cl^- to complex with Sn^{2+} , thereby lowering the potential of the local anodes and also removing any surface film, so that H_2 can be evolved. The rate of local corrosion accompanying the anodic dissolution does not appear to be greatly affected by the impressed current, hence the increase of valence with current density. This is consistent with the assumption that local corrosion is not film controlled*. It is also consistent with proposals that anodic disintegration (which is usually associated with lower than normal apparent valences) results from a combination of normal anodic dissolution and local corrosion^{2,3}.

In the intermediate pH range (0.2–2.2), the apparent valencies do not deviate from the normal value of 2+ by more than $\pm 10\%$. However, this deviation is outside the limit of experimental error and while the normal oxidation of Sn to Sn(II) is the dominant electrochemical reaction, it is not the exclusive one. At pH=2.9, values were obtained that are significantly higher than 2+. Analyses of these anolytes revealed that Sn(IV) was produced as well as Sn(II). At lower pH's only Sn(II) was detected. Considering this and the absence of oxygen evolution, the increased valence is

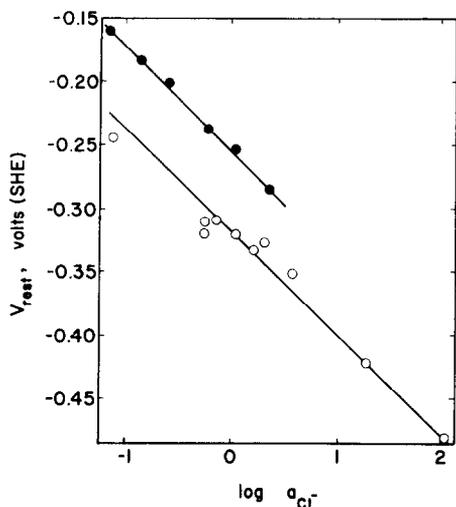
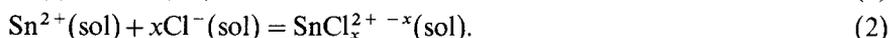


Fig. 3. Rest potentials of the Sn electrode in acid chloride solutions at 25°C. (○, data from this study; ●, Hoar's data for KCl solutions¹.)

* The importance of the hydrogen evolution overpotential on Sn in limiting its self-dissolution can also be easily illustrated by touching a Pt wire to a piece of the metal immersed in the acid Cl^- solutions. Hydrogen is immediately evolved from the Pt.

accounted for by further oxidation of some of the Sn(II) to Sn(IV) or the direct oxidation of Sn to Sn(IV).

An examination of the rest potential data $\text{pH}=0.2\text{--}2.9$ ($C_{\text{Cl}^-}=1.0\text{ N}$) from Table I shows them to be essentially pH independent, *i.e.*, $\partial V_{\text{rest}}/\partial \text{pH}=0^*$. The rest potentials for the remaining solutions (where both pH and C_{Cl^-} are changing) are seen to decrease with increasing Cl^- concentration if one assumes them to also be pH independent. A plot of the rest potentials *vs.* the corresponding Cl^- activities is shown in Fig. 3**. A reasonably linear relationship is obtained in which $\partial V_{\text{rest}}/\partial \log a_{\text{Cl}^-} = -0.085\text{ V}$. Attributing this potential relationship to the complexing ability of Cl^- for Sn^{2+} allows one to estimate the extent of complexing from the reactions***



Combining the Nernst equation for eqn. (1)†

$$E = -0.136 + 0.0295 \log a_{\text{Sn}^{2+}} \quad (3)$$

and the equilibrium relation for eqn. (2)

$$K_2 = a_{\text{SnCl}_x^{2+-x}}/a_{\text{Sn}^{2+}} a_{\text{Cl}^-}^x \quad (4)$$

gives

$$E = -0.136 + 0.0295(\text{p}K_2 - x \log a_{\text{Cl}^-} + \log a_{\text{SnCl}_x^{2+-x}}^+). \quad (5)$$

The partial derivative with respect to $\log a_{\text{Cl}^-}$ of this expression gives

$$\partial E/\partial \log a_{\text{Cl}^-} = 0.0295x. \quad (6)$$

Assuming the measured rest potentials are the reversible values corresponding to eqn. (5), then

$$\partial E/\partial \log a_{\text{Cl}^-} = \partial V_{\text{rest}}/\partial \log a_{\text{Cl}^-} \quad (7)$$

and

$$-0.0295x = -0.085$$

or

$$x \approx 3.$$

The measured rest potentials can now be checked against the reversible values by comparing a potential from eqn. (5) with a corresponding value from Fig. 3. Equilibrium constants for the formation of SnCl^+ , SnCl_2 , SnCl_3^- , and SnCl_4^{2-} from one Cl^- and the adjacent lower complex have been given by Duke and Courtney⁶ as 11.3, 5.1, 0.24, and 1.0, respectively. Thus the value for eqn. (2) ($x=3$) is

$$K_2 = (11.3)(5.1)(0.24) = 13.8$$

and

$$\text{p}K_2 = -1.141.$$

* The rest potentials reported by Hoar (Fig. 3) for KCl solutions ($\text{pH}=7$) differ from the corresponding values in this study by only about 60 mV whilst the pH has changed by 6.9 units.

** The Cl^- activities were calculated using the mean ionic activity coefficients from refs. 4 and 5.

*** The corrosion or "mixed" potential of an active metal at open circuit very closely approaches the reversible value of the metal if the self-dissolution rate is controlled by a high hydrogen evolution overpotential on the local cathodes.

† For the reduction potential.

Substituting in eqn. (5) gives

$$E = -0.170 + 0.0295 \log a_{\text{SnCl}_3^-} - 0.0886 \log a_{\text{Cl}^-} . \quad (8)$$

When a metal is immersed in a solution that initially contains none of its dissolved species, a double-layer activity of 10^{-6} is often assumed to estimate the reversible potential. Using this value for SnCl_3^- in eqn. (8) gives

$$E = -0.347 - 0.0886 \log a_{\text{Cl}^-} . \quad (9)$$

From this equation for $a_{\text{Cl}^-} = 1$, $E = -0.347$ V which compares with -0.32 V from Fig. 3. This is in fair agreement in view of the approximations used* and allows one to attribute the rest potentials primarily to the reaction



This reaction would also represent the overall electrochemical dissolution reaction that occurs.

The Tafel slopes from the linear portions of the polarization curves (Table I) are all approximately 30 mV, *i.e.*, $2.3 RT/2F$. This value is associated with a reaction sequence that has a chemical rate-determining step preceded by two equilibrium charge transfers. A further examination of the Tafel sections also gives information about the species involved in the sequence. In the first place these sections for pH's 1.2–2.9 almost superimpose. Since these are solutions in which $a_{\text{Cl}^-} \approx \text{constant}$, it appears that H^+ , OH^- , or H_2O are not involved in the quasi-equilibrium steps nor H^+ or OH^- in the r.d.s. A semi-log plot of V *vs.* a_{Cl^-} at constant current for the solutions with varying Cl^- concentrations (pH's 0.2 to -2.0) is shown in Fig. 4. The relationship is reasonably linear and gives $\partial V/\partial \log a_{\text{Cl}^-} =$

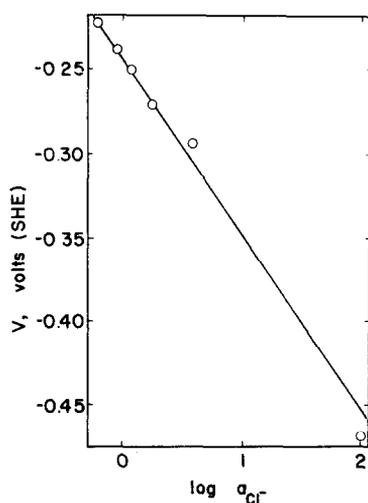
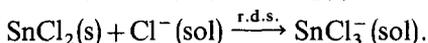
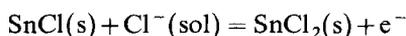
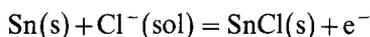


Fig. 4. Effect of Cl^- activity on the potential of the Sn electrode during anodic dissolution ($i = 10^{-2}$ A/cm^2) at 25°C .

* For an assumed double layer activity of $\text{SnCl}_3^- = 10^{-5}$, the calculated and experimental values would be approximately the same.

– 105 mV. A value of – 87 mV would be consistent with a reaction order of 3. This unusually high reaction order is also consistent with the effect of Cl^- activity on the voltamograms shown in Fig. 2. A reasonably linear relationship exists between i and V over the anodic c.d. range 20–80 mA/cm². The ratio of the slopes of the curves, $(\partial i/\partial V)_{1\text{ N HCl}}/(\partial i/\partial V)_{0.001\text{ N HCl}+0.999\text{ N KCl}} \approx 2.3$, should be approximately equal to $(a_{\text{Cl}^-})_{1\text{ N HCl}}^3/(a_{\text{Cl}^-})_{0.001\text{ N HCl}+0.999\text{ N KCl}}^3$ since the reaction is not yet diffusion-controlled at these potentials (no c.d. peak). For 1 N HCl and 0.001 N HCl + 0.999 N KCl, the Cl^- activities can be estimated as 0.809 and 0.604, respectively. This activity ratio cubed is 2.4, very close to the experimental value.

The reaction sequence suggested by these results is



The absence of passivation in the solutions at $\text{pH} < 1$ is explained by the removal of protective Sn oxide (or hydroxide) films through the complexing action of the Cl^- . At these pH's the oxides are unstable and will not re-form^{1,2}. At pH's 2–3, SnO or Sn(OH)₂ are formed at potentials of – 0.3 to – 0.2 V, agreeing closely with the potentials at which the Sn passivates¹. At slightly higher potentials it is also possible to form SnO₂ or Sn(OH)₄, which explains the higher observed valencies and the presence of Sn(IV) species⁷.

ACKNOWLEDGEMENTS

This paper is based on a thesis submitted by one of us (E.C.L.) for the M.S. degree in Chemical Engineering at the University of Missouri, Rolla. It is contribution No. 127 from the Graduate Center for Materials Research, UMR.

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