# INHIBITION OF HYDROGEN ION REDUCTION AT A PLATINUM ELECTRODE BY TIN HYDROUS OXIDE FILM FORMATION

ALLEN J. BARD*

*Harvard University, Cambridge, Mass. (U.S.A.)*

## INTRODUCTION

Among the factors which affect solid electrode reproducibility, platinum oxide film formation and surface changes arising during the plating of metals have received the greatest amount of study. This paper is concerned with yet another cause of variability in solid electrode behavior.

In the course of an investigation of the electroreduction of tin(IV) in acidic halide media with a platinum electrode, evidence of inhibition of hydrogen ion reduction in the presence of tin was obtained. This inhibition was traced to a film of stannic hydrous oxide formed when hydrogen ion was reduced at the electrode, causing the pH to increase in the vicinity of the electrode, and allowing hydrolytic precipitation of tin to occur. The existence, properties, and permeability of this film were investigated, and a mechanism for its formation postulated.

## EXPERIMENTAL

### Apparatus

A Sargent Model XXI Polarograph was used in obtaining current–voltage curves. The conventional H-cell, containing a saturated calomel electrode, separated from the solution compartment by a sintered glass disk and agar plug, was employed in most of the measurements. The platinum microelectrode, 0.51 mm in diameter and 6.0 mm long, was rotated at 600 rev/min in a Sargent Synchronous Rotator. The electrode was cleaned between trials in nitric acid and aqua regia, and rotated about 5 min in the test solution prior to a run. Measurements were carried out at 25.00 ± 0.02°. All solutions were deaerated with oxygen-free nitrogen.

Chronopotentiometry was performed using the conventional type of apparatus[1]. A Varian Model G-10 potentiometer recorder, which had a 2-sec full scale deflection time and a 20 mV intrinsic range was used to record the chronopotentiograms. A Leeds and Northrup Model 7664 pH-meter with a 20 mV output was used in lieu of a potential divider in the input of the recorder. Measurements were made with a bright platinum foil electrode (1.2 × 1.4 cm). The auxiliary electrode, a platinum electrode, was isolated from the test solution by enclosing it in a glass tube with a sintered glass bottom.

The spectrophotometric curves were taken with a Cary Model 11 recording spectro-

* Present address: Dept. of Chemistry, University of Texas, Austin 12, Texas, U.S.A.

ion, while the final current increase is the direct reduction of water. Note that a relatively small amount of tin causes a large decrease in the limiting current of hydrogen ion reduction. Current–potential curves of hydrogen ion reduction, at constant acidity and bromide concentration, at various concentrations of tin(IV) in Fig. 2, show that the amount of suppression of hydrogen ion reduction increases with increasing tin(IV) concentrations. When the stannic ion concentration reaches about 9 m$M$ the limiting current begins to rise again, owing to the reduction of stannic tin. Qualitatively similar effects were observed in a chloride medium, except that large maxima were present on the suppressed hydrogen ion waves.

Suppression of hydrogen ion reduction was also caused by tin(II) in these media, and by both stannic and stannous ions in non-complexing (perchlorate) solutions, and at a stationary microelectrode. In a solution of 3 $M$ NaBr with an acidity as high as 1 $M$ HClO$_4$, a stannic ion concentration of 2 m$M$ decreased the hydrogen ion limiting current from greater than 450 to 168 $\mu$A.

A summary of the suppressive effect in bromide, chloride and perchlorate media is shown in Fig. 3. In general the suppressive effect is greater with tin(II) than with tin(IV), and is greater in perchlorate than in either bromide or chloride. The suppressive effect occurs with tin concentrations 400 to 4,000 times smaller than the hydrogen ion concentration, and the suppression is not directly proportional to the tin concentration.

These observations suggest that hydrogen ion reduction is inhibited by a tin-containing film on the electrode, either a hydrous oxide or basic halide, formed as a result of hydrolytic precipitation in the vicinity of the electrode. That the suppressive effect was indeed caused by a film is indicated by the current–potential curves in Fig. 4. Once the film is formed on the surface, hydrogen ion reduction is suppressed (curves 2 and 3). When the film is removed by acid treatment, the usual hydrogen ion reduction curve is again obtained (curve 4).
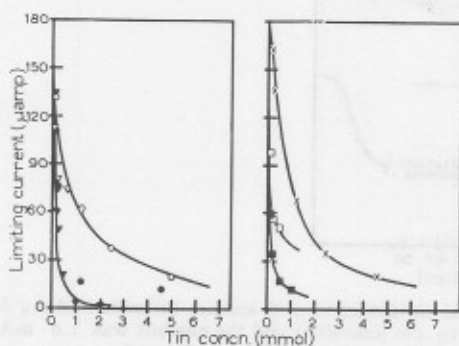


Fig. 3. Suppression effect of tin(II) and tin(IV) in different media: O, Sn(IV), 3 $M$ NaBr, 0.4 $M$ HClO$_4$; ▽, Sn(IV), 2 $M$ NaBr, 0.1 $M$ HClO$_4$; ✕, Sn(IV), 3 $M$ NaCl, 0.4 $M$ HClO$_4$; □, Sn(II), 1 $M$ NaClO$_4$, 0.4 $M$ HClO$_4$; ●, Sn(IV), 3 $M$ NaBr, 0.2 $M$ HClO$_4$; ▼, Sn(II), 3 $M$ NaBr, 0.4 $M$ HClO$_4$; ■, Sn(IV), 1 $M$ NaClO$_4$, 0.4$M$ HClO$_4$.
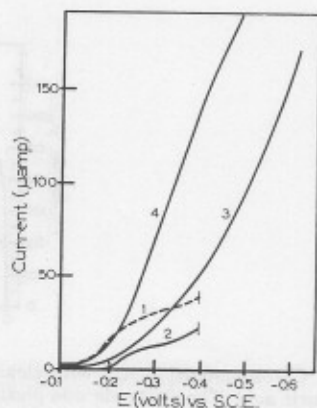
Fig. 4. Effect of electrode pretreatment on hydrogen ion reduction. The solutions contained 3 $M$ sodium bromide and 0.4 $M$ perchloric acid: (1) 0.5 m$M$ tin(II); (2) repeat, immediately after 1; (3) electrode from 2 washed in distilled water, supporting electrolyte alone; (4) electrode from 3 cleaned in aqua regia, supporting electrolyte alone.

trode, prolonged washing (5 min) in HCl or NaOH appeared to partially remove the film. Aqua regia and hot 9 $M$ HBr were most effective in stripping the film.

Mechanically wiping the electrode with filter paper or heating the filmed electrode to 120° for 15 min produced no change in the film pattern. Anodization of the filmed electrode in either the filming solution or the supporting electrolyte was quite effective in removing (or altering) the film. Cathodization appeared to change the nature of the film somewhat, but not remove it (Fig. 5 curve 3).

The observed potential halt in the filmed electrode chronopotentiogram is probably due to both $H^+$ reduction and alteration of the film itself. Measurement of transition times ($\tau$) of 6–123 sec at currents of 0.37–2.12 mA showed a wide variation in both $i\tau$ and $i\tau^{1/2}$. If all of the electricity during the first transition was used in a 2-electron reduction of the film, the amount of tin on the electrode would be 2–5 $\mu$g/sq. cm.

Chronopotentiograms with electrodes manually filmed by smearing hydrous tin oxides onto their surfaces were studied to ascertain whether they were similar to "filmed electrode" reduction patterns, and to elucidate the reactions occurring at these electrodes. Stannic or stannous hydrous oxide was prepared by precipitation from a solution of the chloride with ammonia, separated by centrifugation and washed twice with water. The electrode was coated by smearing the gelatinous precipitate
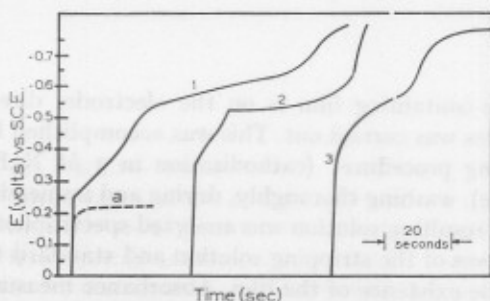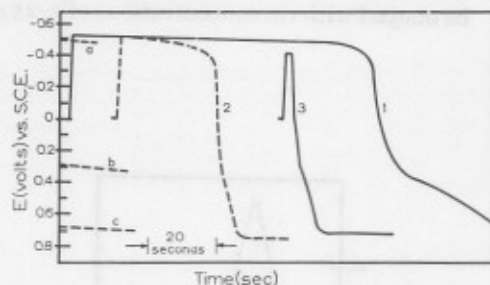


Fig. 6. Cathodic chronopotentiograms with manually coated electrodes. The solution was 3 $M$ sodium bromide and 0.4 $M$ perchloric acid, and the electrode was platinum (1.68 sq. cm): (1) electrode coated with $SnO_2 \cdot xH_2O$, 2.88 mA; (2) electrode coated with $SnO \cdot xH_2O$, 3.06 mA; (3) filmed electrode, 0.92 mA; (a) clean electrode.

Fig. 7. Anodic chronopotentiograms (following cathodization) with manually coated electrodes. The solution contained 3 $M$ sodium bromide and 0.4 $M$ perchloric acid, and the electrode was platinum (1.68 sq. cm): (1) electrode coated with $SnO_2 \cdot xH_2O$, 0.54 mA; (2) electrode coated with $SnO \cdot xH_2O$, 3.09 mA; (3) filmed electrode, 0.98 mA; (a) tin electrode; (b) clean electrode, solution contained 0.1 $M$ tin(II); (c) clean electrode.



completely over the surface of the electrode, and then wiping with filter paper. This procedure leaves a thin, adherent, invisible film.

Chronopotentiograms were taken in an unstirred 3 $M$ NaBr, 0.4 $M$ HClO₄ solution. A cathodic chronopotentiogram was taken (Fig. 6), and immediately afterwards an anodic one (Fig. 7). The duration of the potential halts varied from trial to trial

from a 60 sq. cm (projected area, both sides) electrode, subtracting a blank, prepared from an unfilmed electrode, indicated that the film contains about 3–4 $\mu$g of tin per sq. cm.

Allowing for the uncertainty of the real and apparent areas, we conclude that the film can be as thin as one molecular layer, and is probably not thicker than a few molecular layers.

### Current–time curves; a possible mechanism of film formation

Electrolysis at constant potential at a rotating platinum microelectrode was performed in solutions containing various amounts of stannous tin at several potentials. The potential was set on the polarograph, and the current–time curve was recorded. The curves in Fig. 9 indicate that the current follows an expression of the form:

$$i = k \exp(-bt).$$

A mechanism consonant with this mode of current change is as follows. Cathodization of the rotating platinum microelectrode in acid solutions causes hydrogen ion reduction with the subsequent release of hydrogen gas. As hydrogen ion is reduced, the pH very close to the electrode increases until the solubility product of hydrous tin oxide is exceeded. From the solubility products of the hydroxides[5,6] tin(IV) and tin(II) will precipitate from 1 m$M$ tin solutions at pH's of about 0.9 and 2.6 respectively. Actually the rate of formation of the hydrous oxides must be slow[7], so that after the pH increases past the precipitation point, some time is required for the hydrous oxide aggregates to form.

The primary particles of the hydrous oxides tend to be colloidal and adsorption of hydrogen ion causes these particles to have a positive charge. It has been shown[8] that only small amounts of acid (e.g., 0.004 $M$ HCl) will cause a net positive charge on the surface of hydrous tin oxides. These positively charged particles migrate to the negatively charged cathode and form a film which inhibits hydrogen ion reduction.

The film continues to build up until a state is reached where the amount of hydrogen ion undergoing reduction is just sufficient to keep the film from redissolving. Higher tin concentrations will tend to maintain the electrode at a covered condition and decrease the amount of hydrogen ion reduction. The suppression of hydrogen ion reduction increases in going from chloride to bromide to perchlorate solutions, which is the direction predicted by this mechanism in proceeding to less strongly complexing media.

In chronopotentiometry, when a filmed electrode is cathodized at a constant current, the hydrogen ion available at the unfilmed portions of the surface will rapidly be depleted and the potential will quickly rise to a value where a new reduction may take place.

The usual reduction of a species (e.g. hydrogen ion) at a rotating platinum electrode at a potential corresponding to a point on its limiting current plateau, will rapidly reach a steady current, limited by the rate of mass transfer of the species to the electrode. If a film is forming on the electrode, caused by the electrode reaction and decreasing the area of the electrode available for the reaction, the current will start at its limiting value, but then decay as the film builds up. Since the film forms as a

If the film is conducting[9], reactions where the rate-controlling step involves the acceptance of an electron will proceed essentially unchanged. Reactions where the slow step is adsorption of a reactant onto the electrode, or desorption of products from the electrode, may be considerably altered. Several explanations for hydrogen overvoltage on platinum invoke just such mechanisms, and hence interference with hydrogen ion reduction may take place, while many other reactions occur unhindered.

Current–potential curves taken with a clean platinum electrode in a NaBr medium with and without tin(IV) present, indicate less than 100% current efficiency for the generation of stannous ion. Coulometric titrations with electrogenerated stannous ion themselves proceed with 100% current efficiency however[10], because the film formed on the electrode in the stannic tin solutions greatly increases the hydrogen overvoltage. Estimation of current efficiency using the clean electrode curve at a generation current of 10 mA predicts 87%, whereas the actual current efficiency is greater than 99%.

## CONCLUSION

The phenomenon of film formation by hydrolysis of a species at increased pH in the diffusion layer seems established. Invoking this effect, some apparently anomalous behavior of a platinum electrode is explained. By "filming" an electrode, the cathodic range in acidic solution is extended. Applications to analysis at a rotating platinum microelectrode (e.g. the determination of antimony), chronopotentiometry, and coulometric titrations (e.g. generation of stannous tin) are indicated, although a higher hydrogen overvoltage electrode (e.g. gold) will usually perform equally well. The application of hydrous oxide films as a device for corrosion inhibition merits investigation.

## ACKNOWLEDGEMENTS

## SUMMARY

Evidence is presented for inhibition of hydrogen ion reduction in acidic halide media at a platinum electrode in the presence of tin. This inhibition is traced to a film of tin hydrous oxide formed when hydrogen ion is reduced, causing the pH to increase in the vicinity of the electrode, and allowing hydrolytic precipitation to occur.

The film was investigated employing voltammetry, chronopotentiometry and spectrophotometry. The stability of the film and its effect on other electrode reactions was examined, and a mechanism for its formation proposed.

## REFERENCES

1 C. N. REILLEY, G. W. EVERETT AND R. H. JOHNS, Anal. Chem., 27 (1955) 483.
2 H. J. S. SAND, Phil. Mag., 1 (1901) 45.
3 A. J. BARD, Thesis, Harvard University, 1958.
4 W. NIELSH AND G. BOLTZ, Z. anal. Chem., 142 (1954) 109.
5 W. H. LATIMER, Oxidation States of the Elements and Their Potentials in Aqueous Solutions, 2nd edn., Prentice-Hall, New York, 1952.
6 A. B. GARRETT AND R. E. HEIKS, J. Am. Chem. Soc., 63 (1941) 562.
7 J. GUERON, Bull. soc. chim. France, 1 (1934) 561.
8 B. N. GHOSH, J. Chem. Soc., (1928) 3027.
9 K. FISHBECK, Z. anorg. allgem. Chem., 148 (1925) 97.
10 A. J. BARD AND J. J. LINGANE, Anal. Chim. Acta, 20 (1959) 463.