

Potentiostatic Polarization of Sn-Sb System in Acid Media

A ABDEL RAZIK*, N A DARWISH, A M ALLAM & T H HUSSEIN
Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt

Received 22 October 1984; revised and accepted 11 April 1985

Anodic and cathodic potentiostatic polarization experiments have been carried out in 0.1 M HCl using three thermally prepared Sn-Sb alloys (I-III) containing 1%, 50% and 99% Sb, respectively. In the case of alloy-I, H₂ evolution, with suppressed dissolution of metallic tin, is readily achieved through cathodic polarization. Cathodic protection is accomplished in the ϵ -range of 0.2 to 0.4 V. Anodic passivity is not readily achieved. A protecting Sn(II) oxide film and/or oxychloride is formed at ϵ -values of ≈ 0.87 and 1.87 V. The cathodic curves for alloy-II indicate considerable cathodic protection at $\epsilon = -0.58$ V. At ϵ -value of -1.58 V decomposition of the SnH₄ and SbH₃ formed takes place. On anodic polarization at ϵ -values of 0.02 to 1.52 V, the alloy-II readily gets covered with protecting films of mixed oxide SnO and Sb₂O₃ and/or oxychloride (SnOHCl and SbOCl). The remarkable stability of the electrode surface of alloy-III towards attack by HCl in the whole potentiostatic range is indicative of the establishment of efficiently inhibitive film conferring considerable passivity. Anodic passivity is established at $E_H = 1.6$ V.

The oxidation behaviour of tin anodes in acid media has been extensively studied and investigated. It is found to be affected when tin is alloyed with small quantities of antimony. Incorporation of antimony in tin imparts anticorrosion properties to the latter. Presently we have carried out potentiostatic polarization investigation on Sn-Sb system in order to have an insight into the cathodic and anodic reactions at the metal/solution interface.

Materials and Methods

Anodic and cathodic galvanostatic polarization experiments were carried out using spec-pure tin as well as three thermally-prepared^{1,2} Sn-Sb alloys (I-III) containing 1%, 50% and 99% Sb, respectively. The electrolytic cell used in these experiments consisted of two compartments separated by a sintered glass disc and provided with gas inlet and outlet tubes for passing inert gas. The working electrodes comprised metal/alloy rods (length = 1 cm; diam 0.7 cm), fitted into a glass jacket through polyethylene tubing so that its surface only became exposed. A cylindrical platinum sheet (1 cm² surface area) served as an auxiliary electrode. Freshly polished electrode was introduced into the cell and its open-circuit potential was measured until it reached a steady state using a T₆ Tutorial potentiostat (Witton Electronic Ltd, England). The control potential was imposed by means of a Doran d.c. potentiometer (Derriton, Electronics Ltd, Hastings, England). The change in current with time at each applied voltage was recorded by means of a universal ammeter (England).

Measurements were carried out at $30 \pm 0.1^\circ\text{C}$, under purified N₂ with constant stirring.

Results and Discussion

Alloy systems I, II and III were polarized under potentiostatic conditions in 0.1 M oxygen-free hydrochloric acid solution within the potential range of -1.5 to +1.6 V. The current density (c.d.)-time plots obtained with alloy-I (Figs 1a, 1b) show that both cathodic and anodic curves are characterized by a rapid fall of current density with time, finally attaining a stationary value. An opposite trend in c.d. versus time curves has been occasionally noticed at E_H values of -0.5, -0.7 and 1.6 V (Fig. 1b). Current fluctuations, in certain cases, are observed in the cathodic region, most likely at c.ds near those corresponding to the stage of cathodic protection and prior to hydrogen evolution.

Non-adhering deposits formed during the cathodic polarization range, were readily brought into solution in open circuit. This may be plausibly attributed to hydride formation, e.g. SnH₄ ($2\text{H}^+ + 2\text{e} = \text{H}_2$; $\text{Sn} + 2\text{H}_2 = \text{SnH}_4$), followed by its decomposition to the metal and hydrogen.

Further, for the alloy system-I, the initial open-circuit potential corresponds to limited dissolution of metallic tin, the dissolution being hampered by the considerable hydrogen overpotential associated with the simultaneous discharge of H⁺ ions at the electrode/solution interface. On imposing a potentiostatic field at a potential (ϵ) more negative than the open-circuit potential, a cathodic current would pass to make up for the external field. The main cathodic reaction presumably involves H₂ evolution, with limited dissolution of metallic tin. At an appropriate field, cathodic protection may be imparted by a film of H₂ strongly adsorbed on the metal surface. This is

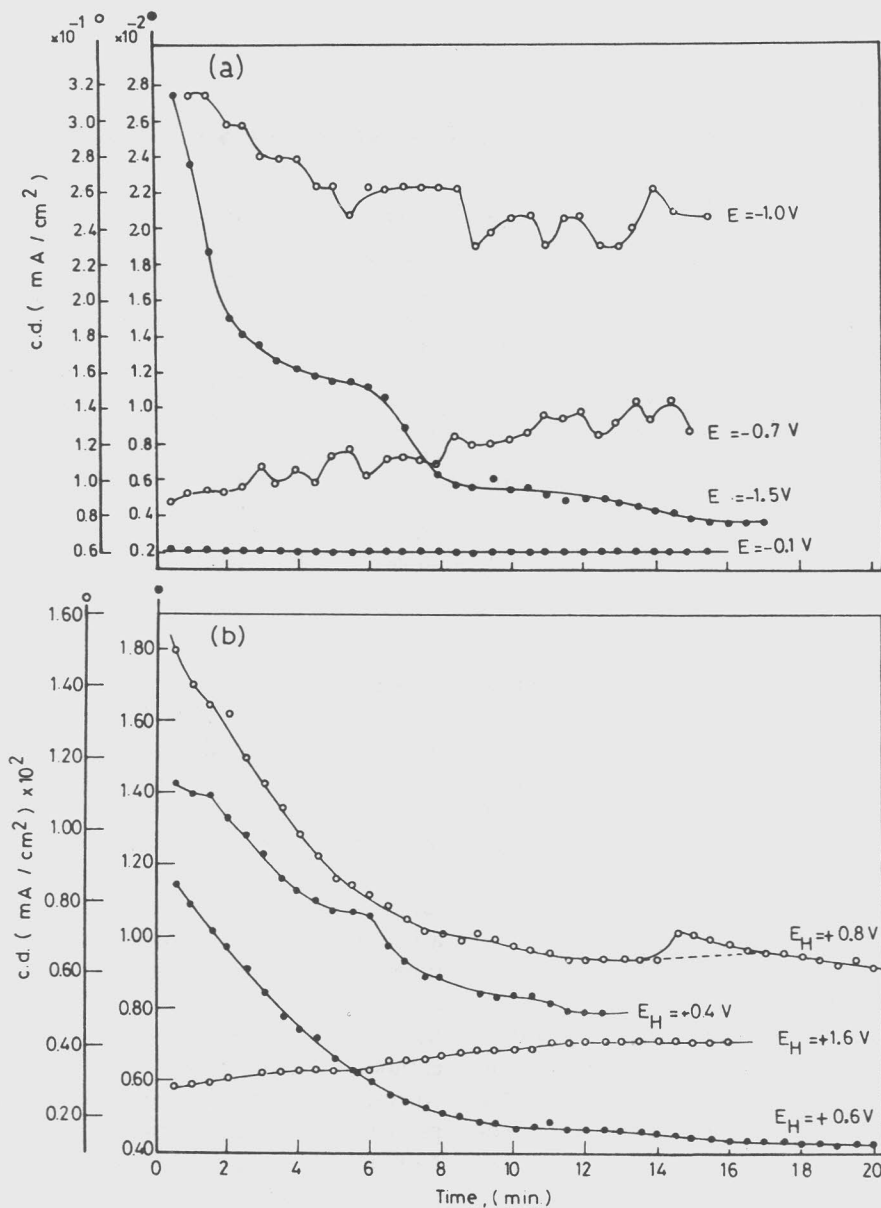
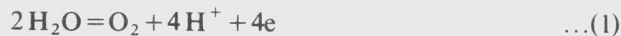


Fig. 1—Current density-time curves for alloy system-I in 0.1 M HCl solution

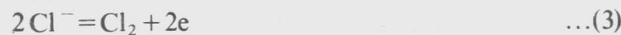
substantiated by a corresponding fall of the cathodic current and the cathodic potentials on the c.d./t curves are observed to pass through two main stages. The immunity brought about by cathodic protection seems to be accomplished in the ϵ -region extending from about -0.2 to 0.4 V, the ϵ -region is in the vicinity of the minimum observed on the ϵ -versus stationary current density (i_{st}) curve (Fig. 2).

The variation of the anodic current density with ϵ shows decrease in anodic passivity achieved. At ϵ -values up to ≈ 0.4 V, the anodic process is dissolution of metallic tin yielding Sn^{2+} ions, which may partly be involved in the formation of a complex of the type SnCl_4^{2+} . The dissolution of metallic tin is apparently

suppressed at ϵ -values of ≈ 0.87 and 1.87 V, which may be attributed to the formation of an Sn(II) anodic oxide and/or oxychloride film on the anode surface. Besides, the oxidation of water yields O_2 (Eq. 1) which may cause the oxidation of Sn(II) to Sn(IV) (Eq. 2).



At the intermediate ϵ range of 1.07 to 1.27 V, the increase in stationary current density values observed due to the reaction (3) at the electrode surface may be attributed to the discharge of Cl_2 .



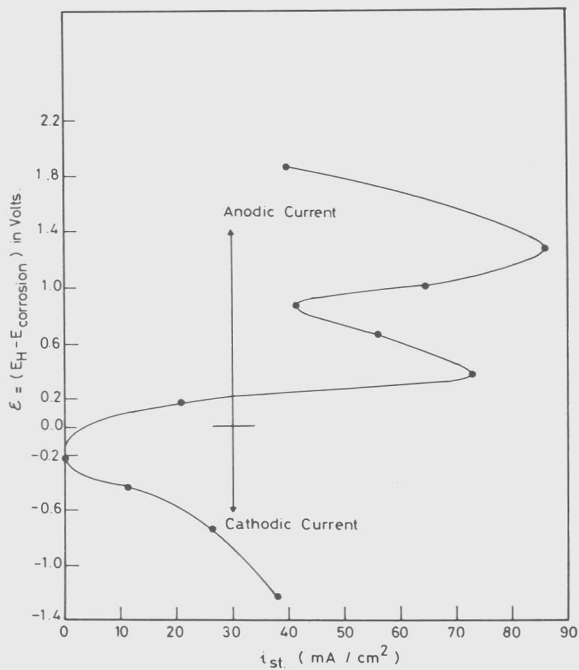
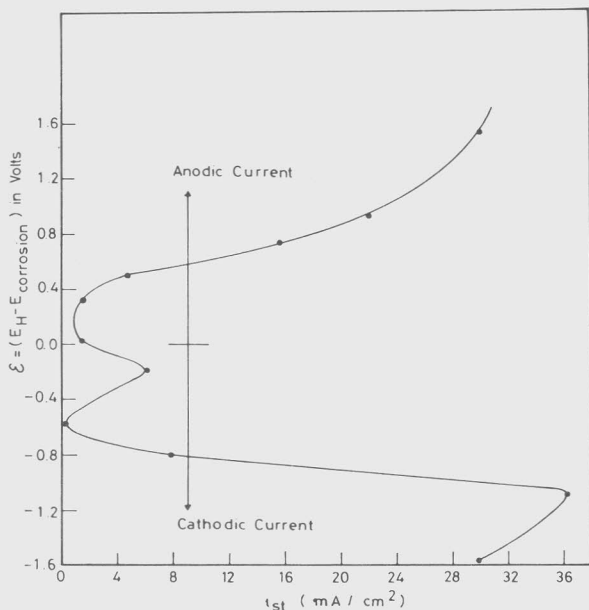

 Fig. 2— ε/i_{st} curves for alloy system-I in 0.1 M HCl solution


Fig. 4—Current density-time curves for alloy system-III in 0.1 M HCl solution

The representative $c.d./t$ curves obtained with the Sb-rich alloys II and III (Figs 3 and 4) show, generally, considerably smaller stationary state current densities than those obtained with alloy-I. With alloy-II, considerable current fluctuations are observed at E_H values of -1.0 and -0.7 V. There is a pronounced fall in the stationary $c.d.$ at an imposed E_H of -0.5 V. This is followed by an appreciable increase in $c.d.$ at

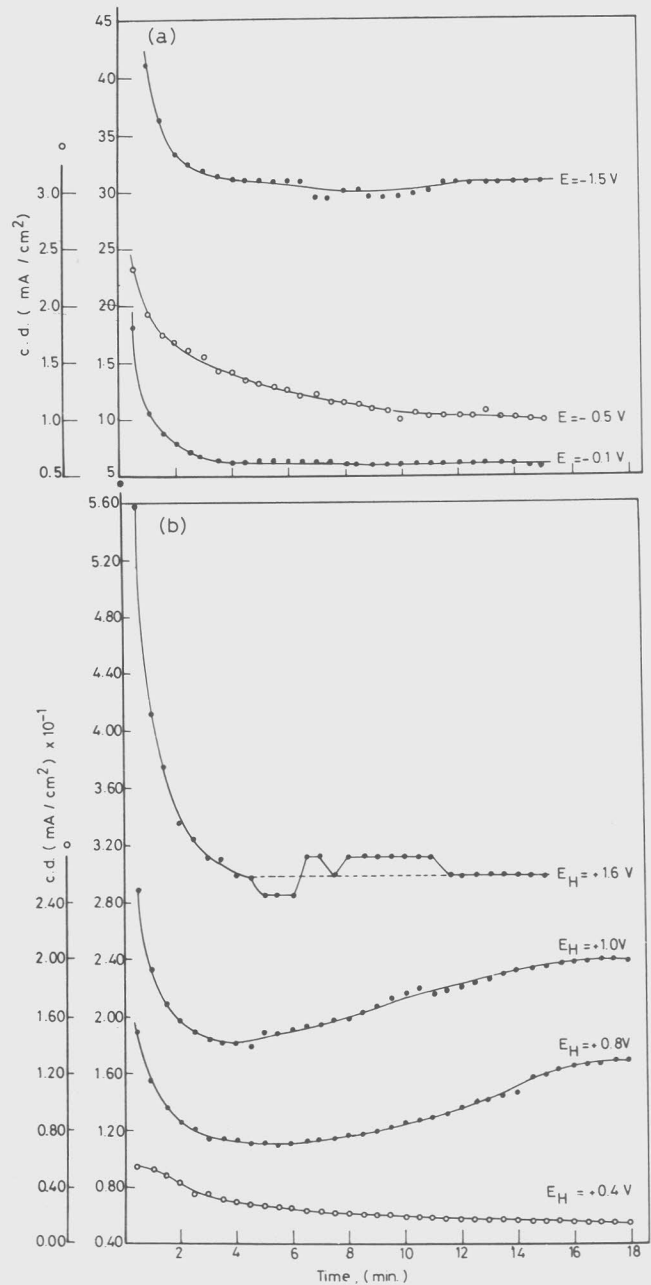
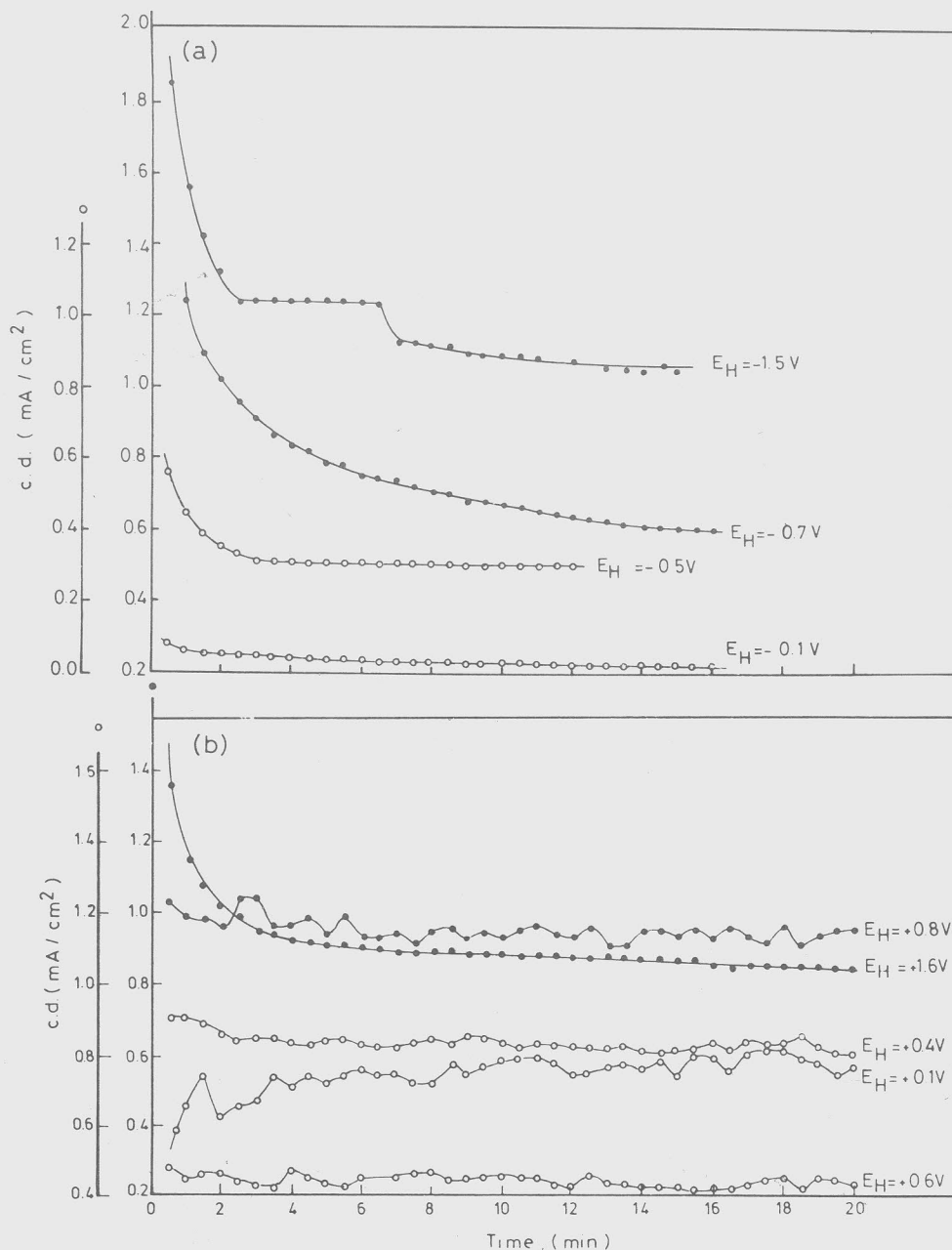


Fig. 3—Current density-time curves for alloy system-II in 0.1 M HCl solution

-0.1 V. Also, the ε/i_{st} curve (Fig. 5) indicates a decrease in the cathodic current with increase in ε from -0.18 to 0.58 V, followed by a sharp increase at more negative ε -values up to -1.08 V. The $c.d.$ falls again to somewhat smaller value at ε -value of -1.58 V. This behaviour indicates that at more negative controlled potential than the mixed static open-circuit corrosion potential, a cathodic current would pass to enhance the H^+ ion discharge process at a current density depending on ε -value. At $\varepsilon = -0.58$ V, the considerable fall of $c.d.$ observed indicates considerable

Fig. 5— ϵ/i_{st} Curve for alloy system-II in 0.1 M HCl solution

cathodic protection of the alloy surface, presumably by the adsorption of H_2 at the electrode surface. At appropriate ϵ -values, H_2 would freely evolve at appreciable c.d.s. One may argue that there exists the possibility of forming hydrides such as SnH_4 and SbH_3 which would decompose under suitable fields yielding the corresponding metal and H_2 . This is clearly substantiated by the fall of the c.d. at $\epsilon = -1.58$ V to a value lower than that observed at $\epsilon = -1.08$ V. A black deposit, most likely made up of finely divided metal, has clearly been noticed near the alloy surface.

The anodic behaviour of alloy-II in 0.1 M HCl, as revealed by the c.d./t curves (Figs 3a, 3b), is indicative

of considerable passivity of alloy surface at ϵ -values in the range 0.02 to 0.05 V ($E_H = 0.1$ to 0.6 V). The alloy surface is well protected, most probably by the formation of slightly porous anodically formed films of a mixed oxide (SnO and Sb_2O_3) and/or oxychloride ($SnOHCl$, $SbOCl$)^{2,3}. At ϵ -values in the range 0.72 to 0.92 V, the discharge of Cl^- ions yielding Cl_2 seems to take place at the passivated electrode surface/solution interface. This is associated with a sharp increase in c.d. at the stationary state (Fig. 5). The break at $\epsilon = 1.52$ V indicates the occurrence of another electrochemical reaction, presumably the oxidation of water yielding O_2 . In this and the chlorine evolution

process the surface film acts merely as a good conductor.

With alloy-III, the remarkable stability of the electrode surface towards attack by the acid, under the whole range of applied potential is indicative of the establishment of efficiently inhibitive films conferring considerable immunity. The cathodic polarisation is characterised by the attainment of considerably low stationary c.ds, as well as by the appearance of adhering gas bubbles on the electrode surface. It seems that the observed immunity is caused by the reduction of a pre-immersion Sb_2O_3 film, followed by discharge of H^+ ions yielding H_2 . The gas molecules form an adsorbed film which imparts cathodic protection to the electrode surface.

Along the anodic polarisation region, corrosion takes place within the pores of the protecting pre-immersion Sb_2O_3 film. The metal suffers limited

dissolution yielding SbO^+ ions which react with Cl^- ions. The resulting oxysalt would clog the pores thereby materially suppressing the corrosion process with concomitant fall of the corrosion current. Along the anodic polarisation region, the electrode attains passivity via a pre-passive stage. Pre-passivation seems to occur in E_H range of 0.1 to 1.0 V, as demonstrated by the current fluctuations on the c.d./t curves (Fig. 4). Anodic passivity is encountered at $E_H = 1.6$ V. Oxygen evolution may then follow, associated under appropriate conditions by the surface oxidation of Sb_2O_3 into Sb_2O_5 .

References

- 1 Khairy E M, Darwish N A, Abdel Razik A & Hussein T H. *J Corrosion Prevention and Corrosion Control* (in press).
- 2 Hansen M, *Constitution of binary alloys* (McGraw-Hill, New York) 1175, 1176.
- 3 El-Wakkad S E S & Hickling A, *J phys Chem*, **57** (1953) 203.