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Reduction of Tin(II) and Antimony(III) in the 1-Ethyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid

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The reductions of Sn(II) and Sb(III) were studied in the air-stable (1-ethyl-3-methyl imidazolium tetrafluoroborate) [EMIm]BF_4 ionic liquid at room temperature. Linear sweep voltammetry (LSV) results show that reductions of Sn(II) and Sb(III) on Pt electrode are electrochemically irreversible behaviour. Diffusion coefficients for Sn(II) and Sb(III) were calculated from LSV data. The Stokes-Einstein products for Sn(II) and Sb(III) are 7.27×10^{-10} and 2.35×10^{-10} g cm s^{-2} K^{-1}. These values indicate that the formation of simpler Sn(II) chloro complex species and higher Sb(III) chloro complexes in the [EMIm]BF_4. The electrodeposition of Sn(II) and Sb(III) was investigated on Pt electrode. Energy dispersive spectroscope (EDS) results show that tin and antimony can be reduced to their metals on Pt electrode simultaneously.

Key Words: Electrochemistry, Tin, Antimony, Ionic liquid, Tetrafluoroborate.

INTRODUCTION

Room temperature ionic liquids (RTILs) are made of only ions at or near room temperature, with desirable properties include wide electrochemical window, good thermal and chemical stability and high ionic conductivity. They have been attracted considerable interest in the field of electrochemistry device as solvent and electrolyte, such as rechargeable batteries, photoelectrochemical cells, electroplating, electrodeposition and electroorganic synthesis[1-4]. Many previous reports[5-11] concerning the use of ionic liquids for electrochemical and electrodeposition studies had focused on chloroaluminate-based ionic liquids which were sensitive to moisture, but the number of reports on air-stable ionic liquids were comparatively small. Therefore, it is necessary to accumulate fundamental electrochemical data of metal ions in air-stable systems.

Tin, antimony and tin-antimony alloy are very important materials for industrial applications. There are numerous investigations of electrochemistry of tin[12,13] and antimony[14,15] from aqueous solutions or high-temperature molten salts can be found in the literature. However, studies on the electrochemistry of tin[5] and antimony[16,17] in ionic liquids are limited. Hussey[5] shows that the deposition of Sn(II) at platinum in aluminum chloride-1-ethyl-3-methyl imidazolium chloride ($AlCl_3$-EMIC) was a quasi-reversible process and the diffusion coefficients of Sn(II) in acidic melt and basic melt were $(5.3 \pm 0.7) \times 10^{-7}$ and $(5.1 \pm 0.6) \times 10^{-7}$ cm^2 s^{-1}, respectively. Osteryoung[17] studied the electrochemistry of antimony on glass carbon in aluminum chloride-N-(*n*-butyl)pyridinium chloride ($AlCl_3$-BPC) at 40 ºC and the reduction of Sb(III) to Sb(II) showed irreversible behaviour while the oxidation to Sb(V) revealed a quasi-reversible behaviour. Yang and Sun[16] reported the electrodeposition of antimony in [EMIm]BF_4 ionic liquid containing an excess of free chloride ions as well as the effects of deposition temperature on the nucleation process and the morphologies of the deposits.

In view of the advantages of the air-stable ionic liquids over the chloroaluminates and a paucity of studies on electrochemistry of tin and antimony in air-stable ionic liquids, this work reports the reduction electrochemistry of Sn(II) and Sb(III) in air-stable [EMIm]BF_4 ionic liquid. In addition, the electrodeposition experiments and the morphologies of the electrodeposits are described.

EXPERIMENTAL

All the electrochemical experiments were carried out under the atmosphere of argon. A CHI 660B electrochemical testing system (CH Instruments, Inc.) with a three-electrode electrochemical cell was employed to conduct the electrochemical experiments. Platinum disk ($A = 1.96 \times 10^{-3}$ cm^2, Aldrich 99.99 %) was used as working and counter electrode. The reference electrode consisted of a silver electrode immersed in [EMIm]BF_4 saturated with $AgBF_4$, which was separated from the test melt with G4 glass or a Teflon menbrance filter. All the potentials in this work were represented against this electrode. Electrodeposition experiments were conducted on platinum wires (0.5 mm diameter, Aldrich 99.99 %). The electroplated wires were immersed in deoxidized acetone for a few minutes, washed with ethanol and deionized water in succession to remove the melt residue. A FEI QUANTA-200 field effect scanning electron microscope (SEM) with an EDAX energy dispersive spectroscope (EDS) working at 30 kV were used to examine the surface morphology and the elements electroplated.

1-Ethyl-3-methylimidazolium tetrafluoroborate ionic liquid was prepared and purified according to the method described in the literature[18]. The density, absolute viscosity, η and conductivity of this ionic liquid at 25 ºC were determined to be 1.2416 g cm^{-3}, 0.357 g cm^{-1} s^{-1} and 1.37×10^{-2} S cm^{-1}, respectively. Anhydrous tin(II) chloride (Aldrich, 99 %), anhydrous antimony(III) chloride (Aldrich, 99 %) were used as received.

RESULTS AND DISCUSSION

Cyclic voltammogram of tin and antimony: The voltammogram of a Pt electrode in [EMIm]BF$_4$ by the linear sweep voltammetry at 50 mV s^{-1} scan rate with Ag/Ag(I) reference electrode is shown in Fig. 1. It exhibits an electrochemical window of 4.3 V ranging from *ca.* 2.7 V to -1.6 V *vs.* Ag/Ag(I).

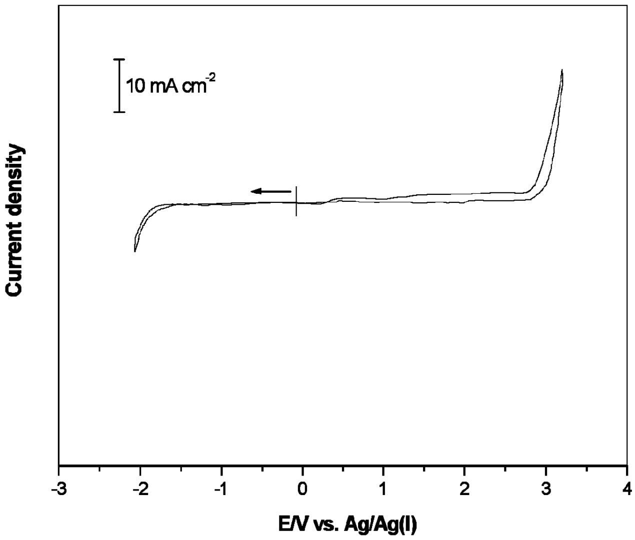

Fig. 1. Voltammogram of Pt electrode in [EMIm]BF$_4$ by the linear sweep voltammetry at room temperature, Scan rate 50 mV s^{-1}

Sn(II) and Sb(III) were introduced into the [EMIm]BF$_4$ ionic liquid by the addition of SnCl$_2$ and SbCl$_3$. Previous literature[19] indicated that Sn(II) exist as [SnCl$_3$]$^-$ and [SnCl$_4$]$^{2-}$, which the former is the most common species and Sb(III)[17] exist as [SbCl$_4$]$^-$ complex anions in chloroaluminate ionic liquids. A typical cyclic voltammogram recorded at Pt electrode for 25 mM Sb(III) in the [EMIm]BF$_4$ at 25 ºC is shown in Fig. 2a. The reduction of Sb(III) occurs at the cathodic wave c$_1$ and the oxidation of the electrodeposited Sb occurs at wave a$_1$. A typical cyclic voltammogram of 25 mM Sn(II) at Pt electrode in the [EMIm]BF$_4$ at 25 ºC is presented in Fig. 2b. This cyclic votammogram reveals that the electrodeposition of Sn (wave c$_2$) occurs at a potential more negative than the deposition of the Sb. On the anodic scan, Fig. 2b shows a oxidation wave, a$_2$, due to the striping of the bulk Sn deposits. Fig. 2c shows the cyclic voltammogram of a solution containing 25 mM Sb(III) and 25 mM Sn(II) in the [EMIm]BF$_4$ at 25 ºC. As can be seen in this votammogram, on the anodic potential scan, the anodic wave a$_2$ for the stripping of bulk Sn deposits and anodic wave a$_3$ for

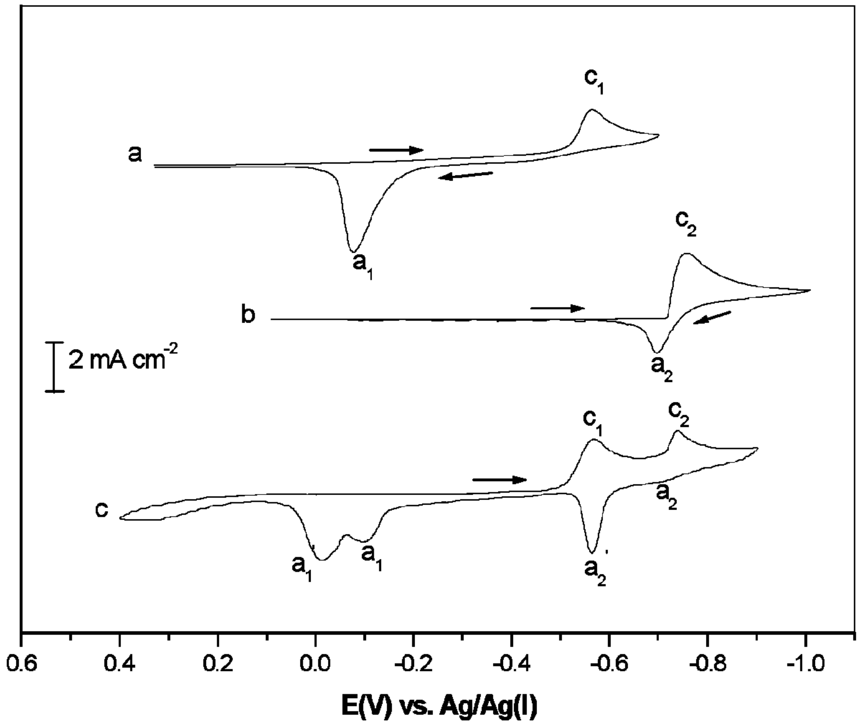

Fig. 2. Cyclic voltammogram of metal ions on Pt electrode in [EMIm]BF_4 at 25 °C. Scan rate 50 mV s^{-1}. (a) M = 25 mM Sb(III) (b) M = 25 mM Sn(II) (c) M = 25mM Sn(II) + 25 mM Sb(III)

the stripping of bulk Sb deposits decreases significantly while a new wave a_2' and a_3' becomes apparent. These changes in the voltammetric features strongly indicate the co-deposition of Sb-Sn.

Reduction of Sn(II) and Sb(III): In the linear sweep voltammetric (LSV) experiments, the cathodic peak potentials of Sn(II) shifted to the more negative side with the potential scan rate increasing. Since the electrolytic current was only a few microamperes, the effect of ohmic drop should be negligible[20]. Thus, the reduction of Sn(II) is electrochemically irreversible process. Some typical data of 25 mM Sn(II) in the [EMIm]BF_4 resulting from a series of LSV experiments with different scan rate, ν (mV s^{-1}), was collected in Table-1.

The transfer coefficient, α, for reduction of Sn(II) to Sn was estimated to be 0.537 from the plot of the E_p^c, for the cathodic peak potentials of the different scan rate and the logarithm of the corresponding scan rate, ν (V s^{-1}), as shown in Fig. 3, according to the following equation[21]

$$E_p = E^{0'} - \frac{RT}{\alpha F}\left[0.780 + 2.303\log\left(\frac{D_O^{1/2}}{k^0}\right) + \frac{2.303}{2}\log\left(\frac{\alpha F \nu}{RT}\right)\right] \qquad (1)$$

TABLE-1
LINEAR SWEEP VOLTAMMETRY DATA FOR THE REDUCTION OF 25 mM Sn(II) in [EMIm]BF_4 ON Pt ELECTRODE AT ROOM TEMPERATURE

ν(mV s^{-1})	10^3 i_p^c (mA)	E_p^c (V)	$E_{p/2}$ (V)	[E_p^c - $E_{p/2}$] (V)
5	1.955	-0.7190	-0.7060	0.013
10	2.771	-0.7450	-0.7260	0.019
20	3.587	-0.7590	-0.7380	0.021
50	5.502	-0.7630	-0.7340	0.029
100	7.049	-0.7940	-0.7610	0.033

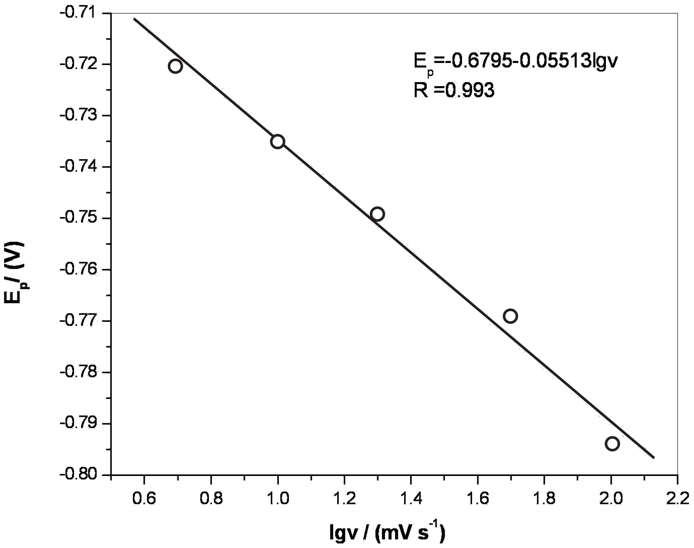

Fig. 3. Dependence of the cathodic peak potential for the reduction of Sn(II) on the logarithm of scan rate in [EMIm]BF_4 ionic liquid containing 25 mM Sn(II) at room temperature

where k^o, $E^{o'}$, D_O, R, T and F are standard heterogeneous rate constant, formal potential in V, diffusion coefficient of substance O, gas constant in J mol^{-1} K^{-1}, absolute temperature in K and Faraday constant in C mol^{-1}, respectively.

The diffusion coefficient of Sn(II) *i.e.*, $D_{Sn(II)}$, in [EMIm]BF_4 was estimated to be 6.07 × 10^{-7} cm^2 s^{-1} from the plot of the peak current density and the square root of scan rate, ν (V s^{-1}), as shown in Fig. 4, from the following equation[21]:

$$j_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} C^*_{Sn(II)} D^{1/2}_{Sn(II)} \nu^{1/2} \quad (2)$$

where α, n_a, $C^*_{Sn(II)}$ are transfer coefficient, the number of electrons involved in the reduction process and bulk concentration of Sn(II) in mmol dm^{-3}, respectively.

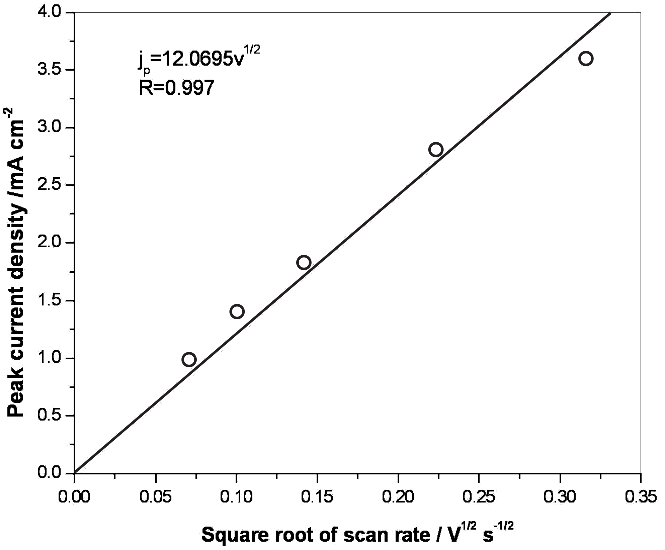

Fig. 4. Dependence of the current density for the reduction of Sn(II) on the square root of scan rate in [EMIm]BF_4 ionic liquid containing 25 mM Sn(II) at room temperature

The diffusion coefficient is related to the viscosity, η and the solvodynamic radius of a spherical diffusing, r_{solv}, by Stokes-Einstein eqn.

$$D = \frac{kT}{6\pi\eta r_{solv}} \tag{3}$$

where k is the Boltzman constant. The Stokes-Einstein product, $\eta D_{Sn(II)}/T$, value is inversely proportional to the solvodynamic radius. The $\eta D_{Sn(II)}/T$ value of Sn(II) in the [EMIm]BF_4 system is 7.27×10^{-10} g cm s^{-2} K^{-1}, which is larger than that of Sn(II) in $AlCl_3$-[EMIm]Cl ionic liquid[5], as listed in Table-2. The comparison of present work with previous reports, the larger $\eta D_{Sn(II)}/T$ value of Sn(II) may be attributed to the simpler Sn(II) chloro-complex species in the [EMIm]BF_4 than in the $AlCl_3$-[EMIm]Cl.

TABLE-2
SOME KINETIC PARAMETERS FOR THE REDUCTION OF 25 mM Sn(II) in [EMIm]BF_4 ON Pt ELECTRODE

System	α	$10^7 D_{Sn(II)}$ (cm^2 s^{-1})	$10^{10} \eta D_{Sn(II)}/T$ (g cm s^{-2} K^{-1})
[EMIm]BF_4	0.537	6.07	7.27
66.7 m/o $AlCl_3$-[EMIm]Cl (Ref. 5)	–	4.60	0.99
44.4 m/o $AlCl_3$-[EMIm]Cl (Ref. 5)	–	5.32	3.55

The typical cyclic voltammogram of Sb(III) in the [EMIm]BF$_4$ ionic liquid at Pt electrode is shown in Fig. 2b. The large peak potential separation, $E_p^{c_1} - E_p^{a_1}$, indicates that the reduction of Sb(III) is a mixed diffusion and kinetic controlled process. The cathodic peak potential, E_p^c, for the reduction of Sb(III) shifts negatively with increasing potential scan rate, as shown in Table-3. Thus, the reduction of is electrochemically irreversible, the reaction rate being controlled by charge transfer rather than mass transport.

TABLE-3
LINEAR SWEEP VOLTAMMETRY DATA FOR THE REDUCTION OF 25 mM Sb(III) IN [EMIm]BF$_4$ ON Pt ELECTRODE AT ROOM TEMPERATURE

ν(mV s^{-1})	10^3 i_p^c (mA)	E_p^c (V)	$E_{p/2}$ (V)	[E_p^c- $E_{p/2}$] (V)
5	0.9395	-0.5110	-0.4840	0.027
10	1.190	-0.5360	-0.5090	0.027
20	1.998	-0.5520	-0.5240	0.028
50	2.964	-0.5710	-0.5400	0.031
100	4.538	-0.5900	-0.5430	0.047

The transfer coefficient, α, for the reduction of Sb(III) to Sb was calculated from the plot of the E_p^c and the logarithm of the scan rate, as shown in Fig. 5. The diffusion coefficient of Sb(III), $D_{Sb(III)}$, in [EMIm]BF$_4$ was accounted from the plot of the peak current density and the square root of scan rate as shown in Fig. 6, which were according to the eqns. 1 and 2. The results of these calculations are summarized in Table-4.

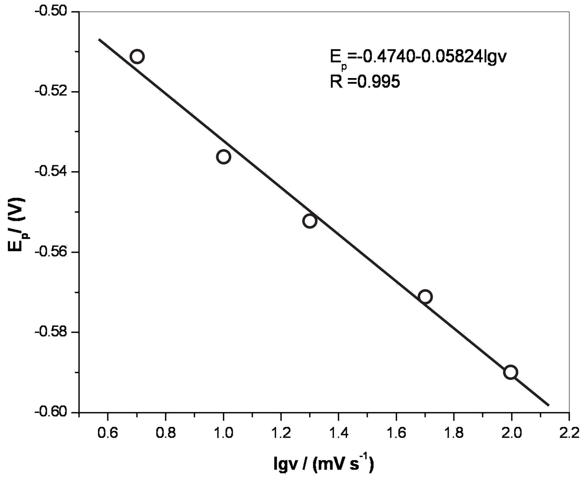

Fig. 5. Dependence of the cathodic peak potential for the reduction of Sb(III) on the logarithm of scan rate in [EMIm]BF$_4$ ionic liquid containing 25 mM Sb(III) at room temperature

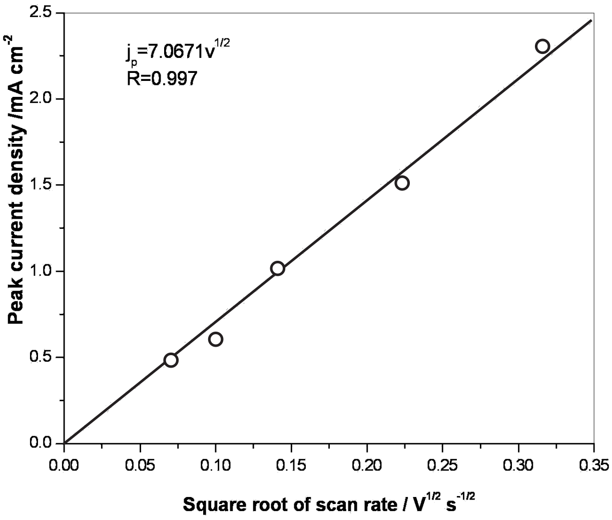

Fig. 6. Dependence of the current density for the reduction of Sb(III) on the square root of scan rate in [EMIm]BF_4 ionic liquid containing 25 mM Sb(III) at room temperature

TABLE-4
SOME KINETIC PARAMETERS FOR THE REDUCTION OF 25 mM Sb(III) IN [EMIm]BF_4 ON Pt ELECTRODE

System	α	10^7 $D_{Sb(III)}$ (cm^2 s^{-1})	$10^{10}\eta D_{Sb(III)}/T$ (g cm s^{-2} K^{-1})
[EMIm]BF_4	0.508	1.96	2.35
1.5:1 acidic $AlCl_3$-[EMIm]Cl melts (Ref. 20)	–	6.88	1.20
0.75:1 basic $AlCl_3$-[EMIm]Cl melts (Ref. 20)	–	0.79	4.06

As shown in Table-4, the small value of Stokes-Einstein products, $\eta D_{Sb(III)}/T$, indicates that the formation of some uncharacterized higher chloro complexes of Sb(III) in [EMIm]BF_4, which commonly happened in high temperature molten salts[19]. Thus, it is possible to carry out the work that conventionally do in the high temperature molten salts but without high temperature.

Electrodeposition of tin and antimony: The electrodeposition experiments were carried out in the [EMIm]BF_4 which contain 25 mM Sn(II), 25 mM Sb(III) and 25mM Sn(II) + 25 mM Sb(III) at room temperature, respectively. Bulk electrodeposits were prepared on 0.5 mm diameter platinum wires under the atmosphere of argon. The potential for electrodeposition experiments was -1.1 V *vs.* Ag/Ag(I). The electrodeposited wires were immersed in deoxidized acetone for a few minutes, washed with ethanol and deionized water in succession to remove the melt residue[15].

The surface morphologies were examined by SEM and the micrographs are illustrated in Fig. 7. The deposits in Fig. 7a-c were Sn, Sb and Sn + Sb, respectively. Energy dispersive spectroscopic (EDS) analysis of the electrodeposit surfaces revealed that they were pure metals with no other elements such as Cl, B and F, indicating that no ionic liquid residue was trapped in the deposits. As shown in Fig. 7a, the deposits of Sn were incompact clusters of needles. In Fig. 7b, antimony electrodeposits adhere well to the platinum and the deposits are dense. As shown in Fig. 7c which obtained from tin and antimony, there are thin clusters of tin crystals on the dense deposits because of the more negative deposition potential of tin. At higher magnification (Fig. 7d), the size of density deposits is *ca.* 300-500 nm. EDS analysis result of the deposit was illustrated in Table-5. The composition of the crystal is tin and antimony and the Sn/Sb ratio is *ca.* 1, namely, tin and antimony can be electrodeposit from the [EMIm]BF_4 ionic liquid together.

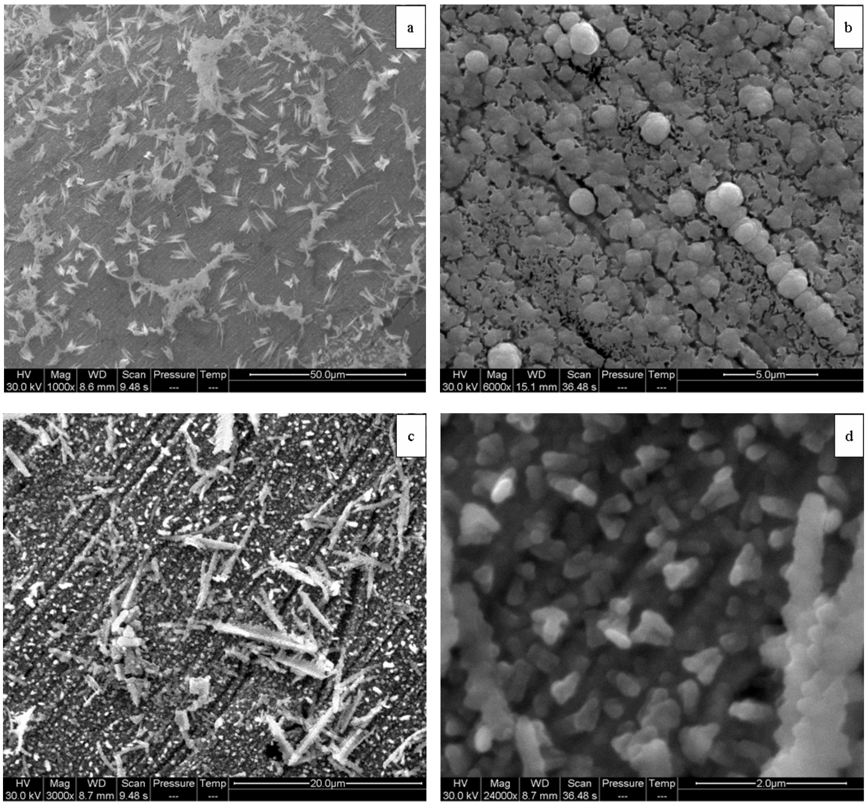

Fig. 7. SEM micrographs of M electrodeposited from 25 mM M ion in [EMIm]BF_4 ionic liquid at room temperature: (a) M = Sn, (b) M = Sb, (c) M = Sn + Sb, (d) the higher magnification of (c) Deposition potemtial was -1.1 V *vs.* Ag/Ag(I)

TABLE-5
ENERGY DISPERSIVE SPECTROSCOPIC ANALYSIS RESULT OF THE DEPOSIT

Element	Wt (%)	At (%)
Sn	13.13	18.44
Sb	14.18	19.42
Pt	72.69	62.14

Conclusition

$SnCl_2$ and $SbCl_3$ can be dissolved in the [EMIm]BF_4 ionic liquid at room temperature. The reductions of Sn(II) and Sb(III) were studied by linear sweep voltammetry (LSV). The Sn(II) and Sb(III) reactions exhibit electrochemically irreversible behaviour on Pt electrode. The diffusion coefficients and Stoke-Einstein products calculated from LSV data for Sn(II) and Sb(III) are comparable to the values reported in basic or acid aluminum chloride ionic liquids, which indicate that the formation of simpler Sn(II) chloro complex species and higher Sb(III) chloro complexes in the [EMIm]BF_4 ionic liquid. The electrodepositions of Sn(II) and Sb(III) were investigated on Pt electrode and scanning electron microscope (SEM) showed that the deposits of tin are incompact clusters of needles, but antimony adhere well to the platinum electrode. EDS analysis reveals that tin and antimony can be electrodeposit from the [EMIm]BF_4 ionic liquid simultaneously.

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