Rapid Determination of Divalent Tin In Alkaline Tin-Plating Solution by Direct Potentiometry

By A. Leung, G. Chen and D. Huang

A novel method for determination of Sn(II) in alkaline tin plating solutions by potentiometry has been developed. Potassium ferricyanide is added to form an equilibrium of both $Sn(OH)_6^{-2}/HSnO_2^-$ and $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$ in the solution. The quantity of Sn(II) in the solution is obtained by measuring the potential of $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$, which is rapid, with a stable reading within three to six min. The potential difference becomes as great as 50 mV when the content of Sn(II) is 0.02 g/L and 0.20 g/L, respectively. The average success rate for the determination of Sn(II) in alkaline tin plating solutions by this method is 95.2 percent, with a relative standard deviation of 1.2 percent.

Sodium stannate is the major ingredient in alkaline tin plating solutions. The electrodeposited coating should become crude and dark, like a sponge, if divalent tin in the plating solution is in excess of 0.1 g/L, which is possible if the tetravalent tin on the cathode is insufficiently reduced, or if dissolution of the tin anode is improper.[1]

Iodometry has been a standard procedure for determination of total tin in plating solutions,[2] but a high-accuracy method for Sn(II) in alkaline tin solution by potentiometry has now been developed.

Theoretical Analysis

The electrode potential of a redox couple can be expressed by Nernst's equation:

(1)

For an alkaline tin plating solution,

$$Sn(OH)_6^{-2} + 2e^- \rightleftharpoons HSnO_2^- + 3OH^- + H_2O$$

(2)

where $E_{Sn(OH)_6^{-2}/HSnO_2^-}$ is 0.96 V,[3] and f is the activity coefficient.

It is possible to analyze the quantity of Sn(II) in an alkaline tin plating solution by measuring the potential. The electrode potential is related only to the divalent tin concentration at constant concentrations of other ions and ionic strength. More time is required, however (more than 20 min), for reading the stable electrode potential of the $Sn(OH)_6^{-2}/HSnO_2^-$ couple.

The electron transfer between $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ is rapid.[4,5] The rate coefficient is $9.2 \times 10^4\ m^{-1}/sec^{-1}$.[6] $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ react with some oxidants or reducers at a rapid rate. Therefore, potassium ferricyanide is added to oxidize $HSnO_2^-$ in the original system $[Sn(OH)_6^{2-}/HSnO_2^-]$ and make that system become the following mixed system: $Sn(OH)_6^{-2}/HSnO_2^-$ and $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$. The reaction is

$$HSnO_2^- + 2Fe(CN)_6^{-3} + 3OH^- + H_2O \rightleftharpoons Sn(OH)_6^{-2} + 2Fe(CN)_6^{-4}$$

In this equilibrium,

$$E_{Sn(OH)_6^{-2}/HSnO_2^-} = E_{Fe(CN)_6^{-3}/Fe(CN)_6^{-4}} \qquad (3)$$

(4)

Their quantitative relation can be expressed in mol/L as

(5)

where b is concentration of potassium ferricyanide added ($b > 2C_{HSnO_2^-}$), which is in excess for divalent tin content. $C_{HSnO_2^-}$ is the concentration of $HSnO_2^-$ in the mixing solution before reaction.

In this procedure, the potential can be measured accurately within three to six min when the platinum electrode reaches equilibrium with the $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$ couple. The reading is stable and reproducible.

Experimental Procedure

Apparatus

Potentiometric measurements were made at a constant temperature with a digital multimeter in stirred solutions. A saturated calomel electrode was used as an external reference in a saturated KCl solution, with a platinum electrode as an

Table 1
Regression Equations for Different Temperatures

Temp. ±0.1 °C	Equation mV	r coeff.	Standard deviation
15	$E = 311 - 3975C + 50813C^2$	0.997	1.58
20	$E = 306 - 4291C + 63292C^2$	0.998	1.34
25	$E = 302 - 4747C + 78960C^2$	0.997	1.73
30	$E = 295 - 4602C + 80933C^2$	0.998	1.12

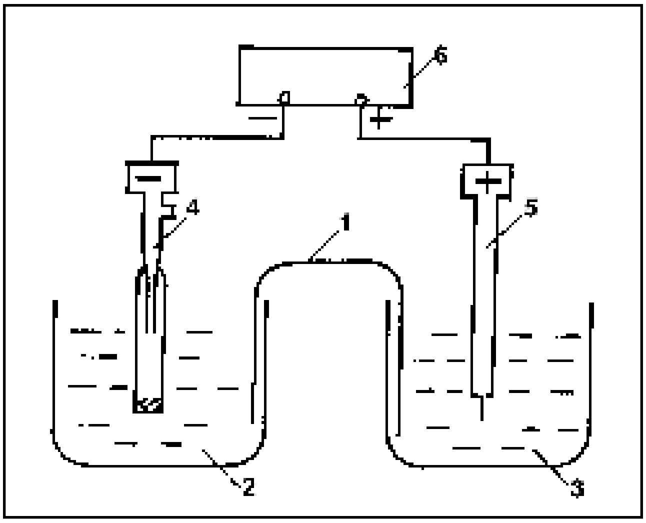

Fig. 1—Schematic of apparatus for determination of potential: (1) Paper salt bridge; (2) saturated KCl solution; (3) test solution or standard solution; (4) saturated calomel electrode; (5) platinum electrode; (6) digital multimeter.

Table 2
Determination of Difference Ratio of $SnO_3^{-2}/Sn(II)$

Temp. ±0.1 °C	Divalent Tin g/L	NaOH g/L	$Na_2SnO_3 \cdot 3H_2O$ g/L	E mV
30	0.090	40	110	258.0
30	0.090	40	97	258.5
30	0.090	40	84.5	259.0

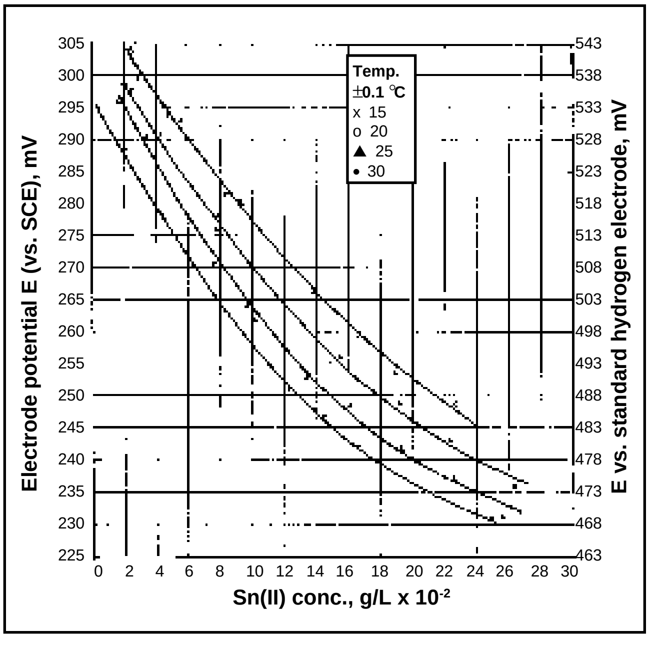

Fig. 2—Calibration curves for potential vs. concentration of divalent tin.

Table 3
Comparison of Potential Determination For Different Alkalinity

Temp. ±0.1 °C	Divalent Tin g/L	NaOH g/L	$Na_2SnO_3 \cdot 3H_2O$ g/L	E mV
30	0.090	40	97	258.5
30	0.090	37.6	97	257.5
30	0.090	36	97	256.5

Table 4
Recovery Values

Sample No.	Divalent Tin g/L	Recovery %	Average Recovery	Standard Deviation
1	0.058	95.6		
2	0.087	96.2	95.2%	1.2%
3	0.092	93.8		

indicating electrode in the test solutions. A junction between the saturated KCl solution and the test solution consisted of a paper salt bridge, 8 x 1.2 cm, made from a filter paper and immersed in the saturated KCl solution prior to use. A new salt bridge was needed for each test. A schematic of this apparatus is shown in Fig. 1.

Reagents and Solutions

The basic solution consisted of 0.5 mol $Na_2SnO_3 \cdot 3H_2O$, 1 mol NaOH and 0.4 mol $NaC_2H_3O_2$/L. Alkaline potassium ferricyanide: 10 mL $K_3Fe(CN)_6$, 90 mL 1.1 M NaOH. Standard solution: 5 mL 0.1 M alkaline $K_3Fe(CN)_6$ and several different volumes of the calibrated sodium stannite were added to 50-mL volumetric flasks containing about 2/3 volume of the basic solution, then the basic solution was added to the mark.

The test solution consisted of 5.00 mL of 0.01 M alkaline potassium ferricyanide and 5.00 mL of the plating solution were added to a 50-mL volumetric flask containing about 2/3 by volume of the basic solution. Then the basic solution was added to the mark.

Results and Discussion

Calibration Curves

Typical calibration curves for the determination of divalent tin at constant ionic strength and temperatures of 15, 20, 25, and 30 °C are shown in Fig. 2. The potential difference becomes as great as 50 mV when the content of divalent tin is 0.02 g/L and 0.20 g/L, respectively. The greater the slope of the calibration curve, the higher the accuracy of the determination. The results show that the accuracy of the method for the determination is satisfactory.

Regression Equations

Four groups of the experimental data were treated by the least squares method. The regression equations were obtained as shown in Table 1. C is the divalent tin content in the plating solution in g/L.

Potential as a Function Of Concentration and Temperature

The equation is obtained from the data treated with the least squares method:

$$E = 330.2 - 4429.8C + 69396.7C^2 - 1.2T, \quad r = 0.997$$

Effect of Concentrations of Na_2SnO_3 and NaOH

The potentials were measured when the divalent tin and NaOH contents were constant and the quantity of SnO_3^{-2} was changed, or vice versa. The results are shown in Tables 2 and 3. In practice, the concentrations of $Na_2SnO_3 \cdot 3H_2O$ and NaOH are without effect on the determination of Sn(II) because the volume of the plating solution in the test solution is small (1/10) and the test solution contains a large amount of $Na_2SnO_3 \cdot 3H_2O$ and NaOH.

Application

The potential of the test solution was measured and the quantity of Sn(II) obtained via the calibration curve. In this determination, it was found helpful to add 0.001 M potassium ferricyanide to improve accuracy.

From the determination of three plating solution samples, an average recovery value for the determination was found to be 95.2 percent, with relative standard deviation of 1.2 percent, as shown in Table 4.

Conclusions

The method of determination of Sn(II) in an alkaline tin plating solution by potentiometry is simple, convenient and fast, and the precision and accuracy are satisfactory. The method can be used for determining Sn(II) in alkaline tin plating solutions containing various concentrations of sodium stannate.

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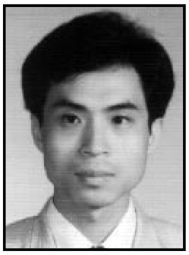

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