ELECTRODEPOSITION OF TIN FROM EMI·BF$_4$·Cl ROOM TEMPERATURE MOLTEN SALTS

M. Morimitsu*, Y. Nakahara, Y. Iwaki, and M. Matsunaga

Department of Applied Chemistry, Kyushu Institute of Technology
1-1 Sensui, Tobata, Kitakyushu 804-8550, Japan

Abstract

The electrochemistry of Sn(II) was investigated with cyclic voltammetry and chronoamperometry in the 1-ethyl-3-methylimidazolium tetrafluoroborate molten salt containing free chloride ions (EMI·BF$_4$·Cl) originated from the mixture of EMIC and NaBF$_4$ (60:40 mol%). The well-defined redox waves for the electrodeposition and dissolution of tin were observed on a platinum electrode at 303 K. The deposition of tin proceeded through a quasi-reversible step with two-electron transfer, and the deposited tin was sufficiently recovered during oxidation. The experimental current-time transient coincided with the theory based on one-dimensional diffusion control.

Keywords: electrodeposition, Sn, cyclic voltammetry, molten salts

1. Introduction

A variety of room temperature molten salts have been developed and has received much attention not only for fundamental interest due to their unique physico-chemical properties but also for possible applications in electroplating, battery, organic synthesis, and so on [1]. Especially, some kinds of molten salts consisting of nonmetallic components possess a low reactivity to air and water, which allows them to handle easily and to use in ambient atmosphere. One of the typical examples is the melt composed of 1-ethyl-3-methylimidazolium cation (EMI$^+$) and tetrafluoroborate anion (BF$_4^-$), originally reported in the literature [2]. The EMI·BF$_4$ melt resulted from the combination of equivalent moles of EMI$^+$ and BF$_4^-$ is water-stable and has a wide electrochemical

window of *ca.* 4 V. Although these favorable properties as an electrolyte have promoted to use the melt for the investigations on the electrochemistry of ferrocene and lithium [3] and silver [4], the EMI·BF$_4$ melt has a low solubility of metal compounds such as metal chlorides, which is essentially caused by the neutrality on Lewis acid-base theory. This makes the limitation for use of the Lewis neutral EMI·BF$_4$ melt as an electrolyte for electrochemical studies. On the other hand, Chen and Sun has recently reported that when excess moles of EMIC is mixed with NaBF$_4$, the melt containing free chloride ions is produced. Thereby, the dissolution of metal chlorides in this melt becomes possible, due to the complexation of the metal chloride with the free chloride ions [5]. They have also found that the obtained melt is a colorless solution and has a low reactivity to air and a wide electrochemical window more than 3 V. While the electrochemistry of Cu(I) [5] and Cd(II) [6] has been investigated in the Lewis basic EMI·BF$_4$·Cl melt, and it has been found that these metals can be electrodeposited, further works on the electrochemistry of other metal species in the basic melt are expected to explore the potential of the melt from fundamental and applied perspectives. In this paper, the electrochemistry of Sn(II) in EMI·BF$_4$·Cl melts was investigated with cyclic voltammetry and chronoamperometry.

2. Experimental

2.1 Chemicals

The 1-ethyl-3-methylimidazolium chloride (EMIC), as supplied, was dissolved in acetonitrile, and the solution was then filtered after refluxing. The filtrate was mixed with ethylacetate so as to precipitate EMIC recrystallized, and the EMIC precipitate was further washed with ethylacetate. After the above recrystallization process had been repeated twice, the obtained EMIC was dried under vacuum at room temperature for 24 h and then at 373 K for 24 h. It should be noted that the preparation and purification of EMIC was originally described in the literature [7]. NaBF$_4$ (Kishida Chemical, 99%) was dried under vacuum at 373 K for 48 h before use.

The EMI×BF$_4$×Cl melt was prepared in the similar procedure to that reported by Chen and Sun [5]. The preparation of EMI×BF$_4$×Cl melts was performed in an L-shape glass cell consisting of two individual compartments, each equipped with an inlet tube, connected each other with a rectangularly bent tube. The appropriate amounts of the purified EMIC and NaBF$_4$ were each added into the compartments through the inlet tubes in an argon filled glove box, so that the mole ratio of EMIC:NaBF$_4$ was 60:40. After removing the L-shape cell from the glove box, the inlet tubes were sealed under vacuum, and EMIC and NaBF$_4$ were mixed together in the closed cell. After 5 days of reacting with stirring at 373 K, the white NaCl precipitate was filtrated, and the filtrate was dried under vacuum at 373 K for 24 h so that the colorless EMI×BF$_4$×Cl melt was

obtained. It is noted that the water content in the resulted melt is believed to be low because no HCl gas was seen as the melt was contacted with an acidic AlCl$_3$-EMIC melt. The obtained EMI·BF$_4$·Cl melt was stored in a Pyrex glass tube sealed under vacuum, and no further treatment was done before use in the glove box. Anhydrous SnCl$_2$ (Aldrich, 99.99%) and AgBF$_4$ (Aldrich, 99.99%) were used as received.

2.2 Electrodes and measurements

Voltammetric measurements of the EMI·BF$_4$·Cl melt, containing of 0.05 mol kg^{-1} SnCl$_2$, were performed using a conventional three-electrode cell: The working electrode was a Pyrex-glass shrouded platinum wire (Nilaco, 99.9%, 0.5 mm in diam.), and the counter electrode was a coiled tungsten wire (Nilaco, 99.95%, 1 mm in diam.). The preparation of the platinum microelectrode was described elsewhere [8]. The reference electrode was a silver wire (Nilaco, 99.999%, 1 mm in diam.) immersed in the EMI·BF$_4$·Cl melt saturated with AgBF$_4$, which was contained in an individual glass tube with a fine glass frit at the bottom so as to separate from the bulk solution. A platinum plate cathode (Nilaco, 99.9%, 0.5 cm x 1 cm) was also used for potentiostatic electrolysis of the melt. Structural analysis of the cathode surface after the electrolysis was undertaken with X-ray diffraction using Cu-Kα radiation.

All electrochemical experiments were carried out in a highly purified argon filled glove box having low contents (less than 5 ppm) of H$_2$O and O$_2$ and conducted with a potentio/galvanostat (EG&G, Model 263A) controlled by a personal computer equipped with a electrochemical software (EG&G, Model 270). Electronic compensation of electrolyte resistance was employed during voltammetric experiments. The temperature was controlled at 30±1 °C with a temperature controller (Omron, Model E5AJ-A2AB).

3. Results and Discussion

SnCl$_2$ was readily dissolved at least up to 0.2 mol kg^{-1} (by visual observation) in the EMI·BF$_4$·Cl melt originated from the mixture of EMIC and NaBF$_4$ (60:40 mol%), resulting in a colorless solution, although the melt, containing 0.05 mol kg^{-1}, SnCl$_2$ was used for voltammetric measurements. Figure 1 shows the cyclic voltammograms of the melt before and after the addition of SnCl$_2$ on the cathodic direction from the rest potential, of which the switching potential was close to the cathodic limit of the melt. The voltammogram of the pure melt presented no cathodic and anodic wave on the forward and reverse scans, suggesting that the water content is sufficiently low after the melt purification. A pair of redox waves were seen in the voltammogram of the SnCl$_2$ added melt, in which the rapid increases in cathodic and anodic currents suggest the electrodeposition and dissolution of metal. The voltammograms of the narrow potential

region around the appearance of the redox waves are also shown in the inset of Fig. 1 in order to determine more clearly the onset potential of the cathodic wave; the cathodic current begins to increase at –1.38 V vs. Ag(I)/Ag reference at the platinum microelectrode. The onset potential was independent of the scan rate, when it was below the maximum value, used in this study (0.1 V s^{-1}).

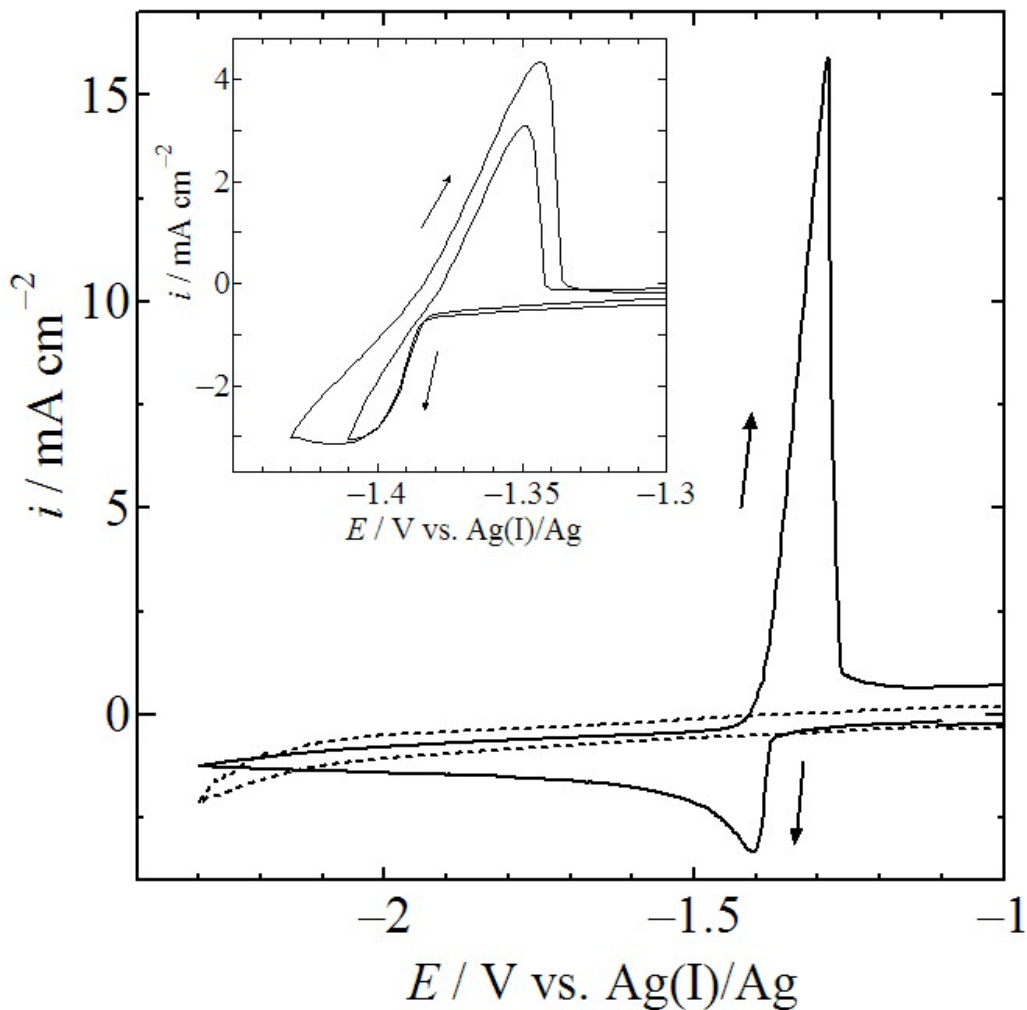From the voltammetric results, the constant potential electrolysis with the platinum

Fig. 1 Cyclic voltammograms of the EMI·BF$_4$·Cl melts with (solid line) and without (dash line) 0.05 mol kg^{-1} SnCl$_2$ at 0.01 V s^{-1} on a platinum electrode at 303 K. The voltammograms of the narrow potential range are also shown in the inset.

plate cathode at –1.5 V was performed for 20 min., of which the total charge passed was 0.9 C cm^{-2}. The cathode after the electrolysis was soaked in acetone to remove residual melt in the glove box and was took out from the glove box. Then the cathode was further washed with distilled water and was dried before submitting to XRD measurements. A silver-white electrodeposit was observed on the cathode surface treated as mentioned above and gave the XRD pattern shown in Fig. 2. The result clearly indicates the electrodeposition of tin from the EMI·BF$_4$·Cl melt as follows.

$$Sn(II) + 2\,e = Sn \qquad\qquad [1]$$

The diffraction peak for SnO$_2$ is also seen in Fig. 2, which is possibly caused by the undesirable oxidation of the electrodeposited tin in the process of washing and drying of the cathode after removing it from the glove box.

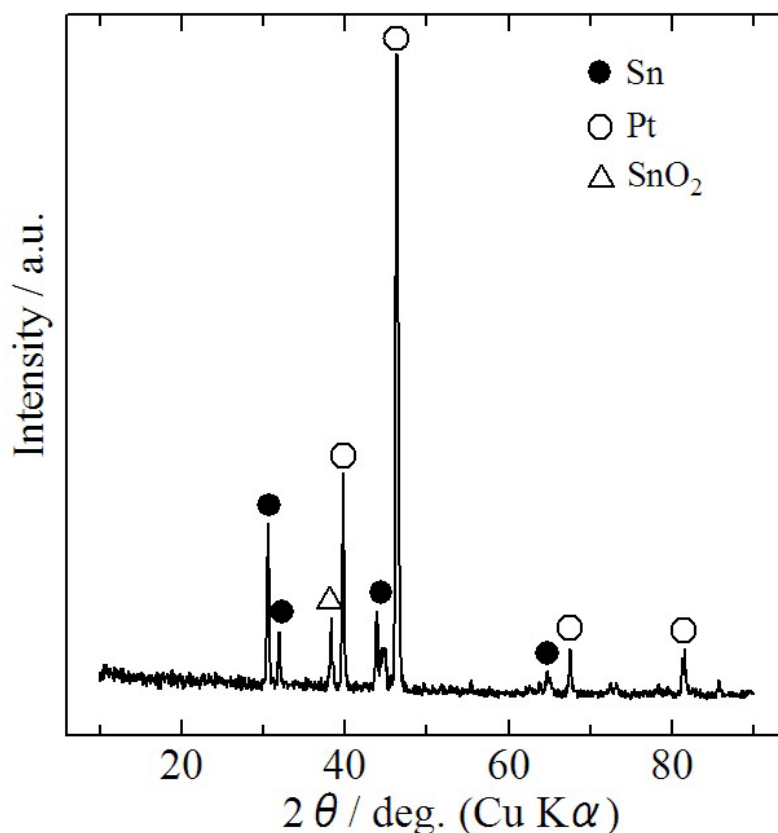The reversibility of the electrodeposition and dissolution of tin on the platinum

Fig. 2 XRD pattern of the platinum electrode after the potentiostatic electrolysis at -1.5 V for 20 min in the EMI·BF$_4$·Cl melt with 0.05 mol kg^{-1} SnCl$_2$ at 303K.

electrode was conveniently evaluated by continuous cyclic voltammetry. A typical result obtained at 0.05 V s^{-1} for continuous potential scans of 10 cycles is displayed in Fig. 3. The voltammograms were completely overlapped, and such a good reproducibility was
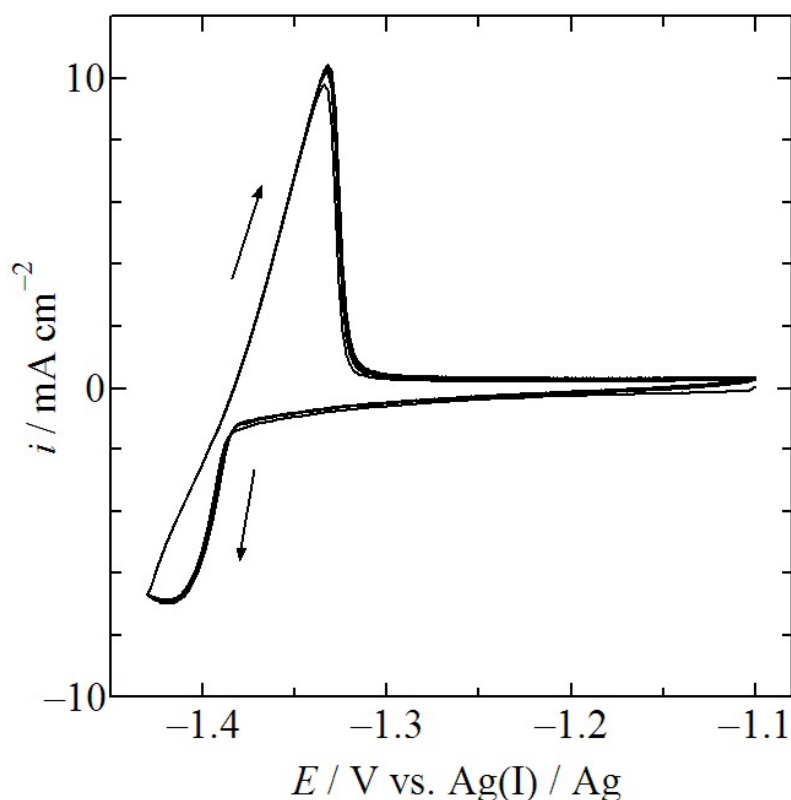

Fig. 3 Continuous cyclic voltammograms (10 cycles) of the EMI·BF$_4$·Cl melt with 0.05 mol kg^{-1} SnCl$_2$ at 0.05 V s^{-1} on a platinum electrode at 303 K.

also seen at different scan rates. From the voltammograms, the cathodic amount of electricity, Q_c, and the anodic one, Q_a, were calculated by the integration of the peak area for each wave to obtain the ratio of Q_a/Q_c. It is noted that the effect of a background current was omitted in the calculation of Q_c. The ratios were 0.97, 0.95, and 0.93 for the voltammograms recorded at 0.01 V s^{-1}, 0.05 V s^{-1}, and 0.1 V s^{-1}, respectively, which suggests that most of the electrodeposited tin is recovered in the EMI·BF$_4$·Cl melt during oxidation. A virtually 100% recovery of the deposited tin for stripping has been also observed on a platinum electrode in acidic and basic AlCl$_3$-EMIC room temperature melts [9]. On the other hand, the scan rate dependences of the potential and current density for the cathodic peak in the cyclic voltammograms obtained were examined. The

peak potential shifted negatively, and the current function, *i.e.*, the peak current density divided by the square root of scan rate, decreased as the scan rate increased. These results imply that the deposition of tin at the platinum electrode is a quasi-reversible process. A quasi-reversible electron transfer process for metal deposition on a platinum electrode in room temperature molten salts has been similarly reported for tin in acidic and basic AlCl$_3$-EMIC melts [9], for cadmium in a basic EMI·BF$_4$·Cl melt [6], or for silver in a neutral EMI·BF$_4$ melt [4].

An initial stage of electrodeposition of tin was further investigated by chronoamperometry. The chronoamperograms obtained at –1.42 V, -1.44 V, and –1.48 V are shown in Fig. 4(a). All of the current transients at different potentials showed a monotonous decay after double layer charging and converged to the same line. The Cottrell plots of the current transients showed a straight line passing the origin, one of which is shown in Fig. 4(b). This suggests that the electrodeposition of tin proceeds under diffusion control in the time scale of the experiments. However, the plots tend to deviate from the fitting line in the short time region (within 2 s) in Fig. 4(b). This implies the tin electrodeposition is not a complete diffusion-limited process, because the voltammetric results indicate the quasi-reversible electron transfer.
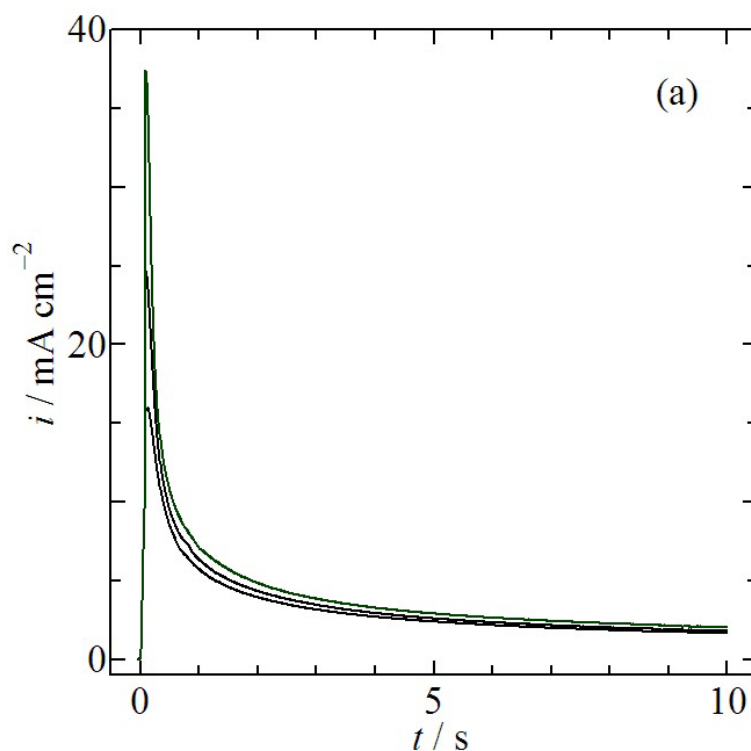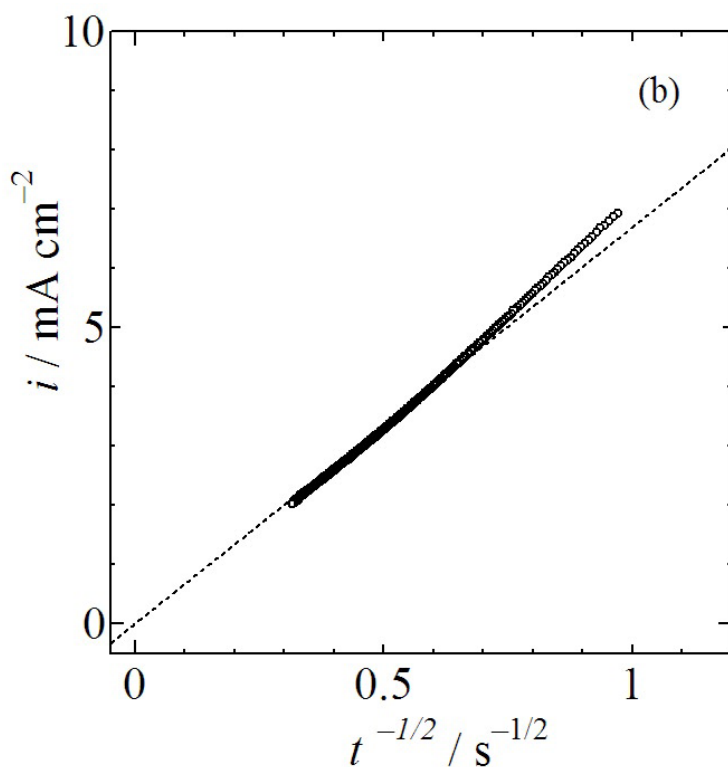
Figs. 4 (a) Chronoamperograms of the EMI·BF$_4$·Cl melt with 0.05 mol kg^{-1} SnCl$_2$ at -1.42 V, -1.44 V, and -1.48 V (bottom to top) on a platinum electrode at 303 K. (b) The Cottrell plots and the fitting line constructed from the chronoamperogram at -1.48 V.

4. Conclusions

The electrodeposition and dissolution of tin in an EMI·BF$_4$·Cl room temperature molten salt with SnCl$_2$ was demonstrated on a platinum electrode. The tin deposition starts at −1.38 V vs. Ag(I)/Ag, and the stripping/deposition efficiency is almost unity. Although the deposition process proceeds through a quasi-reversible charge transfer, the initial stage of the deposition virtually obeys one-dimensional diffusion control of dissolved Sn(II). Further studies on the kinetic and mass transport parameters such as a rate constant and a transfer coefficient for tin deposition and a diffusion coefficient of Sn(II) are now under progress.

Acknowledgements

References

1. *e.g.*, see the review article by R. Hagiwara, *Electrochemistry*, 70, 130 (2002).
2. J .S. Wilkes, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.*, 965 (1992).
3. J. Fuller, R. T. Carlin, R. A. Osteryoung, *J. Electrochem. Soc.*, 11, 388 (1997).
4. Y. Katayama, S. Dan, T. Miura, T. Kishi, *J. Electrochem. Soc.*, 148, C102 (2001).
5. P.-Y. Chen, I.-W. Sun, *Electrochim. Acta.*, 45, 441 (1999).
6. P.-Y. Chen, I.-W. Sun, *Electrochim. Acta.*, 45, 3163 (2000).
7. J. S. Wilkes, J. A. Levsky, R. A. Wilson, C. L. Hussery, *Inorg. Chem.*, 21, 1263 (1982).
8. M. Morimitsu, M.Matsunaga, *Denki Kagaku* (presently *Electrochemistry*), 66, 417 (1998).
9. X.-H. Xu, C. L. Hussey, *J. Electrochem. Soc.*, 140, 618 (1993).