



## Cyclovoltammetry, ATR-IR of $AlCl_3$ /Amide and Thioamide DES and the Morphology of Deposited Aluminum at Variable Potential and Temperature

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### Abstract

Aluminium was successfully electrodeposited from mixtures of aluminium chloride with two amides and two thioamides. Structure identification by ATR-IR spectroscopy suggested the interaction of  $(AlCl_2^+)$  species with oxygen, sulfur and nitrogen respectively which influence the cyclovoltammetry behavior of the mixtures. Morphology of electrodeposited aluminium from the protected mixtures by decane layer examined by SEM and EDX showed variable shapes and microsize due to the effect of variable temperatures ( $30^\circ C$  to  $60^\circ C$ ) and potentials ( $-0.6V$  to  $-1.6V$ ), this in part is related to mass transport limitation and coordinating ligands.

**Keywords:** *DES, Electro-deposition, Aluminium,  $AlCl_3$ -amide,  $AlCl_3$ -thioamide.*

### Introduction

Electro-deposition of aluminium is the preferred method of aluminium coating as it is simple, cost-efficient, low energy consumption, can be used on objects with complex shapes and implies relatively easy control [1]. Other methods performed at elevated temperatures may damage the specimens, has low dissolving capability of Al salts, high volatility, flammability and not suitable to get a thin aluminium films [2]. In addition to the chloroaluminate ILs which is defined as the first generation of ILs an increasing interest in the electrodeposition of metals have been performed in air- and water-stable ILs, especially those reactive metals including light metals and rare-earth metals.

Apart from studying the surface morphology and adhesion strength of deposits, more attention is paid on the kinetic parameters of metal ions and their corresponding nucleation and growth mechanisms [3]. Properties of ILs expected to enable the formation of nanoscale deposits. It was reported that main experimental parameters, e.g. temperature, current density and molar ratio of  $[Im]Cl$  to  $AlCl_3$  effected the surface

morphology of deposited aluminium [4]. Different types of DES were prepared by Abbott [5] and DES in the form of  $[AlCl_2 nAmide]+AlCl_4^-$  was synthesized by mixing  $AlCl_3$  with amine [6] and its physical chemical electrochemical behavior at room temperature were reported.

It was confirmed that the mixtures of  $AlCl_3$  and amide can be easily handled under a layer of decane in a normal humid environment and aluminum deposits can be obtained in this ionic liquid (IL) analogues [7] or deep eutectic solvents [8]. DES also attracted significant research attention as a new type of liquid catalyst because of their tunable Lewis acidity and high catalytic activity. These systems of deep eutectic solvents (DES) are defined as low melting liquids made by combining a salt with a neutral molecule such as  $ZnCl_2/urea$  [9,10].

Following the same concept of DES preparation, other liquids were formed by mixing  $AlCl_3$  or  $GaCl_3$  ( $xMCl_3 = 0.60$ ) with substoichiometric amounts of simple donors (O-donors such as urea, AcA, dimethylacetamide, P8880; S-donors such as

thiourea; P-donors such as trioctylphosphine (P888)), producing viscous liquids [11]. Aluminium chloride ionic liquids based on organic ligands containing atoms possess electron pair such as O, P and S have been formed by coordinating aluminium cationic species with the ligands by the asymmetric cleavage of  $AlCl_3$ . These liquids differ fundamentally from chloroaluminate ionic liquids, since Lewis acidic aluminum dichloride [ $AlCl_2^+$ ] [12] is formed, instead of [ $Al_2Cl_7^-$ ] [5] in chloroaluminum ionic liquids. Due to high aluminium concentration.

The liquid becomes dense, has high heat capacity, high ionic conductivity and exhibits a wide range of Lewis acidity and redox potentials. The most significant feature that makes this class of compounds similar to chloroaluminate ILs is the dependence of Lewis acidity on the metal chloride concentration ( $xMCl_3$ ) [13, 14].

Most of the work related to aluminium electrodeposition in ionic liquids has been performed using chloroaluminate ILs, in which the [ $Al_2Cl_7^-$ ] - complex formed in the Lewis acidic melt reduced to metallic aluminium [15, 16]. The first reported aluminium chloride DES at 2011[6] was less water sensitive liquid than chloroaluminate ionic liquids and has similar reduction behavior of aluminium and catalytic activity [11].

Electrodeposition of aluminium was reported in DES of  $AlCl_3$ /Acetamide (1:1) at 2mA.cm<sup>-2</sup> giving 0.4V with electrodeposition efficiency of 97% suggested that the cationic species [ $AlCl_2.nAmide^+$ ] + are predominantly reduced at the electrode surface [6]. Electrodeposition of aluminium was also reported in  $AlCl_3$ /Amide DES where the amides are (propoamide, butylamide) of (1.3:1) mole ratio on copper substrate at -0.25V and 313K giving thick deposition [16].

Abbott reported the electrodeposition of aluminium on copper from  $AlCl_3$ /Urea (1.5:1) at 25°C diluted with toluene (20vol %) on mild steel electrode with little effect of the diluent on the thick morphology of deposited aluminium unlike the corresponding imidazolium chloridealuminum chloride system [18]. Different system of  $AlCl_3$  with urea or acetamide or their mixtures with or without LiBr, LiCl or LiF were used to electrodeposit aluminium at -0.2V, 313-33K

on copper. They concluded that the morphology is depended on potential and temperature giving compact deposit at most positive potential and lower negative cathodic potential and high temperatures which were related to increase deposition rate [19]. Nanocrystalline aluminium was reported to electrodeposite from  $AlCl_3$ /1-butylpyrrolidine (1.2 or 1.3:1) at room temperature on copper at -0.1V.[20] Deposition of aluminium from  $AlCl_3$ / Urea was reported to have nano to microcrystalline size depending on mole ratio of aluminium chloride , temperatures and potentials of electrodeposition process , while was reported large size of particles with longer time[21].

In this work we have studied the electrodeposition of aluminium from deep eutectic solvents of aluminium chloride with urea, acetamide, thiourea and thioacetamide. This was studied at variable temperatures and potentials to evaluate their influence on the morphology and size of deposited aluminium on copper substrate.  $AlCl_3$ /Thioacetamide was not reported to be prepared up to the best of our knowledge. The cyclic voltammetry and ATR-IR were used to examine the behavior and structure of DES, while SEM and EDX were used to study the morphology of deposited aluminium.

## Experimental

### Chemicals

Urea (Thomas Baker, 99.5%), Acetamide (FLUKA, 98%), Thiourea (MERCK, 99.5%), Thioacetamide (GPR, 98%), Anhydrous Aluminum Chloride (BDH, 99.5%), Acetone (Thomas Baker, 99.5 %), Toluene (Chem\_LB, 99.9%), Acetonitrile (ROMIL, 99.9%), Propanol (BDH, 99.5 %), Hydrochloric acid (HAYMAN, 100%).All material have been used with no further purification.

### Synthesis of $AlCl_3$ -amide IL analogues

$AlCl_3$ -amide (amide = urea or acetamide ) and  $AlCl_3$ -thioamide (thiourea or thioacetamide) with molar ratio (1.5:1) IL analogues were synthesized using same produce as stated in early work [6] when a homogeneous, yellow to brown color liquids were obtained as show in Fig.(2.1). The preparations were performed in a glove box under nitrogen gas. A top layer of decane was added on the liquid to protect it from air.



Figure 1: Optical photograph of (a) AlCl<sub>3</sub>-urea, (b) AlCl<sub>3</sub>-acetamide, (c) AlCl<sub>3</sub>-thiourea and (d) AlCl<sub>3</sub>-thioacetamide ionic liquids

## Potentiostatic Deposition

The electrodeposition was conducted potentiostatically on copper metal sheet of (60 mm x 10mm x 1mm) as positive cathode with an immersed part of about 20mm length in DES, and an anode of aluminium mesh with (40mm length\* 60mm diameter). The cathode was rubbed with sand paper while the anode was abraded with iron brush; both were followed by rinsing with deionised water, then immersed in 0.5% HCl and again rinsed with deionized water and acetone sequentially. After deposition of aluminum in AlCl<sub>3</sub>/urea and AlCl<sub>3</sub>/acetamide DES, specimen when removed from the liquid were immediately treated by dipping in toluene until all ionic liquid was removed and then rinsed with n-propanol then with acetone.

The electroplated cathode removed from AlCl<sub>3</sub>/thiourea or AlCl<sub>3</sub>/thioacetamide liquids was immediately immersed in acetonitrile until all ionic liquid was removed, then washed with acetone and finally dried with stream of air and stored for further analyses, because the rushing washing protocols in AlCl<sub>3</sub>/Amide was not successful with AlCl<sub>3</sub>/Thioamide.

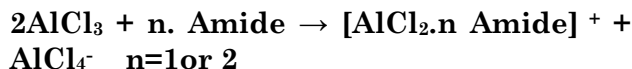
## Measurements

The interaction of AlCl<sub>3</sub> with amide and thioamide examined by ATR-IR Spectrometer by Bruker Optik GmbH, while Cyclovoltammetry (CV) examined using Digily-Dy2300 Bipotentiostat to study the electro redox behavior of all DES. Thurlby 15V-4A, England d power supply was used to control the current and the potential in the potentiostatic electrodeposition process. The surface morphology of specimens of aluminium coatings on copper substrate was investigated with a high-resolution field emission scanning electron microscopy (INSPECT S50)SEM, and the energy dispersive X-ray analysis the (X Flash 6110)

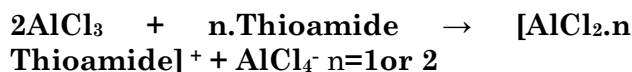
Bruker EDX was used for determination of the composition of samples surface.

## Results and Discussion

The aluminium chloride and amide were found to react immediately due to the strong Lewis acidic nature of aluminium chloride with the amide as the Lewis base. They were found to react exothermically to formed ionic liquid which was reported to be hot with a temperature around 75°C for urea and acetamide[6] while it was measured in this work to reach 40°C for thioacetamide and thiourea. AlCl<sub>3</sub>/Urea and AlCl<sub>3</sub>/Acetamide were reported to contain the cationic species [AlCl<sub>2.n</sub> Amide]<sup>+</sup> and the anionic species AlCl<sub>4</sub><sup>-</sup> as illustrated in the following equation:



The ionic liquids of AlCl<sub>3</sub>/Thiourea and AlCl<sub>3</sub>/Thioacetamide are expected to have analogues species as follow:



Which their interaction will be discussed in the following section.

## ATR-IR Spectra of ionic Liquids

The ATR-IR vibrational spectrum was obtained to study the interaction of the active species for the DES liquids as shown in Fig.(3.2) The vibration frequencies in general were found to shift to either higher or lower frequencies than in the solid of starting compounds reflecting a new interaction in the liquids phase. The main group of the liquids and their starting materials (urea, acetamide<sup>22</sup>, thiourea<sup>23</sup> and thioacetamide<sup>24</sup>) are represented in Table (3.1 and 3.2). It can be seen that the vibrational frequency of C=O at 1674 cm<sup>-1</sup> in free urea or acetamide decreased by 39cm<sup>-1</sup> and 14cm<sup>-1</sup> respectively in the liquid. The N-

H symmetrical and asymmetrical vibrational frequencies have higher vibration in AlCl<sub>3</sub>/Urea and AlCl<sub>3</sub>/Acetamide compared to their vibration in solid amides. The vibrational changes were also observed in AlCl<sub>3</sub>/Thiourea and AlCl<sub>3</sub>/Thioacetamide in comparison to solid thioamides. The C-H vibrational frequency of the (-CH<sub>3</sub>) group in acetamide or thioacetamide liquids formed with AlCl<sub>3</sub> showed almost identical increase towards higher frequency than in acetamide and thioacetamide solid materials. In addition the vibrational band at 1646 cm<sup>-1</sup> in thioacetamide which was attributed to -NH<sub>2</sub> bending vibrational band was shifted to higher frequency to 1660 cm<sup>-1</sup> in the liquid.

The new band appeared at 2513 cm<sup>-1</sup> was assigned to S-H vibration, while the band at 1299, 709cm<sup>-1</sup> for C=S vibrational shifted to 1301, 726cm<sup>-1</sup> respectively. The vibrational band of thiourea at 1610cm<sup>-1</sup> for -NH<sub>2</sub> bending vibrational band was shifted to higher frequency to 1642 cm<sup>-1</sup> in the liquid. Again a new band appeared at 2561 cm<sup>-1</sup> which was assigned to S-H vibration, while the bands at 1195 cm<sup>-1</sup> and 723 cm<sup>-1</sup> for C=S vibrational shifted to 1194cm<sup>-1</sup> and 796cm<sup>-1</sup> respectively. The S-H new band

suggested the formation of teutometric structure of the thioacetamide and thiourea probably result in the interaction of AlCl<sub>3</sub>+2 species with both sulfur and nitrogen atoms. The above IR support the early report that suggested the formation of [AlCl<sub>2</sub>.amide] + species with amide [6]. Therefore, the interaction of positive species assumed to be with sulfur atom in the thioamide. However, in urea and acetamide the C=O was changed the vibration to lower frequencies while the NH<sub>2</sub> groups have higher frequencies compared to solid materials.

In thiourea and thioacetamide the NH<sub>2</sub> and C=S groups have higher frequencies compared to solid materials which support the interaction of the cationic aluminium species in liquid through nitrogen and sulfur atom in the thioamide compounds. The broad bands of amide stretching vibrations between 2900cm<sup>-1</sup> -3500cm<sup>-1</sup> in the urea and acetamide liquids formed with AlCl<sub>3</sub> could be attributed to a hydrogen bond formation while this was not observed in the liquids formed between thioacetamide or thiourea with AlCl<sub>3</sub> when a sharp vibrational bands were observed.

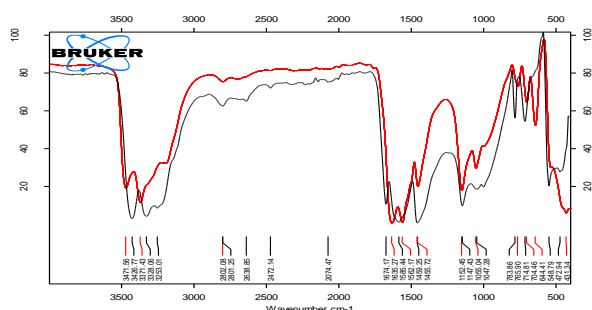
**Table 1: The peaks for urea and acetamide materials with AlCl<sub>3</sub>: Urea and AlCl<sub>3</sub>: Acetamide ionic liquids**

Band assignment	Urea		AlCl <sub>3</sub> :Urea		Acetamide		AlCl <sub>3</sub> :Acetamide	
	Intensity	Vibration (cm <sup>-1</sup> )	Intensity	Vibration (cm <sup>-1</sup> )	Intensity	Vibration (cm <sup>-1</sup> )	Intensity	Vibration (cm <sup>-1</sup> )
N-H	Vs	3426	s	3471	s	3147	m	3435
N-H	vs	3328	s	3371	vs	3295	m	3360
C-H	—	—	—	—	s	2817	s	3073
C=O	s	1674	vs	1635	vs	1674	vs	1660
C=O	vs	1585	vs	1562	vs	1629	vs	1561
NH <sub>2</sub>	vs	1459	s	1455	vs	1457	vs	1493
C-H	—	—	—	—	vs	1390	w	1366
C-N	s	1147	m	1152	vs	1146	s	1126
C-N	s	1047	m	1055	s	1046	m	1045

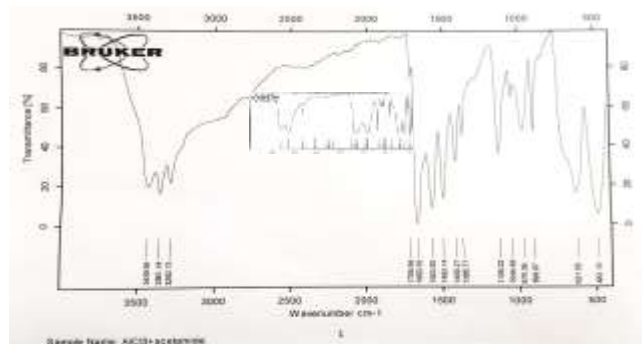
**Table 2: The peaks for thiourea and thioacetamide materials with AlCl<sub>3</sub>: thiourea and AlCl<sub>3</sub>: thioacetamide ionic liquids**

Band assignment	Thiourea		AlCl <sub>3</sub> :Thiourea		Thioacetamide		AlCl <sub>3</sub> :Thioacetamide	
	Intensity	Vibration (cm <sup>-1</sup> )	Intensity	Vibration (cm <sup>-1</sup> )	Intensity	Vibration (cm <sup>-1</sup> )	Intensity	Vibration (cm <sup>-1</sup> )
N-H	vs, vs	3365, 3261, 3149	vs, vs, vs, vs	3436, 3333, 3249, 3172	s, s	3273, 3071	m, m, s	3383, 3341, 3244
C-H	—	—	—	—	vs	2941	m	2974
S-H	—	—	m	2561	—	—	m	2513
NH <sub>2</sub>	vs	1610	s	1642	vs	1646	s	1660
C-N	vs	1463	s	1544	vs	1475	m	1534
CH <sub>3</sub>	—	—	—	—	s, vs	1430, 1375	m, s	1418, 1372
S=C	vs, vs	1195, 723	w, s	1194, 796	vs, vs	1299, 761	s, s	1301, 790

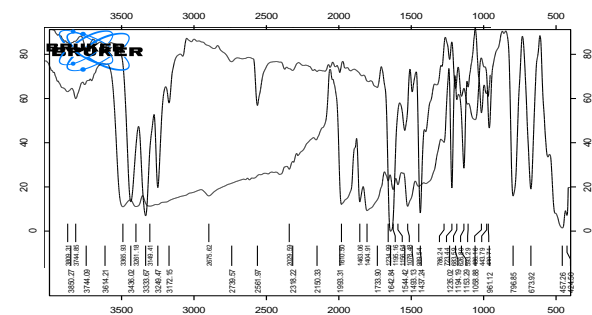
<b>NH<sub>2</sub>,CH<sub>3</sub></b>					<b>vs</b>	<b>1027</b>	<b>w</b>	<b>1203</b>
<b>N-C-N</b>	<b>s,</b> <b>vs</b>	<b>1156</b> <b>1078</b>	<b>m</b> <b>w</b>	<b>1153</b> <b>1058</b>	---	---	---	---
<b>N-C=S</b>	<b>s</b>	<b>989</b>	<b>m</b>	<b>961</b>	<b>vs</b>	<b>969</b>	<b>m,w</b>	<b>985, 929</b>
<b>C=S, C-C</b>					<b>w</b>	<b>761</b>	<b>s</b>	<b>790</b>
<b>Chain</b>	<b>s,</b> <b>m,</b> <b>m</b>	<b>626,</b> <b>443,</b> <b>430</b>	<b>s,</b> <b>s,</b> <b>s</b>	<b>673,</b> <b>475,</b> <b>424</b>	<b>s</b>	<b>500-709</b>	<b>s,</b> <b>s,</b> <b>s</b>	<b>726,</b> <b>666,</b> <b>555</b>



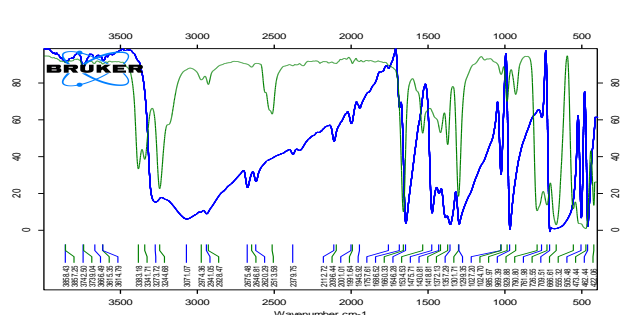
Sample Name: Sample description



Sample Name: AlCl3-acetamide



Sample Name: AlCl<sub>3</sub>: Thiourea Thiourea



AlCl<sub>3</sub>: Thioacetamide Thioacetamide

Figure 2: ATR-IR spectra of (a) AlCl<sub>3</sub>: Urea with Urea, (b) AlCl<sub>3</sub>: Acetamide with Acetamide, (c) AlCl<sub>3</sub>: Thiourea with Thiourea and (d) AlCl<sub>3</sub>: Thioacetamide with Thioacetamide ionic liquid all with (1.5:1) mole ratio

### Cyclic Voltammometry of Ionic Liquids

The cyclic voltammograms of AlCl<sub>3</sub>/amide DES with molar ratio of (1.5:1) at 25 °C was recorded on a Pt electrode using silver wire as quasi reference electrode at a scan rate of 100 mV/sec. The AlCl<sub>3</sub>-urea and AlCl<sub>3</sub>-acetamide showed two reductions, c<sub>1</sub> and c<sub>2</sub> and oxidation two waves at a<sub>1</sub> and a<sub>2</sub> Fig. 3. The cathodic wave (c<sub>2</sub>) may ascribe to the bulk electrodeposition of aluminum, while the anodic current peak at (a<sub>2</sub>) is attributed to the aluminum stripping. In the reverse scan, a crossover loop that is a typical of nucleation process of aluminium was demonstrated by this DES. Wave redox of aluminum from AlCl<sub>3</sub>/urea DES was characterized by under potential deposition (UPD) of aluminum as indicated by wave (c<sub>1</sub>) and aluminium was stripped when the scan was performed at the positive potential at wave (a<sub>1</sub>).

Such UPD was also reported for aluminium deposition from different chloroaluminat

(III) ionic liquids [18].although they have different type of electroactive aluminium species. Both AlCl<sub>3</sub>/urea and AlCl<sub>3</sub>/Acetamide showed a cathodic current with onset potential at about -1.00V while an anodic wave commenced at -0.8V with maximum current at about +0.13V was observed during the anodic scan.

UPD behavior in AlCl<sub>3</sub>/acetamide was also observed (wave c<sub>1</sub> and a<sub>1</sub>) indicating a similar nature of reduction process in both aluminium chloride-urea and aluminium chloride-acetamide DES. The AlCl<sub>3</sub>/thiourea ionic showed that the ionic liquid oxidative current started to be recorded and the reduction of aluminum species started at -0.85V which is less negative than the -1.0V observed in AlCl<sub>3</sub>/urea DES. This difference might be related to the relatively stronger coordination of aluminium positive species [AlCl<sub>2</sub><sup>+</sup>] with sulfur in thiourea than with oxygen in urea. The cyclic voltammetry



behavior of  $\text{AlCl}_3$ /thioacetamide indicated the reduction at  $-1.25\text{V}$  and the oxidation of aluminum at around  $-0.85\text{V}$  without having a cross over loop in contrast to that observed in  $\text{AlCl}_3$ /acetamide DES. In addition reduction process of aluminum from  $\text{AlCl}_3$ /thioacetamide DES indicated the absence of UPD process that found in  $\text{AlCl}_3$ /acetamide, yet, both processes were of quasi reversible reactions.

The different behavior of reduction and stripping of aluminum in all studied DES of  $\text{AlCl}_3$ /urea,  $\text{AlCl}_3$ /thiourea,  $\text{AlCl}_3$ /acetamide and  $\text{AlCl}_3$ /thioacetamide indicated different type of coordinating of the donor atoms of organic molecular with the acidic  $[\text{AlCl}_2^+]$  species as indicated by ATR-IR.

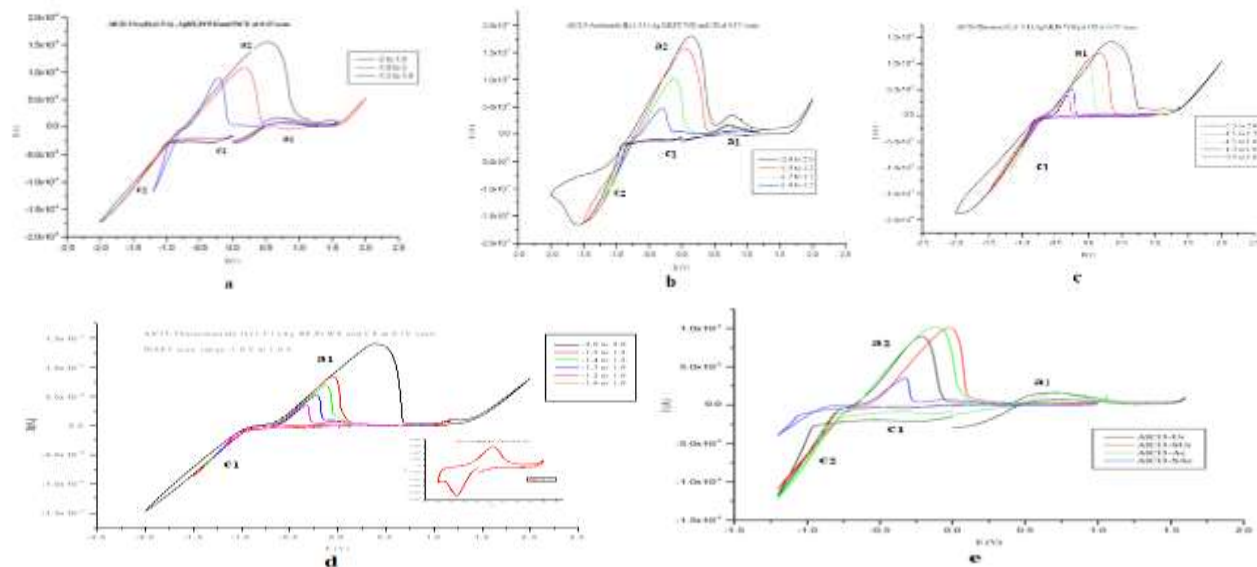


Figure 3: Cyclic voltammetry of (a)  $\text{AlCl}_3$ : Urea (b)  $\text{AlCl}_3$ : Acetamide (c)  $\text{AlCl}_3$ : Thiourea (d)  $\text{AlCl}_3$ : Thioacetamide insert scan range  $-1.0\text{V}$  to  $1.0\text{V}$  and (e)  $\text{AlCl}_3$ :amide and  $\text{AlCl}_3$ :thioamide, ionic liquids all with (1.5:1) mole ratio, Ag RE, Pt WE and CE at  $0.1\text{V}$  scan

### The Surface Morphology of Reduced Aluminum by Potentiostatic Deposition

The electrodeposition of aluminum in DES was studied potentiostatically to determine the effect of coordination complex of the ionic liquid on the morphology of deposited aluminum at different temperatures and potentials. These factors expected to influence the reduction process of growing reduced aluminium cation.

The electrodeposition of aluminum metal on copper substrate in room temperature was conducted in  $\text{AlCl}_3$  with Urea, Acetamide, Thiourea and Thioactamide DES of (1.5:1) mole ratios covered with Decane. All experiments of electrodeposition carried out at different potential i.e. ( $-0.6\text{V}$ ,  $-0.8\text{V}$ ,  $-1.0\text{V}$  and  $-1.2\text{V}$ ) for  $\text{AlCl}_3$ /urea and  $\text{AlCl}_3$ /acetamid and ( $-1.0\text{V}$ ,  $-1.2\text{V}$ ,  $-1.4\text{V}$  and  $-1.6\text{V}$ ) for  $\text{AlCl}_3$ /thiourea and  $\text{AlCl}_3$ /thioacetamid.

In addition the experiments were carried out at  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ ,  $50^\circ\text{C}$  and  $60^\circ\text{C}$  at each potential for 2 hours. Generally the resulted coating was silver-grey or silver-black and dense adherence on the copper in  $\text{AlCl}_3$ /urea and  $\text{AlCl}_3$ /acetamid while in  $\text{AlCl}_3$ /thiourea and  $\text{AlCl}_3$ /thioacetamid the coating was silver-black and dense aluminium with weakly adherence on the copper, as shown in Fig. (4),(5), (6) and(7) respectively.

The current was observed to increase when increasing the temperature reflecting enhancement of reaction rate due to decrease viscosity and increase mobility of reducing aluminium species.

The EDAX spectrum shows the peak of aluminum in  $\text{AlCl}_3$ /urea and  $\text{AlCl}_3$ /acetamide while their spectrum contain less than 2% weight of N,O,C,S and Cl reflecting probably non-removed DES, as shown in Fig.(3).

The weight of aluminium in all DES was found

in  $\text{AlCl}_3$ /thiourea,  $\text{AlCl}_3$ / thioacetamide to increase temperatures and potentials. The surface morphology at  $60^\circ\text{C}$  was smoother than that obtained at lower  $60^\circ\text{C}$ . The surface morphologies of the deposited aluminium show variable shaped at different potential depending on temperature and complexing agent. The size of crystal aluminium grain increase with increasing potentials at all temperatures 30, 40, 50 and  $60^\circ\text{C}$  in all DES. The morphology of deposited aluminium on copper substrate was found to change with potential, temperatures and type of DES.

Thus the shapes in acetamide or urea was used in DES were found to be stone or beads shape or rough and compact, while in thiourea the deposited aluminium was found to be in as cauliflower or beans and compact

but flak or beads when thioacetamide was used. It is worth noted that a sieve shape deposited aluminium with Mm hole size was produced at  $-0.8\text{V}$  and  $-1.0\text{V}$  at  $40^\circ\text{C}$  in  $\text{AlCl}_3$ /acetamide DES only. The different shapes with different experimental conditions expected to reflect the rate of adsorption of reducing aluminium species on the electrode. These reducing aluminium species are of different coordinating complexes resulted due to formation of the DES from urea, acetamide, thiourea and thioacetamide. These complexes are expected to influence the quality of deposited aluminium. The temperature would affect the mass transport in the DES.

In general although the variable condition gave different shapes of deposited aluminium, but there is no general trend can be concluded expect the variable morphology at all there conditions.

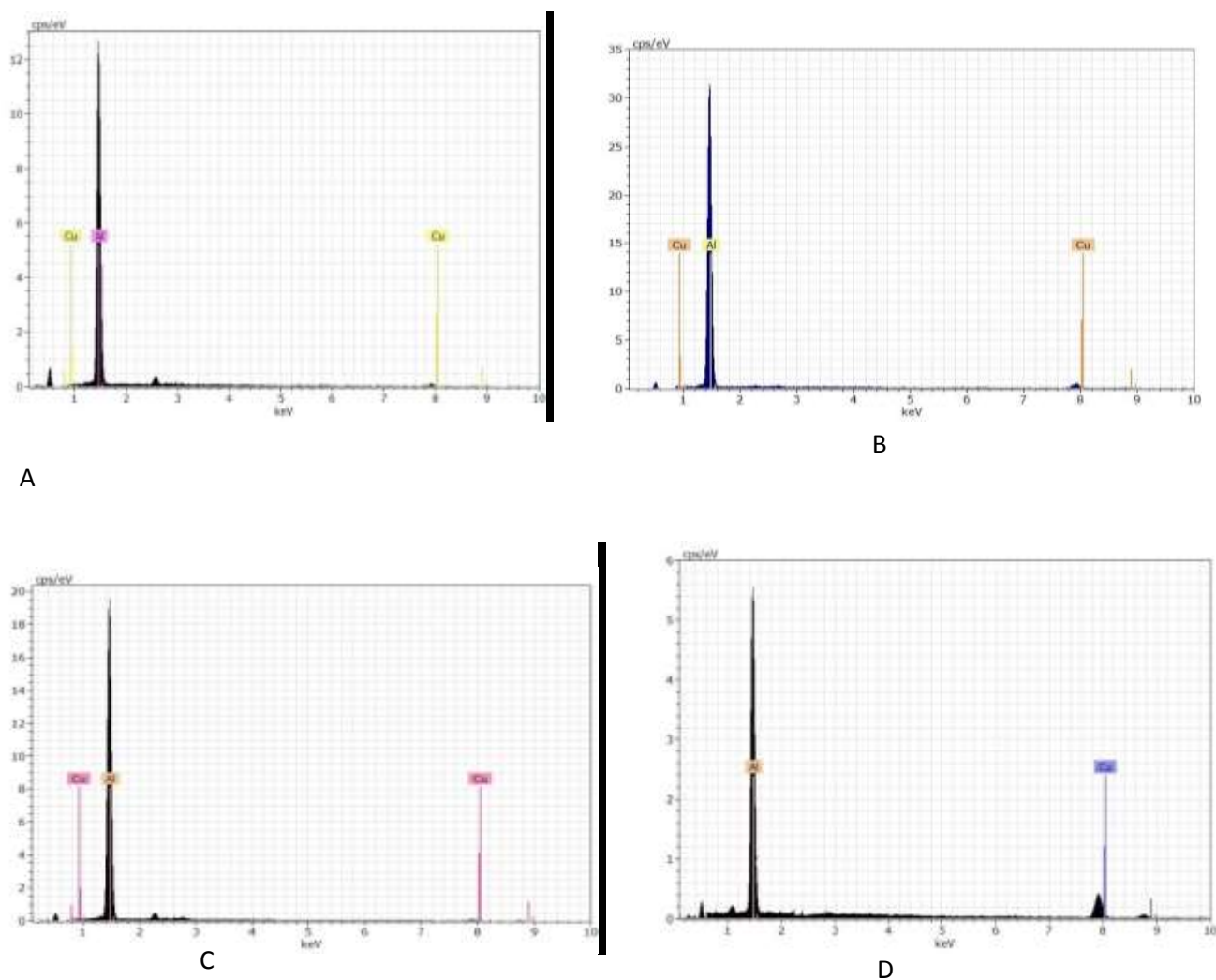


Figure 4: The EDAX spectrum shows the peak of aluminum deposited on copper in (a)  $\text{AlCl}_3$ : Urea (b)  $\text{AlCl}_3$ : Acetamide (c)  $\text{AlCl}_3$ : Thiourea and (d)  $\text{AlCl}_3$ : Thioacetamide DES all with (1.5:1) mole ratio, covered with decane, at  $40^\circ\text{C}$  temperature and  $-1.0\text{V}$  potential for 2hours

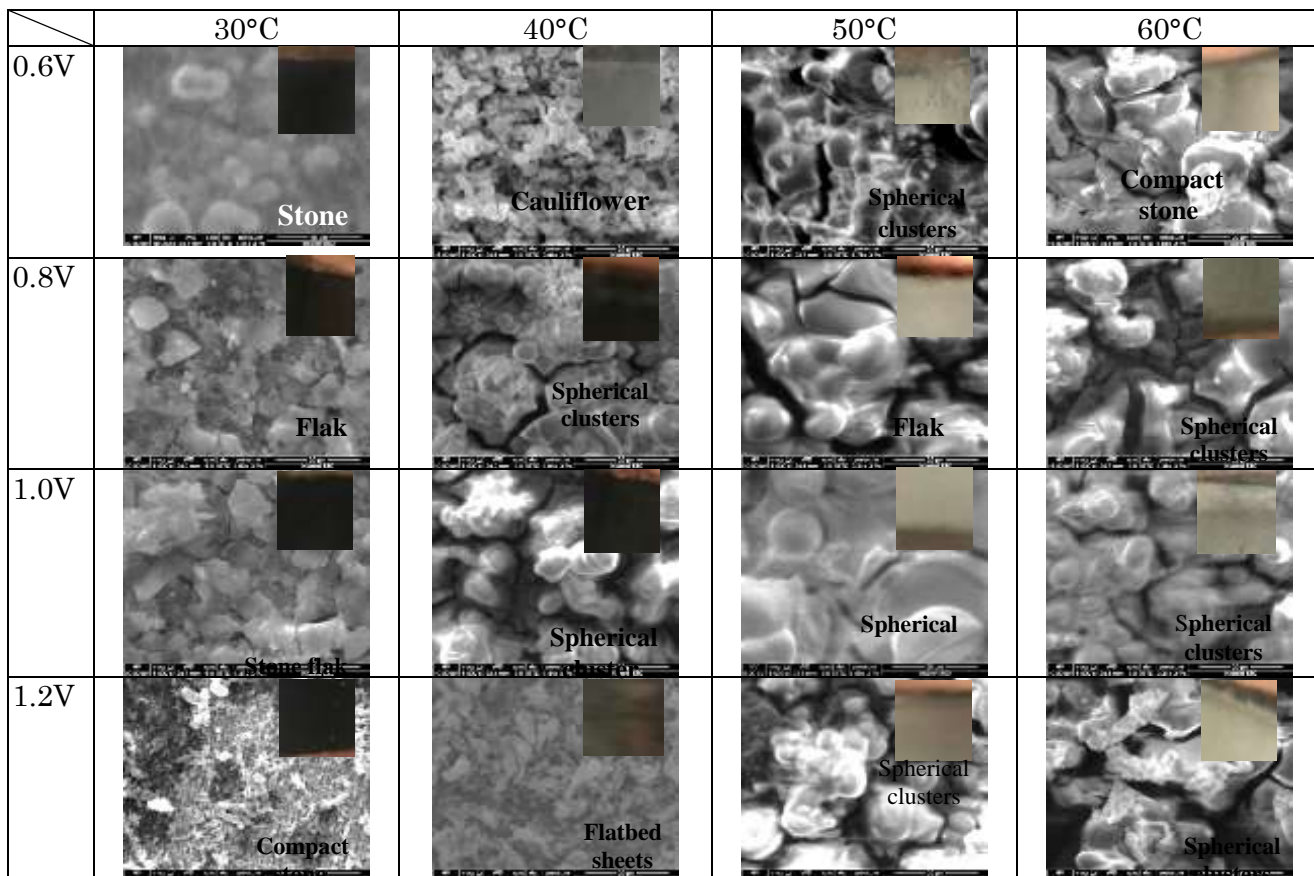


Figure 5: SEM images of deposited aluminium from 1.5:1 mole ratio AlCl<sub>3</sub>:Urea DES covered with decane , at different temperature and potential for 2hours, magnified at 5000x, with the corresponding optical photograph of the deposited aluminium on copper substrate

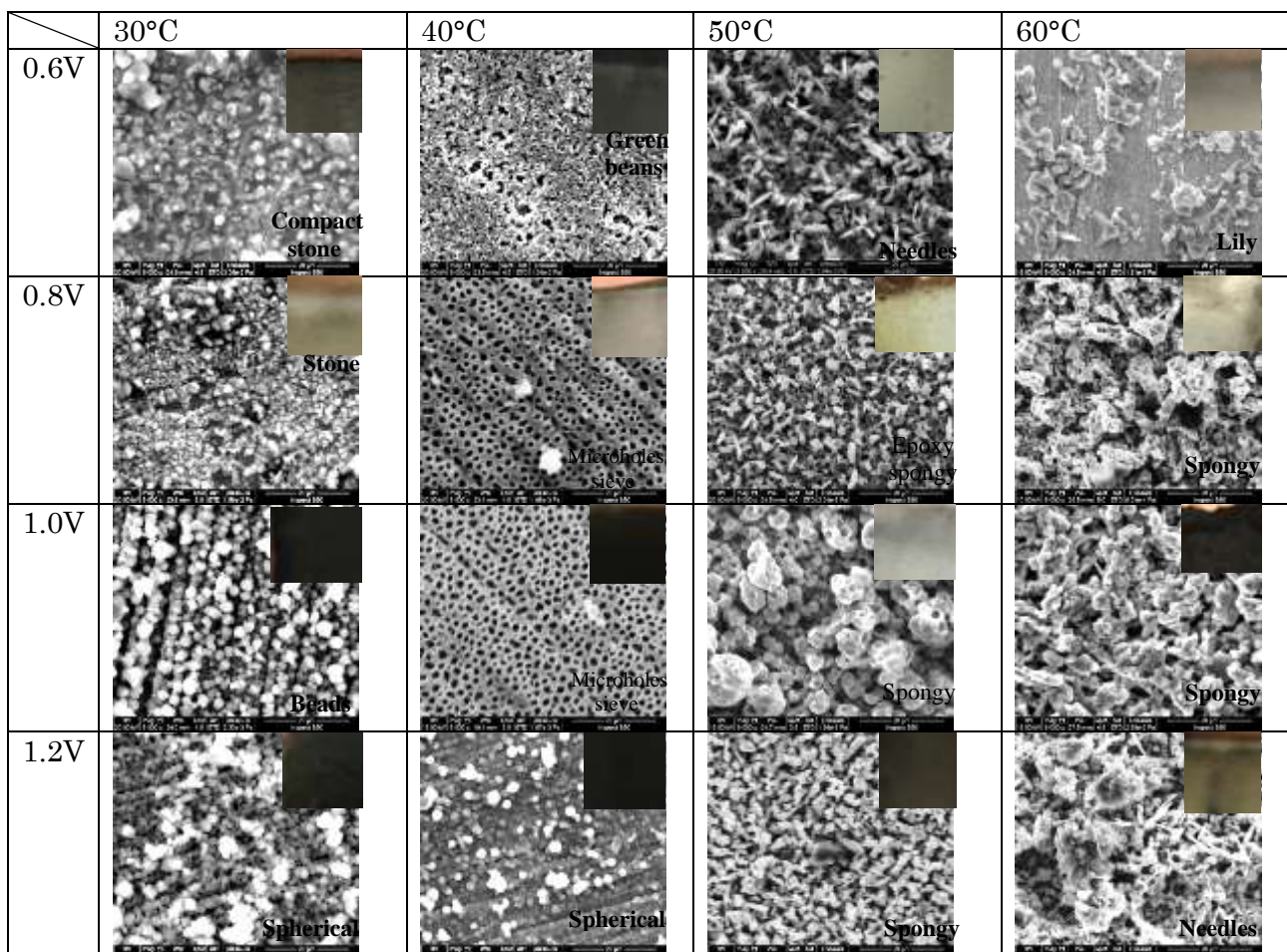


Figure 6: SEM images of deposited aluminium from 1.5:1 mole ratio AlCl<sub>3</sub>: Acetamide ionic liquid, covered with decane, at different temperature and potential for 2hours, magnified at 5000x, with the corresponding optical photograph of the deposited aluminium on copper substrate





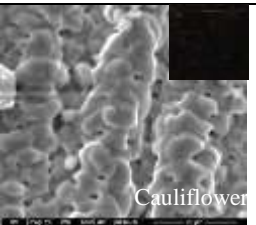
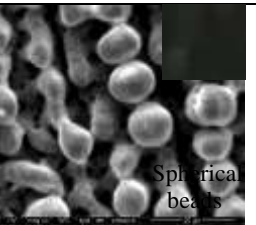
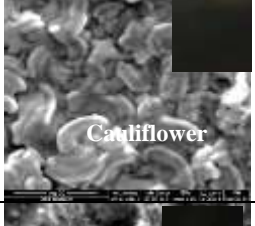
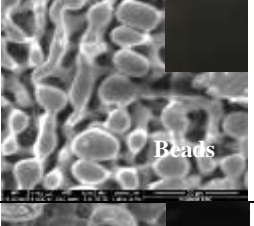

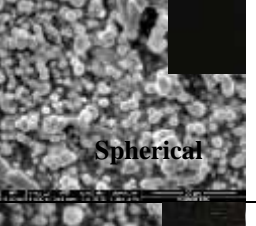





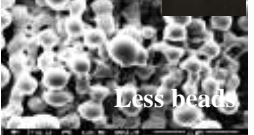


	30°C	40°C	50°C	60°C
1.0V	 Cauliflower	 Cauliflower	 Cauliflower	 Spherical beads
1.2V	 Cauliflower	 Beads	 Flat beans	 Spherical
1.4V	 Flat beans	 Slice mushroom	 Cauliflower	 Spherical
1.6V	 Bean	 Less beads	 Cauliflower	 Beans

Figure 7: SEM images of deposited aluminium from 1.5:1 mole ratio AlCl<sub>3</sub>: Thiourea ionic liquid, covered with decane, at different temperature and potential for 2hours, magnified at 5000x, with the corresponding optical photograph of the deposited aluminium on copper substrate

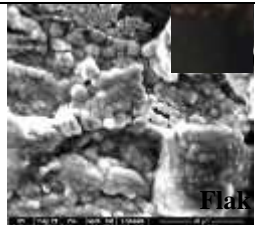
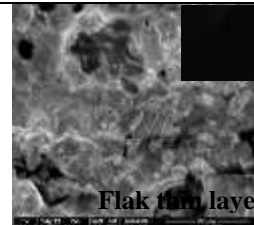
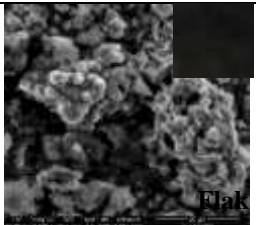
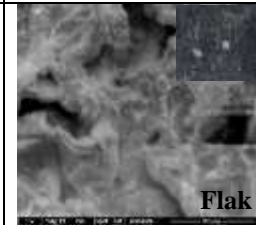
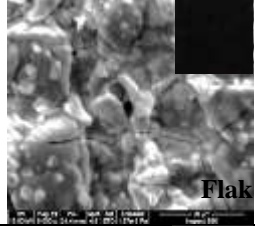
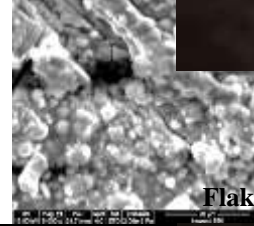
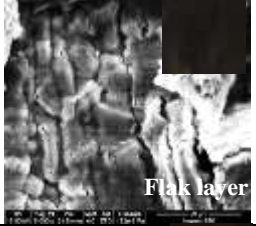
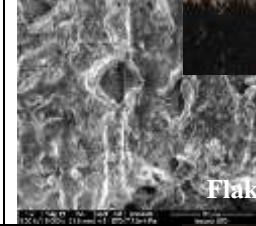


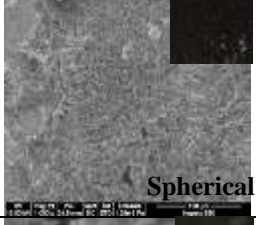

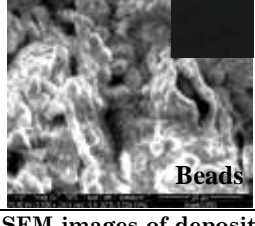
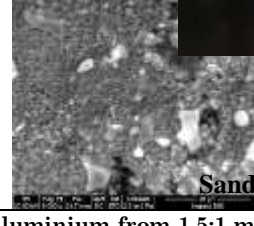
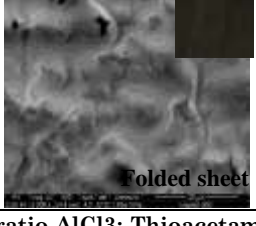
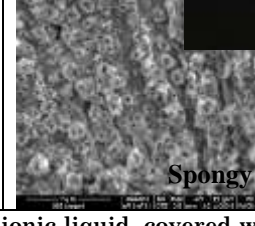
	30°C	40°C	50°C	60°C
1.0V	 Flak	 Flak thin layer	 Flak	 Flak
1.2V	 Flak	 Flak	 Flak layer	 Flak
1.4V	 Sheets	 Flings	 Spherical	 Flak
1.6V	 Beads	 Sand	 Folded sheet	 Spongy

Figure 8: SEM images of deposited aluminium from 1.5:1 mole ratio AlCl<sub>3</sub>: Thioacetamide ionic liquid, covered with decane, at different temperature and potential for 2hours, magnified at 5000x, with the corresponding optical photograph of the deposited aluminium on copper substrate

## Conclusion

Cyclovoltammogram was used to study the reduction of Al (III) ions from DES, while ATR-IR spectrum was used to investigate from interaction between AlCl<sub>3</sub> species and organic. CV results also indicate that Al (III) ions are easier to be reduced from higher molar ratio of AlCl<sub>3</sub>: Thiourea and AlCl<sub>3</sub>: Thioacetamide DES solvent. The deposition of aluminium metal from AlCl<sub>3</sub>: Urea, AlCl<sub>3</sub>: Acetamide, AlCl<sub>3</sub>: Thiourea, and AlCl<sub>3</sub>: Thioacetamide DES with mole ratio (1.5:1) at different temperature and potentials were

found to be smooth, well adhered to copper cathode in AlCl<sub>3</sub>: Urea, and AlCl<sub>3</sub>: Acetamide ionic liquids while in AlCl<sub>3</sub>: Thiourea and AlCl<sub>3</sub>: Thioacetamide ionic liquids were found to be rough, weakly adhered at the studied conditions. Complexing agents gave different morphologies at different temperatures and potentials for each ionic liquid on copper cathode electrode. Each DES also showed different morphology of deposited aluminum on copper cathode electrode. The current density was found to be increased with increased temperatures and potentials for each DES.

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