

# Electrochemical Behavior of Tin in Molten LiCl-KCl at 450 °C

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The electrochemical behavior of tin was studied with cyclic voltammetry at glassy carbon electrodes in the fused LiCl-KCl at 450 °C. Metallic tin deposition on the glassy carbon electrode occurs at a potential of around -0.56 V with Ag/AgCl reference electrode. The diffusion coefficient  $D_{\text{Sn}^{2+}}$  is determined to be  $3.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . At higher anodic voltage,  $\text{Sn}^{2+}$  is oxidised to  $\text{Sn}^{4+}$ . The average number of electrons was determined to be 2 by using the difference between the peak and half peak potentials. Metallic tin was prepared in potentiostatic mode at -0.7 V versus  $\text{Ag}^+/\text{Ag}$  reference for 4 hours. Mass transport towards the electrode is a simple diffusion process and the diffusion coefficient was calculated. The current efficiency for deposition of Sn was as high as 95%.

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**Keywords:** electrochemical behavior, tin, kinetic parameters, electrolysis

## 1. INTRODUCTION

This study is a part of a systematic research into the possibility of using of molten salt LiCl-KCl for the recovery of Sn and In contained in ITO (Indium oxide combining with 10 percent tin oxide) powder. Metal recovery is considered as a profitable process from the waste treatment industry[1]. Molten salt electrolysis has been used for metal production for many years and is already a proven technology. Primary aluminium production is mainly based on this manner all over the world. Molten chlorides are widely used in metal extraction[2,3] and alloy formation[4-7].

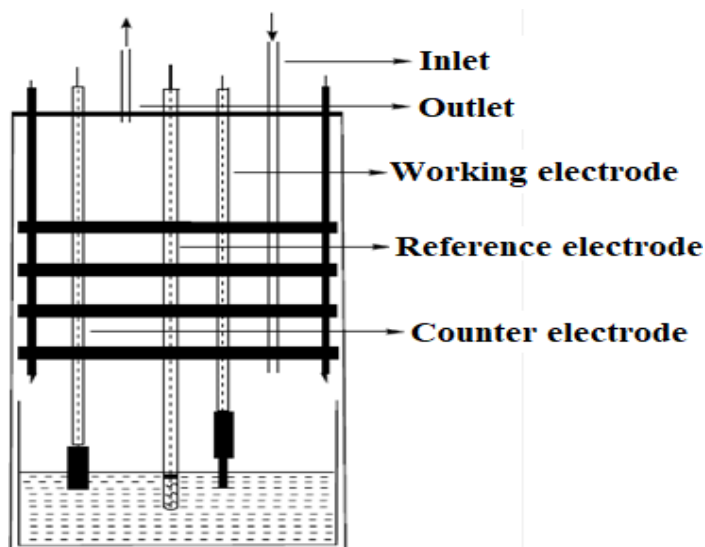
Some electrochemical studies of tin ions had been carried out in aqueous solution[8,9] and molten salts. Pasquier[10] calculated the  $D_{\text{Sn}^{2+}} = (2.1 \pm 0.1) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in LiCl-KCl by chronopotentiograms at 450 °C. Xu[11] got the  $D_{\text{Sn}^{2+}}$  which is  $3.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at the graphite and the molybdenum electrode respectively at 625 °C by chronoamperometry. Ghallali[12] estimated  $D_{\text{Sn}^{2+}} =$

$(2.73 \pm 0.41) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in LiCl-KCl with a vitreous carbon electrode by cyclic voltammetry at 440 °C. The diffusion coefficient  $D_{\text{Sn}^{2+}}$  in LiCl-KCl molten salts seems larger than the one in the  $\text{ZnCl}_2\text{-xNaCl}$  ( $x=1, 1.5, 2$ ) molten salts  $10^{-6} \text{ cm}^2 \text{ s}^{-1}$  obtained by Castrillejo[13] at the same temperature. Cai[14] calculated that the diffusion coefficients of the Sn(IV) and Sn(II) ions were  $2.68 \times 10^{-5} \text{ cm}^2/\text{s}$  and  $5.19 \times 10^{-5} \text{ cm}^2/\text{s}$ , respectively.

As a part of the aim, the present paper is concerned only with results of the electrochemical reduction systems of tin in molten LiCl-KCl melts.

## 2. EXPERIMENTAL

Materials used in this work were analytical grade. LiCl (Sigma-aldrich, >99%): KCl (Sigma-aldrich, >99%) with the eutectic composition (58.2: 41.8mol%) was dried in a heating cabinet at 150 °C for at least 24 hours prior to the start of the experiments. After the salt had melted around 0.1mol%  $\text{SnCl}_2$  (Sigma-aldrich, >97%) were added.



**Figure 1.** Schematic diagram of the experimental cell

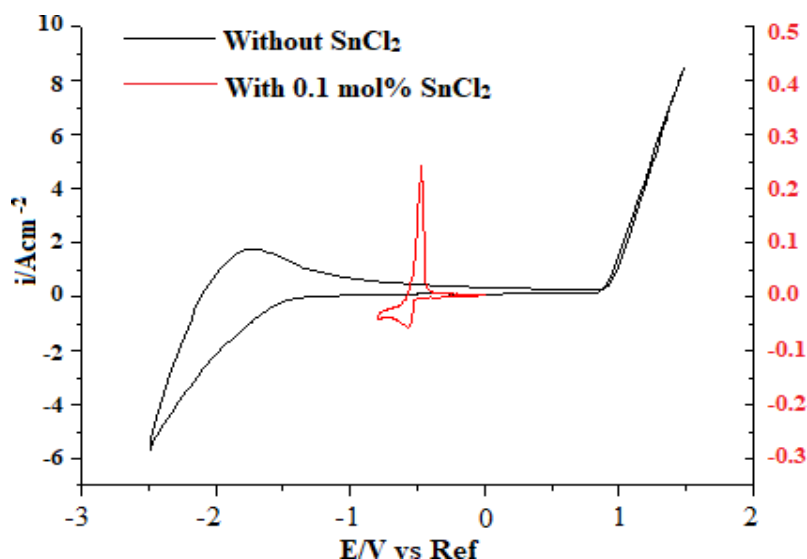
Figure 1 shows the schematic drawing of the cell. The electrolyte was contained in a cylindrical glass crucible and was situated inside a gas-tight quartz container. A three-electrode system was assembled for the cyclic voltammetry testing and the electrodeposition. The cyclic voltammetry studies were performed with a Zahner pp201 computer controlled potentiostat. The sweep rate was from 5-100 mV/s. Experiments were performed under inert argon atmosphere. To minimize the temperature gradient, a total of 4 evenly spaced alumina radiation shields extended from the crucible up to the top of the tube. The temperature in the cell was controlled with a Pt 10% Rh vs Pt thermocouple. The electrochemical studies were performed using a graphite rod (8 mm) as a counter electrode, a tungsten wire (1mm) or a glassy carbon rod (3 mm) as a working electrode. The reference electrode was a silver wire dipped in LiCl-KCl melt containing  $0.75 \text{ mol} \cdot \text{kg}^{-1} \text{ AgCl}$  (Sigma-aldrich, 99.998%) and placed in the mullite tube. The sample was washed by distilled water after 4h of the electrolysis to remove the residual salts and

separate graphite from the crucible. X-ray diffraction (XRD) characterisations were performed with a Bruker AXS D8Focus.

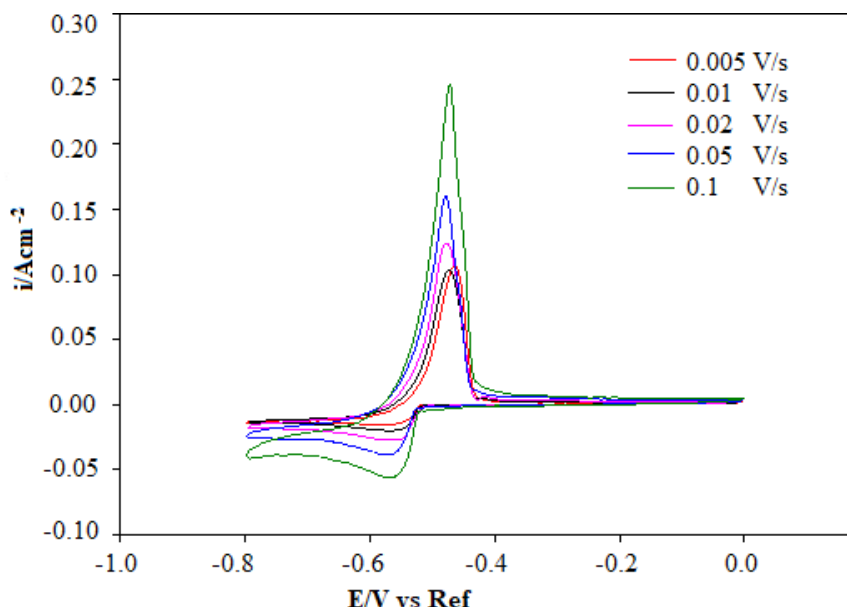
### 3. RESULTS AND DISCUSSION

#### 3.1 Study of $\text{Sn}^{2+}/\text{Sn}^0$ exchange

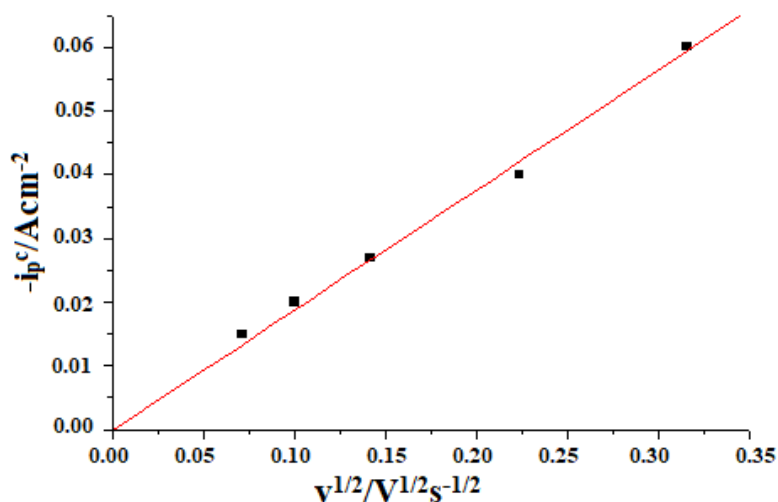
The electrochemical reduction process of  $\text{SnCl}_2$  on glassy carbon electrode in molten LiCl-KCl eutectic at 450 °C was studied by cyclic voltammetry as shown in Fig 2. When adding  $\text{SnCl}_2$  to a pure LiCl-KCl eutectic melt, one cathodic current peak was observed. The shapes of the reduction and oxidation peaks are characteristic of the deposition of an insoluble metal and its oxidation during the reverse scan. Groult[12, 15] reported that the redox reaction of Sn ions is completed by a two-step two-electron exchange, and the two resulting redox couples are  $\text{Sn}^{4+}/\text{Sn}^{2+}$  and  $\text{Sn}^{2+}/\text{Sn}^0$ . Combined with the theoretical decomposition voltage of  $\text{SnCl}_2$ , the couple redox peaks represent the redox process of  $\text{Sn}^{2+}/\text{Sn}^0$  in the negative potential region. Metallic tin deposition on the glassy carbon electrode occurs at a potential of around -0.56 V, as can be seen from the position of the increase of the cathodic current.



**Figure 2.** Cyclic voltammograms obtained with and without  $\text{SnCl}_2$  on a glassy carbon electrode. The potential is swept in the cathodic direction from the open circuit potential. Sweep rate is 100 mV/s.



**Figure 3.** Cyclic voltammograms obtained related to the reduction of SnCl<sub>2</sub> in the fused LiCl-KCl at 450 °C at different sweep rates on a glassy carbon electrode. The potential is swept in the cathodic direction from the open circuit potential.



**Figure 4.** Variation of the Sn(II)/(0) peak current density with  $v^{1/2}$ .

Fig 3 shows a set of cyclic voltammograms obtained for tin deposition over a range of sweep rates. The peak currents increased with increasing the sweep rate and the peak potential deteriorated at a high scan rate. The deposition of tin starts at potentials closer to  $E_{rev}$  at a given sweep rate. There is no obvious nucleation overpotential observed. Loosely speaking, tin nuclei are formed very fast at a fixed overpotential on glassy carbon. The cathodic peak potential of tin deposition remains unaffected by sweep rate. The tin voltammograms are in better conformity with a reversible behaviour.

A plot of the cathodic peak current against the square root of the sweep rate were linear with the slope 0.18 as shown in Fig 4, indicating diffusion-control of the process. In case of a reversible diffusion-controlled process involving deposition of metal, the Berzins-Delahay[16] equation (1) can be used for the calculation of diffusion coefficient:

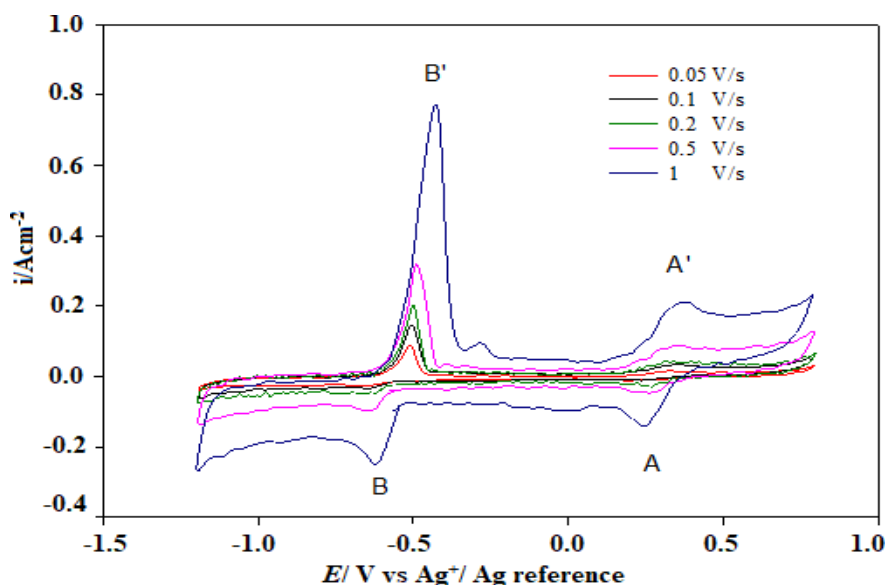
$$I_p = 0.61 n^{3/2} F^{3/2} A (RT)^{-1/2} D^{1/2} C_0 \nu^{1/2} \quad (1)$$

where  $I_p$  is the cathodic peak current (A),  $A$  the surface area of working electrode ( $\text{cm}^2$ ),  $D$  the diffusion coefficient ( $\text{cm}^2\text{s}^{-1}$ ),  $C_0$  the bulk concentration of the species ( $\text{mol}\cdot\text{cm}^{-3}$ ),  $0.0000495 \text{ mol}/\text{cm}^3$  and  $\nu$  the sweep rate ( $\text{V}\cdot\text{s}^{-1}$ ),  $T$  absolute temperature (K),  $n$  the number of electrons transferred in the reaction,  $F$  Faraday constant ( $96485 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$ ),  $R$  universal gas constant ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

From the slope, the diffusion coefficient  $D_{\text{Sn}^{2+}}$  is determined to be  $3.0 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ .

### 3.2 Study of $\text{Sn}^{4+}/\text{Sn}^{2+}$ exchange

Fig. 5 shows cyclic voltammograms obtained related to the reduction of  $\text{SnCl}_2$  in the fused  $\text{LiCl-KCl}$  at  $450^\circ\text{C}$  at different sweep rates. There are two steps for the redox reaction of Sn ions. The redox process of  $\text{Sn}^{2+}/\text{Sn}^0$  is in the negative potential region and the redox process of  $\text{Sn}^{4+}/\text{Sn}^{2+}$  is in the positive potential region [14,15]. In accordance with the negative sweep, the positive sweep of cyclic voltammogram B' is the dissolution of tin. A second wave was also pointed out in the more positive potential window, i.e. two well-defined peaks were observed at  $0.25 \text{ V}$  vs reference and  $0.3 \text{ V}$  vs reference, respectively. They have the typical shape of a soluble/soluble system and may therefore be attributed to the  $\text{Sn}^{2+}/\text{Sn}^{4+}$  redox couple. Ghallali's results for the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  redox couple in melt at less than  $460^\circ\text{C}$  agree with the assumption that a thin insoluble species accumulates onto the surface. At  $460^\circ\text{C}$ , the surface compound becomes soluble and the shape of the peak becomes analogous to a classical diffusion peak. But it was not possible to see the couple A'/A in the lower sweep rates range, because  $\text{SnCl}_4$  is gas at the working temperature and leaves the anode once it is formed.



**Figure 5.** Cyclic voltammograms obtained related to the reduction of  $\text{SnCl}_2$  in the fused  $\text{LiCl-KCl}$  at  $450^\circ\text{C}$  at different sweep rates. The potential is swept in the cathodic direction from the open circuit potential.

**Table 1.** Data obtained by analysing voltammograms of peak A couple from figure for different sweep rates.

$\nu$ [V/s]	$i_p^a$ [A/cm <sup>2</sup> ]	$E_p^a$ [V]	$E_{p/2}^a$ [V]	$n$
0.05	-0.01	0.27	0.34	1.93
0.1	-0.02	0.26	0.32	2.14
0.2	-0.04	0.26	0.32	2.21
0.5	-0.06	0.25	0.32	1.96
1	-0.15	0.27	0.34	1.78

$\text{Sn}^{2+}$  is the intermediate valence state of  $\text{Sn}^{4+}$  reduction. In order to investigate the couple of  $\text{Sn}^{4+}/\text{Sn}^{2+}$ , a representative selection of parameters can be extracted from such voltammograms, some of which are included in Table 1. The number of electrons transferred was calculated by using the difference between the peak and half peak potentials (equation 2). The average number of electrons was determined to be 2 from the data in Table 1.

$$|E_p - E_{p/2}| = 2.2RT/nF \quad (2)$$

### 3.3 Electrochemical deposition of tin

Metallic tin was prepared in potentiostatic mode at -0.7 V versus  $\text{Ag}^+/\text{Ag}$  reference for 4 hours and tin was detected at the bottom of the crucible. After the sample was washed by distilled water to remove the residual salts and separate graphite from the crucible metallic silver-white tin was obtained in Fig 6. Metallic tin had also coalesced to form small balls. The particle size distribution of tin ranged from less than one millimetre to a few millimetres. The appearance view of the cathode electrode also gave a metallic gray colour in Fig 7 and some samples scraped off with a knife were test by the XRD as shown in Fig 8. The XRD shows that there is still some deposited tin on the cathode which didn't sink to the bottom of the crucible.

**Figure 6** The photo of tin obtained by electrolysis.

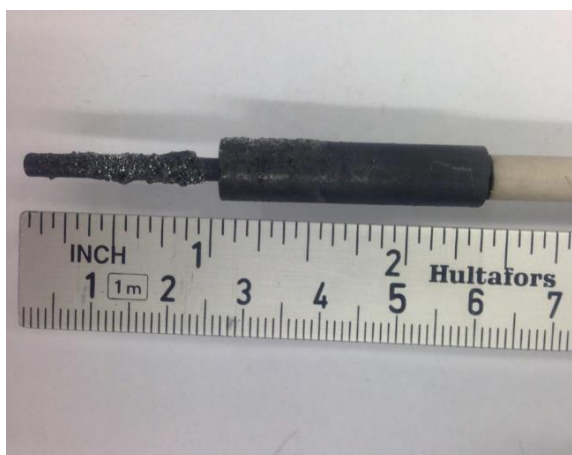


Figure 7. The picture of the cathode after electrolysis.

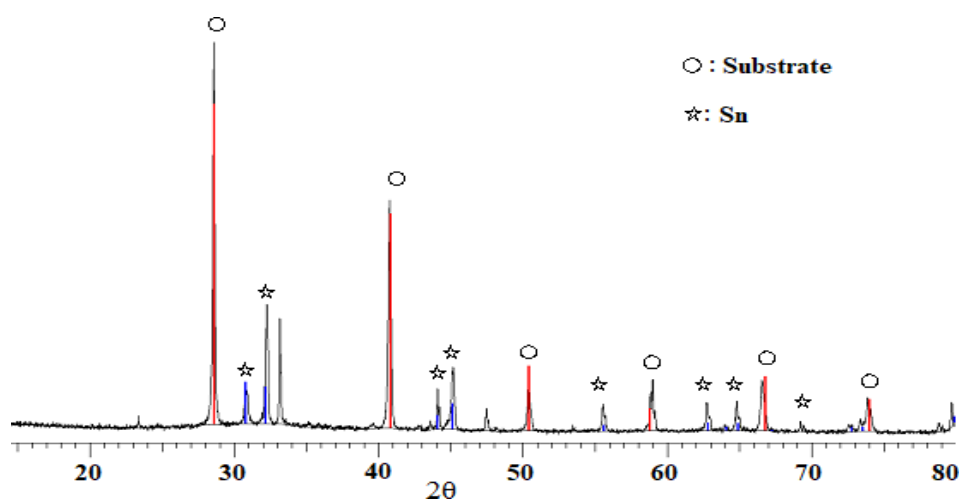


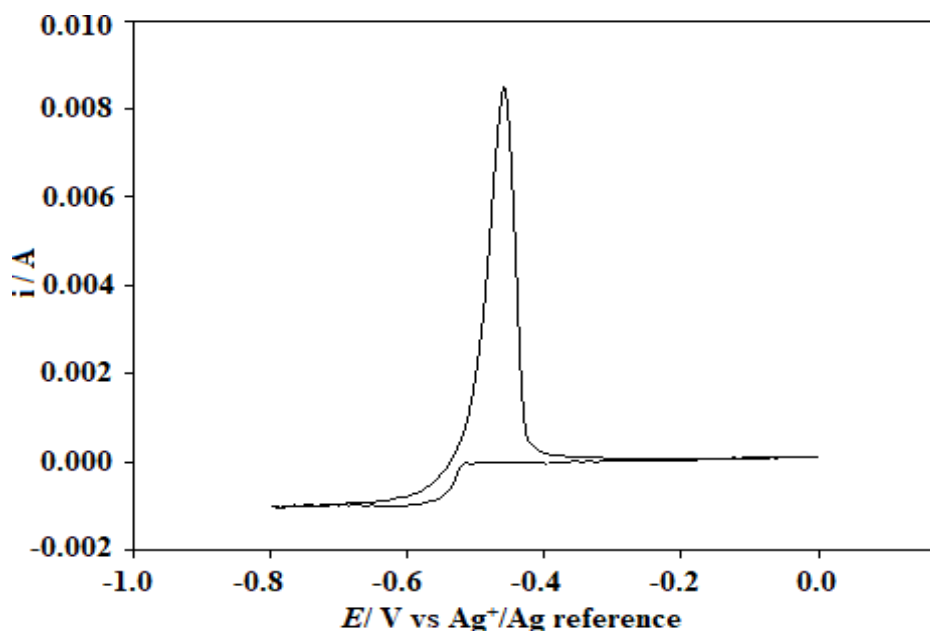
Figure 8. XRD pattern obtained for Sn deposit on the cathode

The current efficiency as the ratio of the actual tin metal produced (1.51 g) and theoretical amount (1.6 g) was around 95%. And the current efficiency between the charges needed for cathodic deposition of tin and anodic dissolution was also investigated as shown in Fig 9.

The charge needed for cathodic deposition of tin calculated from the CV at lower sweep rate  $Q_c$  is  $6.07 \times 10^{-2}$  C and the charge for anodic dissolution of tin  $Q_a$  is  $5.77 \times 10^{-2}$  C. The current efficiency  $Q_a/Q_c$  equals to 95.1%. Considering that tin is liquid at experimental temperature, the actual current efficiency should higher than 95.1%.

In fact, electrochemical deposition of tin has been done in aqueous solution. Acid solutions, such as  $HNO_3$  and  $HCl$ , are commonly used in metal extraction as the solvent. Tin will be reduced at the cathode after the electrolysis process. The percent of tin that was successfully recovered was 99.9% [17,18]. The advantage of this method is more efficient and economic compared to molten salt electrolysis. However, the use of various solvents, including corrosive acids and hazardous extraction substances, increases the potential environmental risks. Tin from the secondary resource is suited for molten salt electrolysis when considering the composition of raw material and environmental factor

because it has a lower melting point (232 °C). Hence, Molten salt also gives an alternative to extract the metals which are produced by aqueous solution.



**Figure 9.** Cyclic voltammograms obtained related to the reduction of  $\text{SnCl}_2$  in the fused  $\text{LiCl-KCl}$  at 450 °C. Sweep rates: 2 mv/s. The potential is swept in the cathodic direction from the open circuit potential.

#### 4. CONCLUSIONS

Metallic tin deposition on the glassy carbon electrode occurs at a potential of around -0.56 V. In the higher anodic voltage 0.3 V,  $\text{Sn}^{2+}$  is oxidized to  $\text{Sn}^{4+}$ . The red/ox couple  $\text{Sn}^{4+}/\text{Sn}^{2+}$  was observed at faster sweep rates range because of formation of gaseous  $\text{SnCl}_4$ . The diffusion coefficient for  $\text{Sn}^{2+}$  was found to be  $3.0 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  obtained by CV. Metallic tin was obtained under constant voltage electrolysis at -0.7 V. The current efficiency for cathodic deposition of tin was 95.1%.

#### ACKNOWLEDGMENTS

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