

## On the Oxidation of Tin(II) in Methanesulfonate Solutions and the Role of Trace Chloride

By Nicholas M. Martyak\* and Robert Seefeldt

**Tin(II) methanesulfonate,  $\text{Sn}(\text{CH}_3\text{SO}_3)_2$ , solutions may contain small concentrations of  $\text{Cl}^-$  originating from commercial methanesulfonic acid,  $\text{CH}_3\text{SO}_3\text{H}$  (MSA), or impure water used during the make-up or replenishment of the acid electrolyte. A problem often encountered using  $\text{Sn}(\text{CH}_3\text{SO}_3)_2$  electrolytes is the unwanted formation of a stannic sludge. Although antioxidants are used to control the kinetics of Sn(IV) formation, the role of chloride in these electrolytes in producing the sludge is unclear. It is shown that chloride does not affect the formation of Sn(IV) to any appreciable extent compared to electrolytes containing no chloride.**

Sulfonic acid plating electrolytes can be used to deposit a thin layer of tin or a tin-alloy on electronic components. Acids such as methanesulfonic,  $\text{CH}_3\text{SO}_3\text{H}$  (MSA), p-toluenesulfonic acid (p-TSA) and phenolsulfonic acid (PSA) are organic acids but exhibit relatively high electrolyte conductivities (high ion mobilities) solubilize tin, lead and most other alloying metals and often control stannic formation better than mineral acids such as hydrochloric and sulfuric acid. Of the three sulfonic acids, MSA is now the most popular acid electrolyte for the plating of electronic components with tin, tin-lead and lead-free tin alloys and is gaining popularity in the tinning of sheet steel. The large interest in MSA is due in part to its high purity and its ability to solubilize metals such as lead and bismuth that are insoluble in mineral acids such as sulfuric acid. Equally important is the reducing nature of this acid in minimizing the formation of tin(IV) oxides and hydroxides. Once formed in the MSA electrolytes, Sn(IV) oxide is insoluble

and may become occluded on the electronic components or clog filters that are used to remove insoluble materials. The plating of electronic components or steel strip with stannous methanesulfonate solutions often uses grain refining additives to produce a matte or bright finish. Antioxidants such as hydroquinone<sup>1</sup> are almost always used to minimize the formation of the stannic sludge. However, even under the best conditions, it is impossible to completely eliminate some Sn(IV) in the plating solutions.

Commercial MSA may be produced from several precursor molecules such as methyl mercaptan,  $\text{CH}_3\text{SH}$ , and chlorine gas as an oxidant:



The methanesulfonyl chloride is then hydrolyzed to produce highly purified methanesulfonic acid:



The hydrochloric acid produced as a by-product is removed producing an organic acid with a very low (<2 mg/L) residual chloride concentration.

Previously, chloride in sulfonic acid plating solutions was shown to increase the kinetics of oxidation of Sn(II) to Sn(IV).<sup>2</sup> This early work used phenolsulfonic acid (PSA) as the plating electrolyte and examined  $\text{Cl}^-$  concentrations from 1.0M to 2.0M and as such, these concentrations of chloride are never encountered in today's commercial MSA plating formulations. For example, the concentration of MSA in matte or bright tin solutions may vary from about 50 to 150 g/L (6.7 to 20.0 oz/gal). Using 70% MSA containing only 2 mg/L  $\text{Cl}^-$  (i.e., ppm) as an impurity, a typical tin plating solution requires only 5 to 15% free MSA, yielding about 0.1 to about 0.3 mg/L  $\text{Cl}^-$  in the operating plating solutions. The effects of chloride on Sn(II)

### Nuts & Bolts: What This Paper Means to You

One of the problems encountered in running a methanesulfonate tin bath, is the buildup of stannic tin sludges. These will adversely effect filtration as well as the quality of the deposit. Originally, it was thought that trace chlorides were the cause, but this work shows otherwise.

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oxidation using oxygen,<sup>3</sup> nitrate,<sup>4</sup> methyl orange,<sup>5</sup> Fe<sup>+3</sup>,<sup>6</sup> and metals in their higher oxidation states<sup>7</sup> showed Cl<sup>-</sup> promotes the oxidation of stannous to stannic but the concentrations of the additives reported<sup>3-7</sup> are not typically encountered in commercial tin plating solutions.

To address the effects of *trace* amounts of chloride in acid tin methanesulfonate solutions, kinetic studies were conducted over a six week period to monitor the loss of Sn(II). The influence of relatively high concentrations of chloride in acid tin methanesulfonate solutions, 10 to 100 mg/L, on the oxidation of stannous was monitored. These high concentrations of chloride were chosen to increase the propensity for stannic generation even though it is highly unlikely that such a high concentration of Cl<sup>-</sup> would ever be seen in a tin methanesulfonate solution.

**Table 1**  
**Free Energies of Formation for Various Tin and Chloro Species**

Species	$\Delta G(f)$ kcal/mol
Cl <sub>2</sub> (a)	1.929
Cl(-a)	-31.09
Cl <sub>3</sub> (-a)	0.683
ClO <sub>2</sub> (a)	29.088
ClO(-a)	-8.1
ClO <sub>2</sub> (-a)	4.784
ClO <sub>3</sub> (-a)	-1.111
ClO <sub>4</sub> (-a)	-1.066
HCl(a)	-31.094
HClO(a)	-18.775
HClO <sub>2</sub> (a)	1.859
HClO <sub>3</sub> (a)	-1.113
HClO <sub>4</sub> (a)	-1.066
Sn	0
SnCl <sub>2</sub>	-68.077
SnCl <sub>4</sub>	-104.629
SnO	-61.136
SnO <sub>2</sub>	-123.666
Sn(+2a)	-6.701
SnCl <sub>2</sub> (a)	-71.275
SnCl(+a)	-39.288
SnCl <sub>3</sub> (-a)	-102.252
SnOH(+a)	-60.767
SnOHCl(a)	-93.326
SnOOH(+a)	-94.421
OH <sup>-</sup> (a)	-37.6

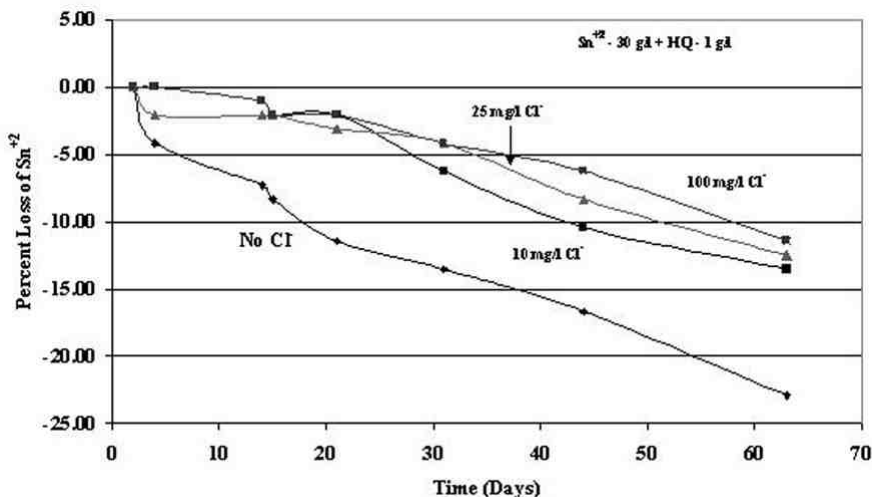


Figure 1—Oxidation of Sn(II) to Sn(IV) and the influence of chloride in solution.

## Experimental

Stannous methanesulfonate solutions were prepared by diluting Sn(II) methanesulfonate and commercially available methanesulfonic acid, CH<sub>3</sub>SO<sub>3</sub>H (MSA) into doubly distilled water. The final Sn(II) and MSA concentrations were 30 g/L and 130 g/L (4.0 and 17.4 oz/gal), respectively and each solution contained 1 g/L (0.13 oz/gal) hydroquinone (HQ) as an antioxidant.

The solutions were periodically analyzed for Sn(II) using an iodine-starch method. A 1-mL aliquot was diluted in 100 mL water and 20 mL of 20% HCl was added followed by mixing for 30 sec. Sodium carbonate, about 1.5 g, was added to the solution and after one min, 1 mL of a starch solution was added and mixed for 15 sec. The solution was titrated with 0.1N iodine to a stable purple endpoint and the concentration of Sn(II) was calculated as follows:

$$\text{Sn(II)} = 5.935 \times \text{Vol. 0.1N iodine solution}$$

Ultraviolet (UV)-visible spectra were recorded after sixty days of exposure to the air. A UV-Visible instrument\*\* along with 1 cm cuvettes were used to record spectra from 250 nm to 950 nm using a scan rate of 1000 nm/min.

## Results and discussion

The change in Sn(II) concentration over a 65-day period is seen in Fig. 1. The solution containing no chloride showed a loss of about 15% of the original Sn(II) concentration whereas those containing from 10 to 100 mg/L Cl<sup>-</sup> showed about a 6% to 10% loss. The loss of Sn(II) in these solutions is considerably less than that reported by Meibuhr and Carter<sup>2</sup> studying the influence of chloride in PSA solutions. This earlier work showed the increase in Sn(IV) was first order with respect to Cl<sup>-</sup> concentration but deviation from first-order kinetics

\*\* Cintra 40 UV-Visible instrument, GBC Scientific Equipment Pty. Ltd., Dandenong, VIC (Australia) [Gilberts, IL (USA)]

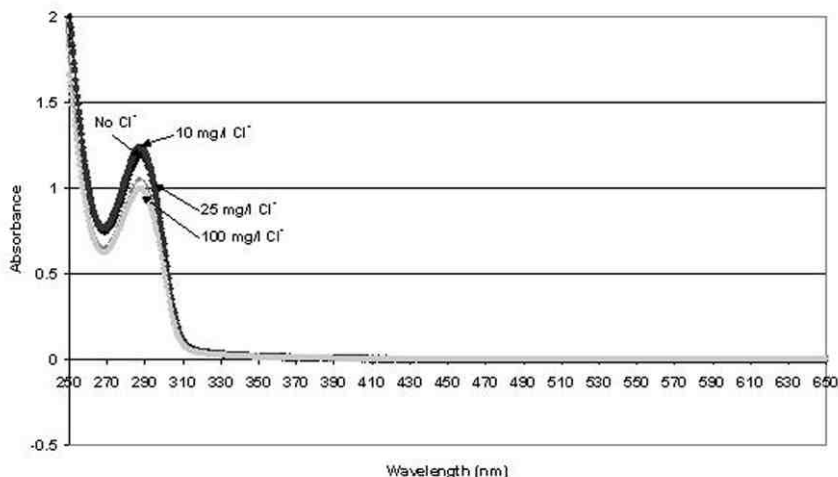


Figure 2—UV-visible spectra of tin solutions after 60 days exposure to air.

was noted at the lower  $\text{Cl}^-$  concentrations. This change in Sn(IV) kinetics is likely due to the decrease in free  $\text{Cl}^-$  that is available for complexing stannous tin in solutions containing low free  $\text{Cl}^-$ .

Changes in Sn(II) concentrations over a 65-day period were monitored using UV-visible spectrophotometry as seen in Fig. 2. The maximum absorbance occurred at about 288 nm and is approximately the same in all four solutions. This absorption is due to the antioxidant used in most commercial tin formulations, namely hydroquinone. There are no other strong absorption bands in the spectra inferring the solutions are still colorless, characteristic of a divalent tin solution. The lack of other absorbance bands in the visible region indicates no soluble Sn(IV) is formed either in the absence or presence of chloride ion. There is a slight decrease in intensity of the HQ absorbance band at the higher  $\text{Cl}^-$  concentrations. Any chloride in the tin methanesulfonate solution apparently causes the HQ to oxidize preferentially over stannous tin as evidenced by the absence of an absorbance band for the Sn(IV) species and the decrease in the HQ intensity band at 288 nm. However, the significantly higher concentration of HQ (1000 mg/L) compared to the trace amounts of  $\text{Cl}^-$  (10 to 100 mg/L) is sufficient to inhibit any Sn(IV) generation.

The oxidation of Sn(II) to Sn(IV) and the role of chloride in the methanesulfonate solutions may be explained using thermodynamics. For general reaction:



The change in free energy of the reaction is: [4]

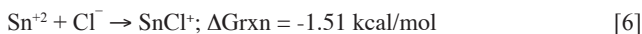
$$\Delta G_{\text{rxn}} = [\Sigma((c\Delta G_f^\circ(C) + d\Delta G_f^\circ(D))) - \Sigma((a\Delta G_f^\circ(A) + (b\Delta G_f^\circ(B)))]$$

where  $\Delta G_f^\circ$  is the standard free energy of formation the individual reactants or products. A computer program<sup>8</sup> was used to generate the free energies of various Sn(II) and Sn(IV) compounds as seen in Table 1. There are several possible step-wise or overall reactions leading to stannic tin. It was previously shown that the reaction product between stannous and a chloro species is oppositely charged to the oxidizing agent.<sup>9</sup> For example, Duke and Pinkerton<sup>6</sup> and Krishna<sup>9</sup> reported the oxidation of Sn(II) by  $\text{Fe}^{+3}$  produced the  $\text{SnCl}_3^-$  complex. Meibuhr and Carter, using a modified Job's method of continuous variation<sup>10</sup> studied the kinetics of oxidation using the following general reaction:



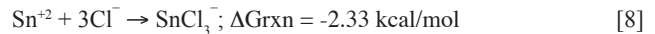
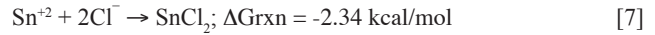
where A is Sn(II), X is  $\text{Cl}^-$ , O is an oxidant such as dissolved oxygen and  $\text{AmXn}$  is a stannous chloro species. From the ratio of the amount of Sn(II) oxidized to the molar amount in solution, the product was determined. For example, if the ratio was 0.33, the product was likely  $\text{SnCl}_3^-$ , but their work concluded the product was  $\text{SnCl}^+$  (*i.e.*, the ratio was close to 1:1). Dissolved oxygen in the PSA solution was likely the oxidant and may exist as a peroxide-type compound,  $\text{HO}_2^-$ .<sup>9</sup>

Therefore, assuming dissolved oxygen also exists as a peroxide-type compound in the MSA solutions, which is reasonable since PSA is very close in structure and reactivity to MSA, the initial product between Sn(II) and  $\text{Cl}^-$  must be positively charged. One possible mechanism for the oxidation of Sn(II) to Sn(IV) involving chloride and dissolved oxygen calculated from the data in Table 1 is:

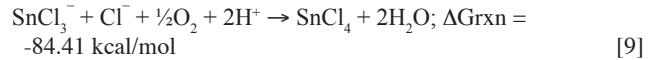


The product is oppositely charged from the  $\text{HO}_2^-$ , in agreement with previous work.<sup>2,9</sup> The mono-chloro species can then further

react with available trace chloride to produce a series of Sn(II)-Cl complexes:



The above stanno-chloro complexes likely form in the methanesulfonate solution in agreement with Meibuhr and co-workers.<sup>11</sup> They studied the effects of chloride in acid tin sulfate plating solutions and showed that at 0.02M chloride (~700 mg/L), the concentrations of the various tin(II) chloro complexes were:  $\text{SnCl}^+ = 1.7 \times 10^{-2}\text{M}$ ,  $\text{SnCl}_2 = 10^{-4}\text{M}$  and  $\text{SnCl}_3^- = 10^{-8}\text{M}$ . It is well known that the Sn(IV)-chloro species are more stable than the Sn(II)-chloro molecules<sup>12,13</sup> so the Sn(II)-chloro entities are likely oxidized:

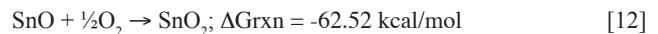


This stannic complex,  $\text{SnCl}_4$ , will eventually hydrolyze to stannic oxide and hydrochloric acid starting the oxidation cycle all over again:



The overall free energy change for the formation of  $\text{SnO}_2$  from Sn(II) is -117.2 kcal/mol.

In the absence of any chloride, the direct oxidation of Sn(II) to Sn(IV) by oxygen is also thermodynamically favorable:



resulting in an overall  $\Delta\text{Grxn}$  of -116.96 kcal/mol. The two oxidation pathways, chloride-free and in the presence of trace chloride, result in an almost identical  $\Delta\text{Grxn}$ . Therefore, it is hard to say with any certainty that the stepwise oxidation of Sn(II) via chloro intermediates is favored over the direct oxidation route.

The slightly lower oxidation rates seen in Fig. 1 in the presence of chloride may be due a slow step in the above oxidation process. If one of the chloro addition steps, Eqs. 7 or 8, forming a higher Sn(II)-chloro complex is slow or the oxidation of the Sn(II)-chloro species to the Sn(IV)-chloro species is kinetically hindered, Eq. 9, the overall rate of Sn(II) to Sn(IV) oxidation would also be slowed.

The data presented in Table 1 was used to generate potential-pH diagrams for the tin-water, Figure 3, and the tin-water-chloride, Figure 4, systems. These diagrams show the thermodynamic domains of stability for the various tin-chloro and tin hydroxide species in solution. It is apparent the species prevalent in aqueous solutions at low pH is stannous ion yet equilibrium calculations suggest stannous-chloro complexes are also in the plating solutions.

The role of the antioxidant used in this study is critical in slowing the formation of  $\text{SnO}_2$ . Keeping the concentration of dissolved oxygen at a very low concentration slows the oxidation of the Sn(II)-chloro complex, Eq. 9, or SnO to the  $\text{SnO}_2$ , Eqs. 11 and 12. It appears the effects of the HQ masks the effects of *trace* chloride in the tin methanesulfonate solutions on the kinetics of stannous oxidation.

There are other accelerated experimental procedures to monitor the effects of plating solutions components on the oxidation of stannous to stannic. For example, continuous bubbling or air or

oxygen would certainly increase the kinetics of oxidation but the results may not truly reflect production-plating lines unless these plating lines have relatively high solution agitation and thus be exposed to a continuous supply of fresh oxygen. Perhaps mild solution agitation via mechanical mixing might be more realistic in simulating production-plating lines and should be explored. Finally, another accelerated test method includes studying the influence of oxidation of stannous tin at the anode and to what extent, if any, chloride may have on this process.

## Conclusions

The oxidation of stannous tin is not influenced to any large measure by trace amounts of chloride in a tin methanesulfonate solution. The chloride probably reacts with stannous tin, forming soluble tin chloro species followed by their slow oxidation to stannic. HQ is important in minimizing the rate of Sn(II) oxidation.

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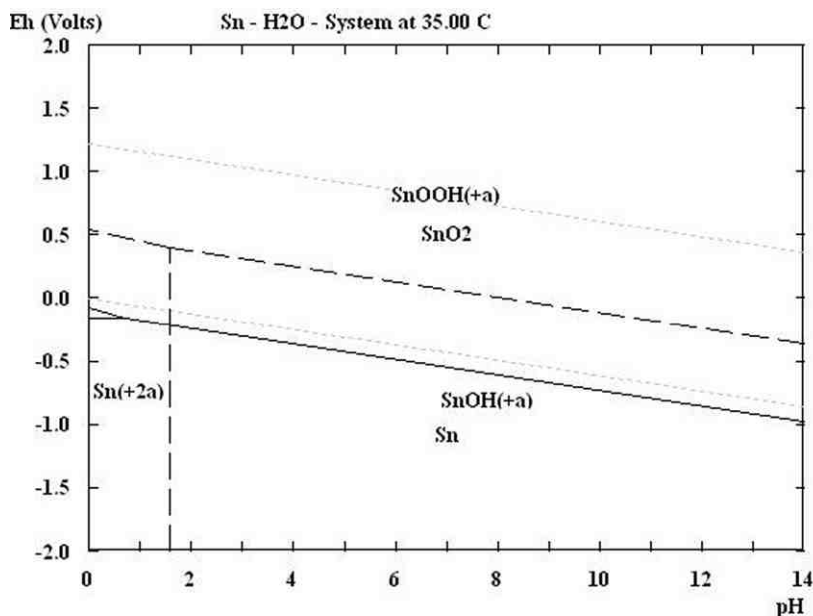


Figure 3—Aqueous species diagram for the Sn-H<sub>2</sub>O system  $\bar{D}$  No chloride.

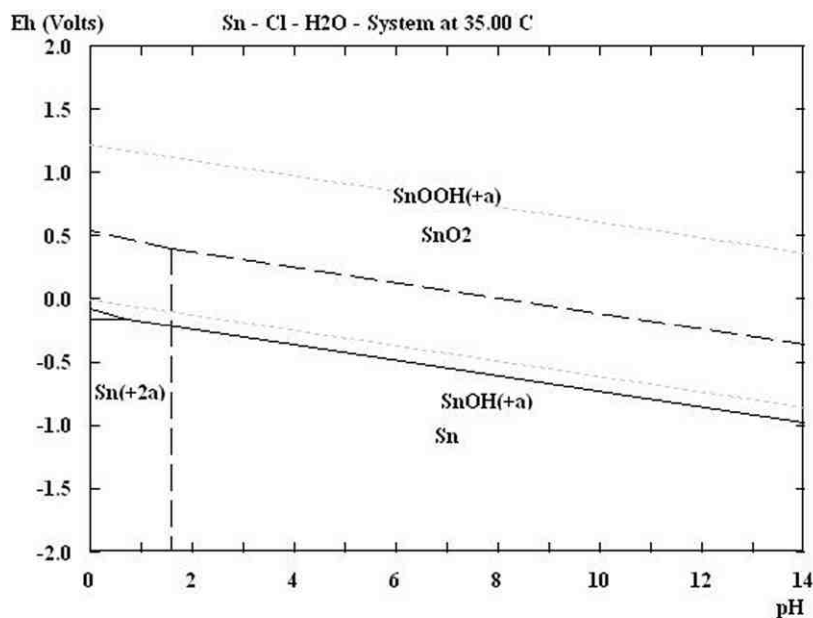
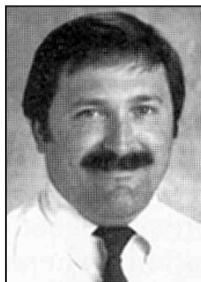


Figure 4—Aqueous species diagram for the Sn-H<sub>2</sub>O system  $\bar{D}$  100 mg/L chloride, showing no soluble Sn-Cl complexes.

## About the Author



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