INTRODUCTION

Introduction

Tin metal is silver white, soft, ductile, nontoxic, lubricity, with excellent corrosion resistance in air, and able to form many useful alloys (1). With its low melting point, 232°C, and high boiling point, 2270°C, tin has a liquid range exceeded by just few metals. It readily alloys with many metals to form several intermetallic compounds of commercial importance. Copper, nickel, silver, gold, and palladium are soluble in liquid tin. Molten tin wets and adheres readily to clean iron, steel, copper, and copper-base alloys.

There are two allotropic forms of tin: white (β) and gray (α). White or ordinary tin, the familiar form, crystallizes in the body-centered tetragonal system, and possesses properties that make it useful. Gray tin has a diamond lattice, it is considerably less dense than β-tin and has a nonmetallic appearance and properties. Gray tin has also semiconductor properties. The allotropic transformation between the two forms occurs at 13°C and is extremely slow. The allotropic change is known as "tin pest", probably because it appears to spread from the center of "infection". The transformation is inhibited or prevented by the incorporation of few tenths of percent of antimony, lead or bismuth into the tin. The atomic number of tin is 50 while its atomic weight is 118.69. Due to its electronic configuration, $4d^{10}\ 5s^2\ 5p^2$, tin has four electrons available for bonding. Accordingly, tin is tetravalent in many of its compounds; as with its homologies germanium and lead. However, the 5s electrons may act as inert pair, consequently tin is also divalent. In this respect tin is intermediate between germanium and lead; with the former, bivalency is uncommon and lead exhibits tetra-valency only in its organic compounds. For tin, the two valence states are almost equally stable and readily inter-convertible. Solutions of stannic tin, Sn (IV), are readily reduced to stannous tin, Sn (II), by many reducing agents, especially metals such as antimony and nickel. On the other hand, solutions of Sn (II) are just as readily oxidized to Sn (IV) by common oxidants including air.

Tin is amphoteric, it reacts with acids and bases while relatively resistant to neutral solutions. The over potential of hydrogen evolution on tin is quite high, about 0.75V, so that the attack by acids and bases is slow unless in the presence of an oxidizing agent to depolarize the evolution of hydrogen. Distilled water has no effect on tin, and so it is the preferred medium for preparing and storing it.

In acidic solutions, Sn (II) compounds probably exist in the form of Sn^{2+} aqua ion, but Sn (IV) probably does not exist as such. It is either hydrolyzed or complexed as in $[SnCl_6]^{2-}$ and $[Sn(OH)_6]^{2-}$. In alkaline media, Sn (IV) is the most stable; alkaline stannite, or stannate (II) solutions disproportionate according to:

$$2[Sn(OH)_4]^{2-} \rightarrow [Sn(OH)_6]^{2-} + Sn + 2(OH)^-$$

This reaction is important in plating from alkaline stannate solutions. All tin compounds tend to hydrolyze in aqueous solutions. Alkaline solutions must be stabilized by the presence of excess alkali, acid solutions of excess acid.

Uses of Tin

Tin has attracted considerable attention during the past several decades because of its desirable physical properties such as high hardness, good wear, corrosion resistance and in some cases attractive gold like color. Some of the more important applications (1, 2) include:

-The manufacture of tin plate e.g. the tin plated steel products which are used in canning fruit, meat, etc. Very large quantities of tin-plate, having only a thin layer of tin, are used for containing food. Thicker coatings are used for milk churns, petrol tanks, etc.

-Tin is used for the preparation of different alloys e.g. brass (consists of Cu 70-80% & Sn 30-20%) which is used in making utensils, bronze (consists of Cu 80-90% & Sn 20-10%) which is used in making status and parts of machinery, bell metal(consists of Cu 72-80% &Sn 28-20%) which is used also in making statues etc., solder (consists of Sn 50-70% & Pb 50-30%) which is used in making containers of food stuffs and also for soldering, and type metal (consists of Sn 5% & Pb 75% & Sb 20%) which is used in making types.

-Tin is also used as coating for different metals such as:

terne plate which is steel coated with lead-tin alloys containing 5-25% tin. They have good resistance to atmosphere containing sulphurous compounds.

-Sn-Zn coatings which are good for tool components, aircraft under carriage.

-Sn-Ni coatings contain 65% tin, have good resistance to atmospheres containing sulphurous compounds.

-Tin foils are used in wrapping cigarettes, confectionary etc.

In 1984-1985(3-5), Tin-sulphide is potentially an interesting material for use in solar cell due to their relatively low band gap, so that a significant interest is done to electro- deposit the semi-conducting metal-sulphide for use in photovoltaic and photochemical cells.

Electrochemical Behavior of Tin in Acid Solutions:

The anodic behavior of pure tin, and a Pb-10wt. % tin alloy have been studied in sulfuric acid solutions using the ring-disk technique and potential decay measurements(6). For tin in sulfuric acid, the results showed that this metal passivated partly at acid concentrations above 3M. Tin was found to dissolve mainly as Sn (II) ions, but to some extent also as Sn (IV) if the potential is more than 3V. The ex-situ analysis of the corrosion layer formed on pure tin showed that the layer consisted mainly of amorphous SnO. The results for Pb-Sn alloy showed that tin dissolves from or through the corrosion layer formed on the alloy as Sn (II) ions. Tin was found to inhibit the formation of PbO_2. The effect of tin ions dissolved in the solution seemed to be similar to that of tin as an alloying agent. The ring-disk voltammetric measurements showed that a tin-containing compound is formed on the Pb-Sn alloy. This product is probably a mixed Pb-Sn oxide or tin doped PbO_n.

The impedance response of a tin electrode in 4.5 and 6M sulfuric acid solutions has been studied at the rest potential(7) as well as during anodic polarization in the active dissolution and passivation regions. The validity of a model for the active dissolution of tin advanced earlier is proven and extended to explain the mechanism of the open circuit corrosion process. In the passivation range, the impedance spectra observed were complex, and very dependent on the (+ve) potential and acid concentration. The high frequency response is ascribed to darker-like film formed on the electrode surface, through which ions are transported by high field-assisted migration. The low frequency response suggests an intricate coupling between the passivation and activation-dissolution process at the film-solution interface.

The anodic behavior of tin in 4.5-8M sulfuric acid was studied using rotating ring-disk voltametry, steady state polarization measurements, and surface analytical techniques. The region of active dissolution was determined and a reaction mechanism was advanced to explain the Tafel slopes obtained. The ring-disk electrode measurements showed that tin dissolves as bivalent ions, both in the region of active dissolution and in the passivation range. Using X-ray photoelectron spectroscopy and secondary ion mass spectrometry, it was shown that the anodic layer is mainly amorphous SnO with some HSO_4^- and/ or SO_4^{2-} adsorbed or incorporated.

Giannetti *et al* (8) studied the electrochemical behavior of tin in deaerated 0.5M citric acid by means of the potentiodynamic method. They reported that the anodic oxidation of tin in citric acid is a complex process associated with dissolution of the metal and formation of passivating film. It was shown that, despite of the simplicity of the (E/I) profile; the anodic oxidation of the metal involves the formation of a soluble Sn (II) species which is subsequently oxidized to Sn (IV). The nature of the soluble species is the object of some investigations by different authors (9, 10). It was reported that, passivation occurs via the hydrolysis of Sn (IV) to yield $Sn(OH)_4$ or SnO_2.

Gianneti *et al* (11), also studied the electrochemical behavior of tin in 0.5M citric acid solutions by electron microscopy techniques in addition to potentio-dynamic method. The observed electrochemical dissolution is quite similar to pure chemical dissolution when metallographic practices were used and takes place distinctly between the grains. They concluded that the film growing process follows dissolution/precipitation mechanism. The local reactivation process occurs primarily along the tin grain boundaries locations.

SEM associated with electrochemical studies on the tin electrode in citric acid support the conclusions based on pure electrochemical measurements. When the electrode was submitted to relatively slow linear potential sweeps the oxidation current is due essentially to metal dissolution, which occurs distinctly on the different crystallographic planes. Tin oxide film which is either formed naturally in air or by a potentio-dynamic oxidation is very thin and is not observable by SEM. However, the film grown under stationary conditions seems to be hydrated and shows characteristics of films formed by precipitation.

Bojinov *et al*(12) studied the influence of tin on the formation of the corrosion layer on lead with a Pb –10% Sn electrode in 0.5 and 4.5M sulphuric acid using voltammetry, rotating ring disk electrode and potential decay measurements, as well as photo-electrochemistry and ac impedance. The results obtained support the conclusion that in the presence of tin the amount of non-stoichiometric oxide formed in the corrosion layer in the vicinity of the equilibrium potential of the system $PbO_2/PbSO_4$ is increased. According to the results of the impedance measurements tin catalyses, the oxidation of Pb(II) to Pb(IV) by 0.1-0.2V. It was suggested that the resulting, electronically conducting oxide is a mixed Pb-Sn oxide containing mainly Pb(IV).

Bojinov *et al* (13) studied the passive state of the tin electrode in concentrated sulphuric acid solutions using electrochemical and photo-electrochemical measurements, photo-current spectroscopy and impedance spectroscopy. At high anodic over potentials (more than 1.6V vs. $Hg/Hg_2SO_4/ K_2SO_4$-(sat.)) the passivating layer becomes photoactive. This phenomenon is believed to be due to the formation of a high valency tin oxide. Experimental impedance spectra were compared with simulated spectra using a physical model of the interface based on the so-called surface charge approach. This model describes the growth of a barrier film under kinetic and high-field-assisted migration limitations, as well as its dissolution at the film-solution interface.

The anodic behavior of tin in H_2SO_4 solutions, using electrochemical and surface analytical techniques have been studied (14). The ultimate aim of these studies is to gain a better understanding of the anodic behavior of Pb-Sn alloys, which are used in lead-acid battery plates. Ring-disk electrode measurements have provided evidence that tin dissolves as Sn(II) in both the active dissolution and passive regions, but these measurements also showed that at sufficiently high anodic over potentials some formation of soluble Sn (IV) takes place in addition to oxygen evolution(15). Ex-situ surface analyses using scanning electron. Microscopy (SEM), electron surface for chemical analysis (ESCA) and secondary ion mass spectrometry (SIMS) indicate that the structure of the passivating surface film is mainly amorphous with a composition close to SnO.

Impedance spectra measured in the region of passivity (-0.8 to 0V vs. Hg/Hg_2SO_4) are complex and depend strongly on the electrode potential and the acid concentration, indicating that the reactions leading to passivation are multi-step processes (16). The authors proposed that a barrier-like film is formed through high field-assisted migration and that a locally coupled dissoultion-passivation reaction at the film-solution interface determined the low frequency response of the system. When the rates of formation and dissolution of the film become equally fate, a steady state is reached and the film stops growing. This state is dynamic and is expected to be influenced by the potential and the quantity of charge passed through the electrode.

The effects of antimony on the corrosion of tin in deaerated 0.33M citric acid was investigated by **Leidheiser**, *et al* (17). The role played by antimony in accelerating the corrosion of tin was studied. The corrosion rates of Sn-Sb alloys were determined from polarization data. The corrosion rates were linearly related to the Sb-content in the alloy. A mechanism was proposed in which small amounts of Sb-oxide on Sn-substrate were found to catalyze the hydrogen evolution reaction. Addition of NO_2^- to deaerated citric acid greatly accelerated the corrosion rate of unalloyed tin. A relation was proposed to relate the effect of NO_2^- on the corrosion rate to the concentration of this ion. The results of NO_2^- and Sb in connection with corrosion rate were attributed to a partially oxidized surface which could serve as a very effective catalyst for the hydrogen evolution reaction on tin.

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Electrochemical Behavior of tin in neutral media:-

***Sziraki**, et al* (18) investigated a reliable comparison for the corrosion rates of different Sn-Zn alloys in de-aerated/aerated 0.5 mol.dm^{-3} Na_2SO_4 solutions. The kinetic consistency of the polarization resistance (R_p) determined by the conventional linear polarization technique (LP) was supported by electrochemical impedance measurements (EIS). The corrosion potentials (E_{corr}) was found to be close to that of the pure Zn down to 5% Zn content, either in aerated or de-aerated solutions. Consequently the Zn dissolution governs the corrosion mechanism of the alloys. In addition the steady-state E_{corr} is near the equilibrium potential of the Zn^{2+}/Zn electrode reaction [E^o = -1.08 V (SCE) in Zn^{2+} ion free solution]. The possible contribution of the zinc exchange rate (i_o) depends mainly on the extent of the i_{corr} to the standard i_o and the surface Zn^{2+} ion concentration. The Tafel constants were determined simultaneously at the E_{corr} by the Faradic distortion method. From the data obtained, the anodic process was found to be a charge transfer controlled Zn oxidation, e.g. the corrosion layer did not yield a complete passivation.

The corrosion behavior of tin in salt solutions at various temperatures and in the presence of air, nitrogen and oxygen atmosphere was investigated (19). For this purpose, model salt solutions containing sodium chloride (2wt %) and sodium chloride with 0.002 wt % nitrite and nitrate were prepared. The system was chosen to perform the corrosion processes which could take place during the thermal treatment of some food products in tin plate cans, in the presence of oxidizing salts and different atmospheres. Electrochemical investigations were performed using potentiostatic and galvanostatic polarization methods. From the experimental data, the corrosion current, corrosion potential, polarization resistance and electron number were calculated. Augar electron spectroscopy and the XPS techniques were used to determine the chemical composition of the solid surface. It was found that The presence of nitrite and nitrate at concentration of 0.002 wt% in 2wt % NaCl acts as the accelerators on the tin corrosion with increasing temperature. The salt mixture (Cl^-, NO^-, NO^{-2}) showed a slightly inhibitory effect. Generally, the highest corrosion current values of tin electrode in salt solutions were recorded in a nitrogen atmosphere and the lowest in an oxygen atmosphere indicating that the formation of a certain protective film occurs. According to the electrochemical data, it could be assumed that tin is present in the form of oxide or hydroxide. The presence of Cl^- ion also suggests formation of tin-hydroxychloride, as well as $SnCl_2$ species. These results have been confirmed by XPS analysis.

The electrochemical characteristics of ternary-oxide electrodes with a general formula $RU_{0.2}$ $Ti_{0.8-X}$ Sn_X O_2 for chlorine evolution from NaCl solution were examined as a function of x by CV and ac impedance measurements (20). It was found that introducing SnO_2 into the electrodes improves the performance of the electrodes. The Morphology of the Ru- Ti-Sn ternary- oxide electrodes depended significantly on the content of SnO_2-among these electrodes. It has been concluded that

$Ru_{0.2}$ Ti_{07} $Sn_{0.1}$ O_2 gave the best performance.

Pyun and Chun (21) studied the anodic behavior of homogeneous Cu-Sn alloy in an aqueous 3.5 wt % NaCl Solution by potentiodynamic polarization, cyclic voltammetry, and potentiostatic cuurrent-time experiments and compared the results with the behavior of pure Cu. Speccimens were subjected to various anodic potentials and subsequent analyses by scanning electron microscopy supplemented with energy dispersive spectroscopy. At active potentials, the alloy and the pure cu either dissolve directly or through an adsorbed meta stable CuCl layer by transport of $CuCl^-_2$ ions. The active-passive transition at higher applied anodic potential resulted in the formation of a thicker and more stable CuCl salt layer. With further increases in anodic potential, the compact CuCl salt layer on the Cu-Sn alloys impedes the formation of CuO or $Cu(OH)_2$, thus maintaining perfect pasivity.

Evgenys, *et al* (22) have investigated transport properties and composition of passivating films, formed on the surface of Li-Sn, and Li-Sn-Cd alloy electrodes in propylene carbonate-based solutions, using electrochemical and secondary-ion mass spectrometry techniques. The profile of polarization curves obtained by using the single-pulse current technique showed that the transport rate of mobile Li^+ ions through a passivating film solution is limited by the space charge of ions injected in the latter from the electrode or from the for anodic and cathodic currents, respectively. The values of mobility and concentration for mobile Li^+ ions in passivating film have been determined. It has been stated that introduction of $MoCl_5$ into solution leads to a modification of the passivating film composition and to an improvement of its transport properties on account of an increase in the Li^+ ion mobility.

Kliskic et a l, (23) studied the cathodic polarization of two Al-Sn alloys in NaCl solutions. The results presented in that paper were obtained with two Al-Sn binary alloys (0.02 and 0.4 wt % Sn) which had been prepared on super pure (99.999%) Al base. Study of the behavior of these alloys at cathodic polarization in 2M NaCl solution by means of electrochemical methods complemented by SEM and EDAX analysis provided an insight into the effect of addition of tin on the electrochemical behavior of aluminum. It has, also, been observed that a low tin content causes aluminum to behave hyperactively at high negative potential values. This leads to crevice formation and conditions favorable for further dissolution the result of the change of potential in the negative direction with the alloy containing 0.4 wt % tin is super activation of aluminum as consequence of de-filming processes.

***Elshayeb** et al* (24) investigated the electrochemical behavior of pure aluminum and three of its alloys with zinc and tin in 0.6 M NaCl in the presence and absence of In^{3+} ions. The study comprised polarization and potentiostatic current-time measurements complemented by SEM-EDAX investigation. In 0.6 M NaCl the corrosion resistance of the alloys decreases in the following order:

$$\mathrm{Al} < \mathrm{Al-Sn} < \mathrm{Al\text{-}Zn} \cong \mathrm{Al-Zn-Sn}.$$

The addition of In^{3+} to the test electrolyte revealed activation of pure Al which increases with increase of In^{3+} concentration. Similar results were obtained for the binary Al-Zn and the ternary Al-Zn-Sn alloys, while Al-Zn alloy displayed a higher activation effect with In^{3+}.

***Ammeloot** et al* (25) characterized the oxide layers formed on a cu-13Sn (wt%) alloy in 0.5M NaCl aqueous solution to compare their properties to those obtained on pure copper and pure tin samples. It was found that for Cu-13Sn alloy, Cu_2O and SnO_2 were simultaneously present at the surface, for short immersion times in the NaCl solution. This result was confirmed by XPS measurements. Nevertheless the predominance of copper (I) oxide became clear after 48h immersion. For comparison, similar measurements were performed and discussed in the presence of BTA, an inhibitor of the copper corrosion. Coulometric analyses and impedance measurements showed that the behavior of a Cu-13Sn alloy is very similar to the behavior of pure copper in a 0.5 M NaCl solution with and without BTA. A main difference between the two materials consists in a different thickness of the corrosion layer. The photo electro- chemical method showed interesting possibilities as an in-situ analytical tool in the field of oxide growth, not only on pure metals but also on alloys. The simultaneous presence of SnO_2 and. Cu_2O on a Cu-13Sn sample was inferred from this method and checked by XPS measurements, while potentiodynamic experiment was unable to distinguish between the two oxides. A p - type semi conductivity was observed for copper and for bronze at low immersion times in NaCl. Differences appeared for longer immersion times. The semi conductivity remained of the p- type in the case of bronze, while it was the p- n type in the case of copper. The differences in the behavior between pure copper and Cu-13Sn alloy were explained in correlation with the growth mechanism of the oxide layer under cationic migration control.

Electrochemical Behavior of Tin in Alkaline Media:

The anodic oxidation of tin was studied galvanostatically in NaOH solutions of different concentrations (26). Primary passivity was attained in all solutions when the metal is covered with a film of $Sn(OH)_2$ or SnO. Permanent passivity sets in when $Sn(OH)_4$ was formed as a continuous layer on the electrode surface. In concentrated alkali solutions larger quantities of electricity are charged to the electrode to compensate the chemical dissolution of the hydroxides.

The anodic behavior of the tin electrode in solutions containing stannite and stannate is similar to that in solutions devoid of these ions. An increase in the tin content of the solutions is equivalent to the elevation of the polarizing current, passivity sets in more readily in the concentrated solutions.

X-Ray photoelectron spectroscopic studies of tin electrodes after polarization in sodium hydroxide solution were given by ***Ansell, et al*** (27). The results indicated the formation of stannous oxide and hydroxide in the prepassive region. At higher potentials stannic oxide and hydroxide are formed. The thickness of the layer is evaluated over the potential range -0.95 to +0.40 v using various models and is in the range 30-86°A.

The electro-deposition of tin sulphide on poly crystalline tin from alkaline solution was investigated by Ederio *et al* (28), using cyclic voltammetry. The first anodic peak in the cyclic voltammogram is associated with the deposition of a SnS monolayer from the adsorption of hydro sulphide on the electrode surface. At more (+ve) potentials there is a second anodic peak related to a SnS_2 film over the electrode. The growth of the anodic film has been interpreted by the hopping-motion model for a high field assisted ionic migration process with the rate limiting energy barrier located at the metal film interface.

***Suter** et al* (29) investigated the corrosion and layer formation of the alloys Cu-15Ni-8Sn and Cu-5Al-5Sn in 0.1 M NaOH solution upon exposure to air using X-ray photo-electron spectroscopy. For the alloy Cu-15Ni-8Sn an enrichment of the Ni and tin ions is revealed if the sample is prepared electrochemically in 0.01 M NaOH solution. Nickel acting as a barrier hinders the migration of the tin ions and as a result a thin and protective tarnishing film consisting of Cu (I) compounds is formed. In the 0.1 M NaOH solution a strong tin dissolution is observed for the alloy Cu-5Al-5Sn and a thick and porous oxide film consisting of Cu (II) compounds is formed. An exposure to air results in tin enrichment. As a consequence, a higher corrosion rate is observed for the alloy Cu-5AL-5Sn in the 0.1 M NaOH solution and an improved corrosion behavior under atmospheric conditions which is most probably due to the presence of tin.

Chorles et al (30), investigated cyclic polarization of tin electrodes in 6 M KOH at room-temperature. The study revealed a relatively large anodic and cathodic over potentials for water decomposition that depend on the surface structure of the material. Polished tin electrodes also underwent a slow reaction during anodic polarization above the reversible potential for O_2 evolution that involved the formation of a reaction product film. The film was uniform over the surface of the electrodes and contained hydrous potassium titanate. A corrosion product, similar in composition but less uniform in appearance, was formed on tin after 4 months under open-circuit conditions in the same solution. Results indicated that the film was formed slowly by a dissolution-precipitation mechanism and that the dissolution step gives rise to an oxidation peak observed in the cyclic voltoammogram during anodic polarization. Since the film is formed above the reversible potential for O_2 evolution and since the over voltage for O_2 evolution depends on surface structure, it is not yet clear whether the formation of the corrosion film will compete with electrolysis reactions during the charging of structurally tailored, high surface area, tin electrodes that are under development for ultra capacitor applications.

Electrochemical Behavior of Tin in Buffer Solutions:

Numerous studies of tin have been focused on passivation in strongly and slightly alkaline solutions, less with neutral solutions. According to these studies, passivation and properties of the passive film grown on tin strongly depend on experimental conditions, especially the pH of a solution. Reports also show that various properties of the passive films are closely related to their composition. However, there is disagreement in the literature data on the composition of the electrochemically formed passive films on tin.

The anodic behavior of tin in buffered phosphate electrolyte (pH=3.1) was studied by **Stirrup** *et al* (31) using a variety of techniques. A number of anodic processes were occurred. On anodic polarization the electrode initially filmed with a phosphate layer, was found to undergo dissolution, probably forming Sn (H_2PO_4, HPO_4) species. Impedance data gave a Tafel slope of 0.046V/decade for this process. At more positive potentials, three consecutive passivating processes occurred, involving blocking the surface by $Sn_3(PO_4)_2$.

Doduc, *et al* (32) examined the anodic behavior of tin in neutral phosphate buffer (pH= 6.7) at 37 ^{0}C by cyclic voltammetry , potentiostatic and galvanostatic pulse techniques. The anodic reaction was diffusion/controlled, and passivation was caused by precipitation of species from solution, followed by nucleation and growth processes at more anodic potentials. The passive film consisted of tin hydroxide and phosphate. The same authors (33) investigated the dissolution reactions of tin in neutral phosphate solutions in the region before passivation using rotating disk, and ring – disk electrodes. During the anodic reaction on the disk a cathodic current was observed on the ring resulting from the reduction of soluble species produced on the disk at both low and high potential. The low ring – disk current was attributed to the formation of an insoluble product. They also investigated the dissolution of Sn in alkaline phosphate by the rotating ring – disk technique (34). Soluble tin species were produced on the first and second stages of passivation. Evidence was also given that, during the second stage, a small amount of Sn (II) species was formed and was quickly oxidized to Sn (IV).

Kapusta, *et al* (35) studied the anodic oxidation of Sn in 0.2M borate buffer solution by potentiodynamic, poteniostatic, and galvanostatic techniques. Although a large amount of charge was consumed during anodic oxidation, only a fraction of this charge was used in film growth. The initial stages of metal passivation under dynamic conditions were best described by Muller's dissolution – precipitation model (36). Under potentiostatic conditions, two different equations were proposed to describe the kinetics of film formation. For anodic potentials < 1.6V vs. SCE a logarithmic dependence was found to hold between cathodic charge and time. At higher potentials, the growth rate was controlled by nucleation process and the rate law was more complicated. Under galvanostatic conditions, the logarithm of the growing time was proportional to the inverse of the cathodic charge. The results were discussed in terms of the theories of film growth.

Gouda *et al* (37) studied the corrosion behavior of a tin-steel couple in stagnant deaerated solutions of oxalic, citric and tartaric acids at pH 2-6. The variations of both the open-circuit potential and the galvanic current of the couple in these solutions were followed as a function of time until the steady-state values were reached. In 0.1 M citric acid and oxalic acids at pH 2- 5, and in 0.1 M tartaric acid at pH 2-4, as well as in 10^{-3} M oxalic acid at pH 2 and 3, steel was found to be cathodic with respect to tin. The corrosion behavior in these solutions was determined by both the complexing strength of the acid anion and the kinetics of inhibition of the cathodic reaction. In 10^{-3} M citric and tartaric acids at pH 2 and 3, as well as at pH 4 in tartaric acid, tin was the more noble electrode of the couple. This result was attributed to the weak complexing of tin in these solutions. In 10^{-3} M citric, oxalic and tartaric acids at pH 5 and 6 and in 10^{-1} M solutions of these acids, as well as in 0.1 M tartaric acid at pH 5 tin was initially anodic with respect to steel. However, reversal of polarity occurred after some time and steel became the anode of the couple. The behavior was attributed to film formation on the tin electrodes when immersed in these solutions.

Varsanyi *et al*(38) made some measurements on the passivation of tin in borate buffer using potentiodynamic curves recorded at high scanning rate (9V min^{-1}, 3.6V min^{-1}). The most important features of these curves were the presence of a current peak at around - 1180mV (vs. SCE) which had not been previously observed. The nature of the passive film formed in the vicinity of this potential was characterized using in situ. Moessbauer measurements. In borate buffer the passive film formed at the more negative range of potentials (-1180 to -780mV) was a duplex, consisting of highly amorphous $Sn(OH)_2$ or hydrated stannous oxide and SnO_2 or $Sn(OH)_4$. At the more positive potentials, the passive layer consisted only of Sn (IV) hydroxide or oxide which ensured a more efficient passivation.

Chan *et al* (39) have obtained cathodic and anodic polarization plots for the corrosion of pure tinfoil and tinplate in deoxygenated aqueous solutions containing various quantities of citric acid, tri-sodium citrate and sodium bisulphate from potentiodynamic measurements. Open circuit potentials for the corrosion of tin surface in such solutions at 25 ^{0}C become more negative with increasing pH. At sufficiently anodic potentials, in the presence of citrate ions, passivation characteristics were observed in the anodic polarization plots when a white solid material, probably a tin citrate complex compound, was formed on the electrode surface. SEM micrographs of the coated surface indicated that the solid was crystalline in nature. Cathodic Tafel slopes for the hydrogen evolution reaction on tin for the different solutions were determined.

Seruga, *et al* (40) studied the passivation of tin in 0.05 M citrate buffer solutions pH(3-6) by means of cyclic voltammetry, photopolarization, resistance and capacitance measurements . The passivation and properties of the passive film grown on tin is strongly dependent on the pH of the buffer. In buffers with pH 6 and 5 the formation of semiconducting or insulating films can be described by a mechanism controlled by IR drop inside the film pores. In buffers with pH 3 and 4 weakly protective films are formed through a dissolution/precipitation mechanism which controlled by diffusion. The passive films grown on tin contain an excess of tin ions and show n–type semi-conducting properties.

Quantitative analysis of the results of the capacitance measurements (made on the basis of the band structure model of passive thin films) fitted a simple space charge capacity model. The values of the flat – band potential and donor concentration were estimated.

Seruga *et al* (41) studied passive film formation as a function of applied potential on tin in citrate buffer solution by x-ray photoelectron spectroscopy (XPS) and cylcic voltammetry. In order to avoid air oxidation and to minimize contamination of the samples, an electrochemical preparation and transfer system attached to the ultrahigh vacuum system was used. Quantitative evaluation of the electrochemical and XPS data showed a characteristic change of the spectra in the prepassive and in the passive potential range. The prepassivation correlated with the clear presence of Sn^{o}, Sn^{2+} and Sn^{4+} species, while true passivation correlated with the presence of Sn^{4+} species only, as expected on thermodynamic grounds. Three different O_2 – containing species were found in both the prepassive and passive regions: tin- oxide (characterized by the O 1s peak at 530.4eV), Tin- hydroxide species (oxygen peak at 531.5eV), and adsorbed water (peak at 532.7eV). The tin- hydroxide species are dominant film components of both samples.

In this study on the passivity of tin in citrate buffer solution, pH 6, showed that dissolution – precipitation kinetics, having a diffusion controlled rds, play an important role in the stepwise oxidation of Sn(O) – Sn (II) to Sn IV) in the prepassive range . As a result, the initial prespassivating, purely protective film is formed and its thickness was less than one monolayer. True passivation under dynamic conditions resulted in the formation of a thin $Sn(OH)_4$ film which is one to two layers thick. The thickness estimated by cathodic removal of the surface film formed up to an upper potential limit $E_{I, a}$ = 1.8V is ca. 3nm. Electrochemical measurements clearly showed that the potentiodynamically passivated and established tin electrode, scanned for more than ten cyclic, exhibited a chemical and physical transformations. There are sufficient grounds for the assumption that the initially formed $Sn(OH)_4$ film dehydrates with time and with increasing the positive potentials to a more thermodynamically stable state. Dehydration of $Sn(OH)_4$ to SnO_2 involves a Gibbs energy change of –38Kjmol^{-1}.

Refaey(42) studied the corrosion and passivation of tin in sodium borate ($Na_2B_4O_7$)solutions at pH = 8.35 by potentiodynamic and cyclic voltammetry techniques. The effect of the following factors on the anodic dissolution and passivation of tin metal are discussed in different ranges of concentration of borate ion, pH, potential scan rate, successive cyclic voltammetry, switching potential and progressive additions of halide ions. The primary passivation was attained when the metal is covered with a film of Sn $(OH)_2$ and /or SnO_2. Permanent passivity occured when $Sn(OH)_4$ and /or SnO_2 forms a continuous layer on the electrode surface. The anodic dissolution reactions were controlled by diffusion. In all experiments, the aggressive action of the halides decreased in the order $Cl^- > Br^-$. SEM examination confirms the occurrence of pitting corrosion in the presence of halide ions. The pitting potential (E_{pit}) is decreased with increasing halide ion concentration.

Almeida *et al* (43) established the inhibiting effects of citric acid on the pitting corrosion of tin by potentiostatic and potentiodynamic studies. The critical potential (E_{crit}), which leads to pitting or general corrosion, was determined in sodium perchlorate solution in the pH range 1.0 to 4.0. Pit nucleation and growth, at pH= 4.0, was described by instantaneous nucleation followed by progressive nucleation. The results showed that the minimum acid concentration needed to inhibit pitting of tin is 10^{-2}M. Pitting occurrence by direct interaction between metal and perchlorate anions was observed. The results showed that the type of corrosion, pitting or general was dependent on pH. At pH 3.0 and 4.0 the pit initiation is preceded by the formation of an oxide layer, described by a dissolution–precipitation model for metal passivation. Pit nucleation and growth involve a number of contributions which were distinguished through the analysis of current transients at constant potential. In general compounds which inhibit pitting can promote general corrosion. The inhibiting effect of citric acid on pitting corrosion was recognized by the shift of the critical potentials to more positive values. Actually, the type of corrosion is closely related with the quantity of citrate anions.

General corrosion of tin is observed in pure citric acid revealing a surface that shows an isotropic reflection of polarized light. Several authors reported that pitting corrosion occurs when the surface is exposed to aqueous solutions containing aggressive anions such as halides (44). However, this form of localized corrosion may also occur in the presence of other species such as per chlorate, sulphate and nitrate anions (45-48).