

The Electrochemistry of Tin in the Zinc Chloride-1-ethyl-3-methylimidazolium Chloride Molten Salt

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Low temperature molten salts can be prepared from mixtures of zinc chloride and 1-ethyl-3-methylimidazolium chloride (EMIC)¹ Because zinc chloride is a Lewis acid, the Lewis acidity of ZnCl₂-EMIC melts can be adjusted by varying the molar percentage of zinc chloride. Previous studies indicate that the ZnCl₂-EMIC melts can be employed for the electrodeposition of various metals and alloys in a temperature range between 40 – 150 °C.²⁻⁴ It is well known that the most popular ambient temperature AlCl₃-EMIC molten salts are extremely sensitive toward moisture and air.⁵ On the other hand, the ZnCl₂-EMIC melts do not react vigorously with water and air. This fact makes the ZnCl₂-EMIC melts easier to handle: the electrodeposits obtained from ZnCl₂-EMIC melts can be washed directly with water without causing cracks in the deposits.

The electrochemistry of tin has been investigated previously in high-temperature alkali chlorides and in alkali chloroaluminates.⁶⁻⁸ More recently, it was also reported that Sn(II) could be reduced to tin metal and oxidized to Sn(IV) in both the acidic and basic AlCl₃-EMIC room temperature melts.⁹

In this report, the electrochemistry of Sn(II) was investigated in the 40-50 mol% ZnCl₂-EMIC melt at 90°C at tungsten and glassy carbon electrodes. The Sn(II) was introduced into the melt by dissolution of SnCl₂. Typical cyclic voltammograms recorded at a tungsten electrode are presented in Fig. 1. Fig. 1a indicates that when the potential was scanned negatively from the rest potential, the reduction of Sn(II) to tin metal occurred at about 0.1 V (vs. Zn(II)/Zn) and the deposited tin metal could be stripped off upon potential reversal. Fig 1a indicates that the deposition of Sn was complicated by nucleation. The nucleation process of tin on the GC electrode was further studied with chronoamperometry. Fig 2 shows that the current-time transients data obtained from these experiments are in good agreement with theoretical model based on instantaneous three-dimensional nucleation with diffusion controlled growth of the nuclei. Fig. 1b shows that when the potential was scanned positively from the rest potential, Sn(IV) was oxidized to Sn(IV) at about 1.4 V. Fig 1b also indicates that the Sn(IV) could be reduced back to Sn(II) at a potential right before the reduction of Sn(II) to Sn metal. The sluggish kinetics of the Sn(IV)/Sn(II) redox reaction can be realized by the wide peak potential separation of this couple. The cyclic voltammograms shown in Fig. 3 indicates that the oxidation of Sn(II) to Sn(IV) at the tungsten electrode was hindered by the adsorption of Sn(II).

References

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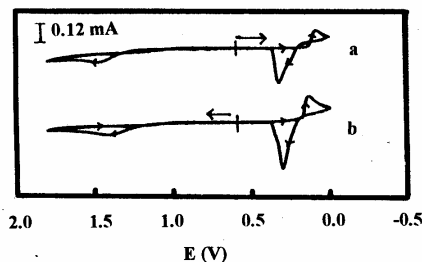


Fig. 1 Staircase cyclic voltammograms of 30mM Sn(II) in 40-60 mol% ZnCl₂-EMIC melt at tungsten electrode at 90°C: (a) the potential was scanned negatively from the rest potential (b) the potential was scanned positively from the rest potential. Scan rate was 50mV/s

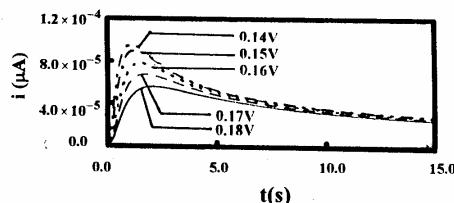


Fig. 2 Current-time transients resulting from chronoamperometry experiments recorded on glassy carbon electrode for 40.0-60.0 mol% ZnCl₂-EMIC melt containing 30mM Sn(II) at 90°C. The potential was stepped from 0.5 V to the potential region where deposition of tin only occurs (between 0.14 V and 0.18 V).

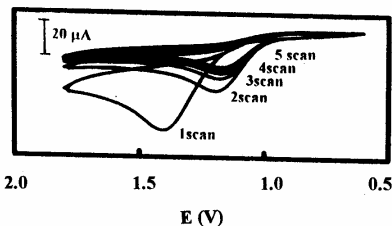


Fig. 3 Multiple staircase cyclic voltammograms for oxidation of Sn(II) at tungsten electrode in 40-60 mol% ZnCl₂-EMIC melt containing 30mM Sn(II) at 90°C. Scan rate was 50mV/s.