



RECOVERY OF ALUMINIUM FROM BAUXITE RESIDUE: DISSOLUTION AND ELECTROWINNING OF ALUMINIUM USING PYRROLIDINIUM IONIC LIQUID

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SUMMARY: Aluminium within bauxite residue represents one of the major losses in Bayer process. The proposed process development of recovering aluminium from bauxite residue involved pyro-, hydro- and iono-metallurgical routes. In this paper, iono-metallurgical route is used to investigate the identification of the appropriate aluminium salt that can be dissolved in pyrrolidinium ionic liquid (*BMPTFSI, 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide*). The characterisation of the resultant solution and electrowinning of aluminium on copper cathode were also investigated. It was found that $\text{Al}(\text{OTf})_3$ salt was able to be dissolved relatively easily in the ionic liquid, creating a solution of 0.09 mol/L concentration. Following that, the solution density, viscosity and conductivity were measured and FTIR spectra of solution was characterised. The cyclic voltammetry in the $\text{Al}(\text{OTf})_3$ solution indicated a visible cathodic peak at -2.8V vs Ag/Ag^+ in Acetonitrile. The solution was then subjected to an electrolysis test under constant cathodic potential in ambient temperature, with SEM/EDS analysis confirming presence of aluminium on copper cathode.

1. INTRODUCTION

Aluminium's (Al) robust demand in the global market has been fuelled in recent years by advancements towards lightweight vehicles and buildings, increased demand in consumer products such as electronic equipments, as well as the recent trends of cost-effective switches from copper to aluminium by power industries (Onstad, Obayashi et al., 2016). Freshly exposed aluminium metal reacts rapidly in the presence of oxygen to form a protective aluminium oxide film and thus, protecting metals from corrosion. With the global aluminium production hitting approximately 57,9 million metric tonnes per year during 2015 (World Aluminium, 2016), the challenge to reduce aluminium losses within the industry is a priority in Bayer processing.

Bauxite residue, also known as red mud, is the by-product of alumina production through the Bayer process. Gibbsite ($\text{Al}(\text{OH})_3$), boehmite ($\gamma\text{-AlO}(\text{OH})$) and diaspore ($\alpha\text{-AlO}(\text{OH})$) are the main mineralogical phases that contains aluminium (Al) within bauxite ores (Gräfe, Power et al., 2011; Klauber, Gräfe et al., 2011). Bauxite ores also contain as significant portion of iron-bearing minerals that gives bauxite its characteristic red appearance (Gräfe, Power et al., 2011). In addition, a significant range of existing minerals within bauxite are made of silicates, titanium, calcium, other minor elements such as sodium and rare earths (Gräfe, Power et al., 2011; Liu and Naidu, 2014). Unavoidable inefficiencies during the bauxite digestion in Bayer process such as incomplete dissolution of refractory aluminium phases i.e. diaspore, formation of desilication products; and further aluminium losses occurring during bauxite residue separation from the sodium aluminate liquor (Mishra, Staley et al., 2002).

This study is focused on developing an alternative process involving the recovery of aluminium from bauxite residue beginning with pyro- and hydro-metallurgical approaches. This is followed by the ionometallurgical approach using ionic liquids. The four modules are broken down into: (1) recovery of aluminium in the form of a dissolvable species i.e. sodium aluminate (NaAlO_2) from bauxite residue via roasting in the presence of Na_2CO_3 and mild alkaline leaching, (2) synthesis of aluminium salts dissolvable within ionic liquid from the pregnant liquor which is a super saturated solution of sodium aluminate (NaAlO_2), via precipitation (3) dissolution of aluminium salts within ionic liquid and (4) electro-winning of pure aluminium from ionic liquid at ambient condition. The scope of this research will be based on module (3) and (4).

The Hall-Heroult process is the traditional electrolytic technique of winning aluminium from aluminium oxide, developed in 1886. It often consists of an electrolytic bath in which aluminium oxide (Al_2O_3) is dissolved at temperatures of 930-1000°C in an electrolyte containing molten cryolite (Na_3AlF_6) and aluminium fluoride (AlF_3). Despite its enormous success in extracting Al with high output rates, the is drawbacks of the Hall-Heroult process include major cost and environmental drawbacks such as energy demands, anode degradation, anode effect that increases the carbon footprint by producing an electrically insulating gaseous layer of 70-80% carbon monoxide as well as perfluorocarbon compounds, and passivation of electrolytes (Endres, Zein El Abedin et al., 2008; Kvande and Drabløs, 2014).

Ionic liquids are molten salts with low melting temperatures (some even at ambient temperature) consisting entirely of ions, i.e. cations and anions in strong association. The technological potential of these ionic liquids that had certainly piqued research interest though it has its advantages and disadvantages. The advantages include electroplating a range of metals that are inhibited by hydrolysis, low energy consumption due to low temperature operations, increased quality of coatings from negligible hydrogen gas generation, and cost-saving benefits of reusing ionic liquids. However, the cost of manufacturing ionic liquid have so far been a larger drawback of uptake in industry (Endres, Zein El Abedin et al., 2008). One of the largely investigated ionic liquid usage is in the advancements of electrodepositing Al, with most of the literature focused on tetrachloroaluminate-based (AlCl_4^-) ionic liquids (Schubert, Zein El Abedin et al., 2008). The composition and acidity of

chloroaluminate ionic liquid, presence of moisture and decomposition rate are known to affect the electrodeposition of aluminium (Rocher, Izgorodina et al., 2009).

There are four groups of cation-grouped ionic liquids; imidazolium, pyrrolidinium, ammonium and the phosphonium-based ionic liquids (Bourbos, Giannopoulou et al., 2014). Al has been known to be electrodeposited in water-stable ionic liquid, despite mechanism of occurrence not fully understood (Rocher, Izgorodina et al., 2009). Pyrrolidinium-based ionic liquids are known for its low cost compared to other ionic liquids, as well as low toxicity rating and a larger range of electrochemical window compared to protic ionic liquids (Anouti, Caillon-Caravanier et al., 2008). For this research, a pyrrolidinium-based BMPTFSI (*1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide*, $C_{11}H_{20}F_6N_2O_4S_2$, Molecular weight: 422.41g/mol) is used as the solvent and electrolyte. BMPTFSI has a wide electrochemical window, low viscosity in ambient conditions, is aprotic and hydrophobic, and exhibiting thermal stability up until 200°C and above (Anouti, Caillon-Caravanier et al., 2008; Mao, Nulwala et al., 2012; Salgado, Parajó et al., 2014).

2. EXPERIMENTAL METHODOLOGY

Analytical grade chemicals of a range of aluminium salts (>99%wt; Alfa Aesar for $Al_2(SO_4)_3$ anhydrous, $Al(NO_3)_3 \cdot 9H_2O$, AlF_3 anhydrous, $AlCl_3$ anhydrous, $AlBr_3$ anhydrous, AlI_3 anhydrous, $Al(CF_3SO_3)_3$ anhydrous (i.e. $Al(OTf)_3$), and Solvionic for $Al(C_2F_6NO_4S_2)_3$ (i.e. $Al(TFSI)_3$) and BMPTFSI (99%wt., Iolitec) was used to prepare Al solution. High purity argon gas (>99%wt.) was used to deaerate during dissolution experiment for 24h. Deionised water (1.5µS/cm electroconductivity), Acetone (>99.5%wt, Chem-Lab) and 2-Propanol (>99%wt., Scharlau) were used to clean the electrodes prior to cyclic voltammetry and electro-winning of Al. Hydrochloric acid (>37%wt., Sigma Aldrich) and nitric acid (65%wt., Chem-Lab) were used in aqua regia digestion to determine the aluminium content within the ionic liquid solution.

A 0.1M solution of aluminium salts in BMPTFSI was prepared by dissolving a range of aluminium salts in 50mL of BMPTFSI at 150°C±10°C in Trallero and Schlee mini-reactor for 24h deaerated with argon gas using a stirring rate of 300rpm. The solution is then vacuum filtered and sealed in glass bottles for subsequent analysis. The chemical analysis of aluminium was performed on 0.5mL sample solution using a 3-step digestion procedure, with 5 mL concentrated HNO₃ digestion repeated four times, followed by 40mL of aqua regia digestion diluted with 20mL of deionised water, and finally, boiling in 100mL 15%wt. HCl.

The density, viscosity and electrical conductivity of both the ionic liquid and the solution of $Al(OTf)_3$ salt in the ionic liquid were measured using the following methods: (1) density was evaluated by measuring on a high precision scale with the mass quantity of 3 mL of liquid sample solution under three repetitions, (2) viscosity measurements were done in a Brookfield LVDVI+ viscometer. The viscosity was measured between temperature ranges of 20°C≤T≤120°C; (3) conductivity measurements were performed with the SI Analytics HandyLab 200 conductivity meter attached with LF713T probe (cell constant, K = 100cm⁻¹±10%) in the temperature range between 25°C ≤ T ≤ 50°C. FTIR analysis was completed using Perkin Elmer FTIR Spectrum 100 between wavenumber range of 4000cm⁻¹ to 650cm⁻¹ (step 16cm⁻¹, 16 repetitions).

Next, the electrochemical window of the solution was defined by performing cyclic voltammetry. Firstly, 5mL of solution is pre-treated and is placed in a Nüve EV 018 Link Lab vacuum furnace at T:100°C for 24h. The cyclic voltammetry (CV) and chronoamperometry (CA) set-up consists of a potentiostat, current-to-voltage converter, data acquisition system (provided by VersaStat3 Ametek Princeton Applied Research). Electrolysis cell for CV uses platinum (Pt, φ: 1.98mm) as working and counter electrode and reference electrode of Ag⁺/AgNO₃ in Acetonitrile. CV potential scan (vs Ag⁺/AgNO₃ in Acetonitrile) was begun at 2V, reversed at -3.5V, and then terminated at 2V, at a scan rate of 20mV/s. Electro-winning tests via CA under two different durations (5h and 32h) were

performed with copper used as deposition substrate. Inert gas (Argon) is used to sparge the headspace and constant potential of -2.8V vs Ag/Ag^+ in Acetonitrile was applied at room temperature.

The cathode (copper wire) is firstly cut and cylindrical area of cathode covered thermally with plastic tubing. The exposed area is then polished using P400 and P1200 grain size SiC abrasive paper, and thoroughly rinsed with distilled water, 2-propanol and acetone to remove any residual material. ALMEMO 2470 AHLBORN with AMR Control data logger is then connected to cathode and anode, and potential difference between cathode and anode were measured for the duration of the CA experiment. After CA experiment is completed, cathode surface is once again washed with deionised water, 2-propanol and finally placed in 20mL acetone until subsequent analysis. The surface morphology of the cathode was investigated using Jeol6380V Scanning Electron Microscope with energy-dispersive X-ray spectroscopy (SEM/EDS) under back-scattering mode (Accelerating voltage: 15kV, Filament heating: 80-82 μt , Low vacuum control: 30Pa).

3. RESULTS AND DISCUSSION

3.1. Dissolution of Aluminium Salts

Figure 1 shows the final concentration of Al in BMPTFSI from the dissolution of various Al salts as indicated. The salts that showed the least amount of solubilisation were $\text{Al}_2(\text{SO}_4)_3$ (0.007M) and AlF_3 (0.0039M), followed by $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.044M). The rest of the aluminium halides, AlCl_3 , AlBr_3 and AlI_3 achieved 0.059M, 0.073M and 0.069M respectively. The highest concentration was achieved using aluminium trifluoromethanesulfonate (Common name: Aluminium triflate; Chemical formula: $\text{Al}(\text{CF}_3\text{SO})_3$ or $\text{Al}(\text{OTf})_3$), reaching up to 0.09M of Al dissolved in BMPTFSI. This salt solution was then chosen for characterisation and electrowinning of Al.

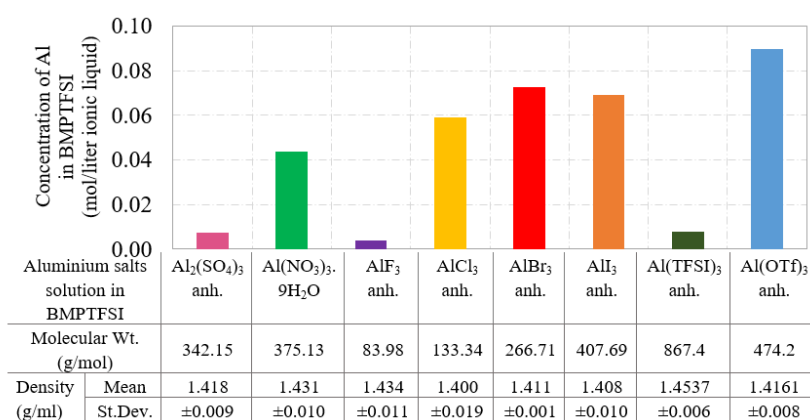


Figure 1: Concentration of Al salts (mol/L ionic liquid) in BMPTFSI and density of solutions.

3.1. Characterisation of $\text{Al}(\text{OTf})_3$ dissolved system vs pure BMPTFSI

3.1.1 Physical and Electrochemical Characterisation of $\text{BMPTFSI}/\text{Al}(\text{OTf})_3$ System

In Figure 2(a), cathodic and anodic peaks of pure BMPTFSI indicate single reversible TFSI anions adsorption and desorption phenomena (in the area -2V to -2.5V vs Ag/Ag^+ in Acetonitrile) on the cathode, while an irreversible peak occurs after -3.5V vs Ag/Ag^+ in Acetonitrile indicating the reductive destruction of BMP cation of the ionic liquid on the cathode surface (Hayyan, Mjalli et al., 2013). A prominent downward irreversible peak (-2.8V vs Ag/Ag^+ in Acetonitrile) in the cathodic region for the $\text{Al}(\text{OTf})_3$ solution, however, indicates that there is a potential electroactive species reduced in $\text{Al}(\text{OTf})_3/\text{BMPTFSI}$ system that could be attributed to aluminium. It is evident that Al

reduction potential is higher than the potential of the reductive destruction of the BMP^+ cation, supporting BMPTFSI as a suitable electrolyte for Al electrowinning.

Figure 2(b; Viscosity) shows that pure BMPTFSI is less viscous compared to $\text{Al}(\text{OTf})_3/\text{BMPTFSI}$ solution. Compared to aqueous electrolytes, the viscosities of ionic liquids are substantially higher especially at ambient temperature, repressing electromobility of Al species in ionic liquid solution. This is supported as Isono (1984) reports the viscosity of several aqueous electrolyte solutions with concentration of 0.1M at 25°C are close to 1cP whereas the order of magnitude of ionic liquid solution is larger by a factor of 100 at similar conditions. At 120°C , the $\text{Al}(\text{OTf})_3/\text{BMPTFSI}$ solution viscosity diminishes to 10cP and still is comparatively higher to aqueous electrolyte solutions at ambient temperatures.

Figure 2(b; Conductivity) shows the conductivity of pure BMPTFSI is slightly higher than $\text{Al}(\text{OTf})_3/\text{BMPTFSI}$ for the investigated temperature ranges. However, the value of conductivity even

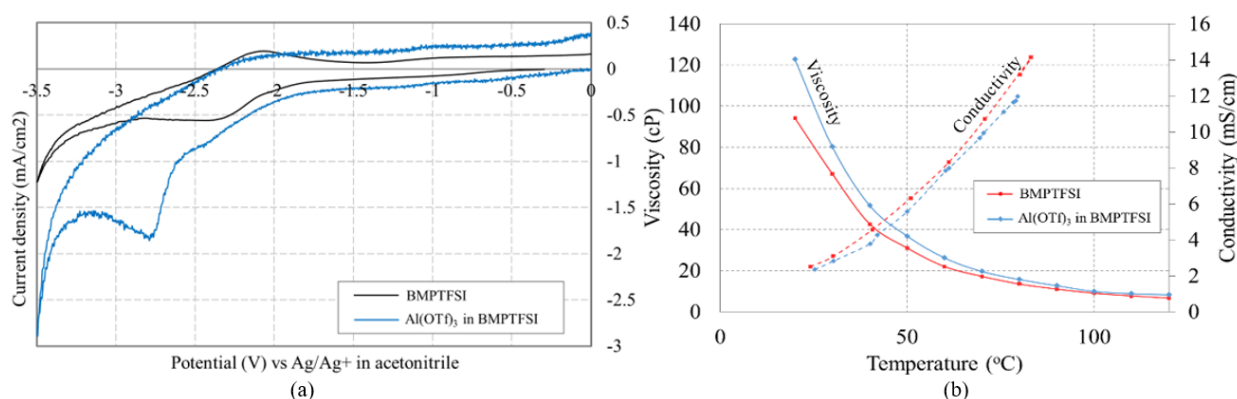
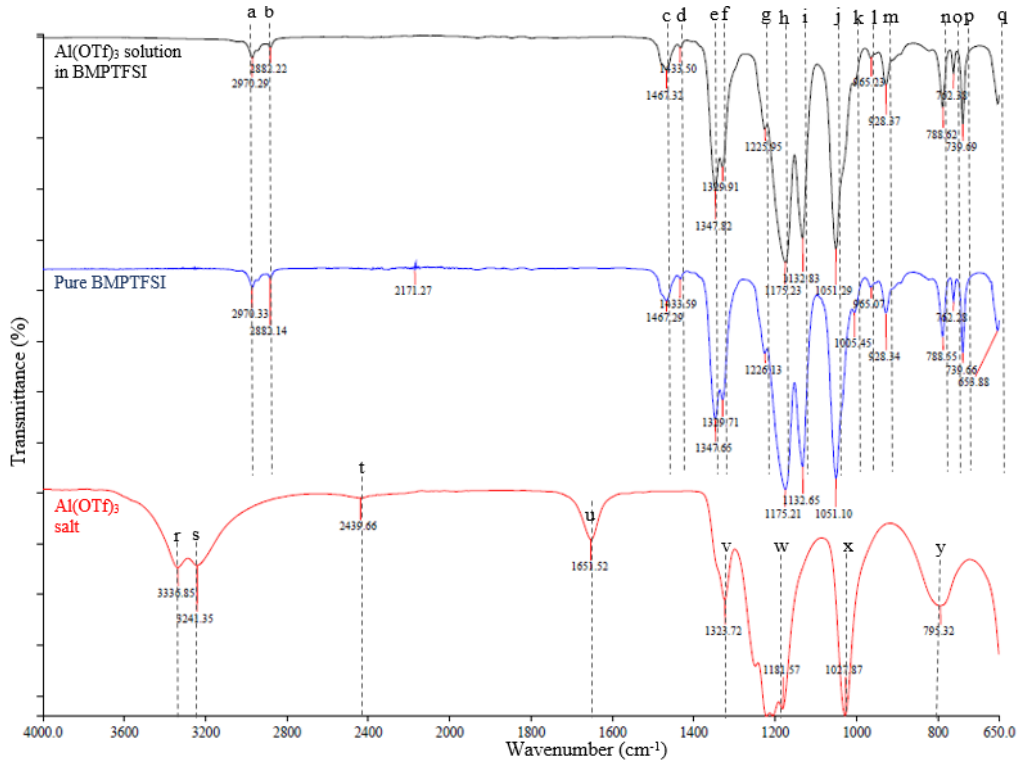


Figure 2: (a) Cyclic voltammetry of aluminium triflate ($\text{Al}(\text{OTf})_3$) system and (b) Conductivity and viscosity ($\text{Al}(\text{OTf})_3$) solution and pure BMPTFSI

at ambient temperature is comparable with the one of some aqueous solutions. Isono (1984) also reports that at ambient temperature, the electrical conductivity of the strong electrolytes with the concentration 0.1M at ambient temperature are within the range of 10-30mS/cm, which is 2 to 15 times larger than ionic liquid-based solution (2mS/cm). At 80°C , the electrical conductivity increases substantially for ionic liquid-based solutions (14mS/cm) with values on par with aqueous electrolytes at 25°C . In conclusion, the viscosity and electrical conductivity measurements show that electrowinning of metals from ionic liquid solutions could be more efficient at higher temperatures where the diffusion and the electromigration of metal species are easier meriting to lower viscosity and higher conductivity values.

3.1.2. Fourier transform infrared spectroscopy (FTIR) of $\text{Al}(\text{OTf})_3$ solution and pure BMPTFSI

Infrared spectroscopy does not offer any information for the speciation of aluminium in the $\text{Al}(\text{OTf})_3/\text{BMPTFSI}$ system. As is seen in Figure 3, the FTIR spectra of pure BMPTFSI as well as of $\text{Al}(\text{OTf})_3/\text{BMPTFSI}$ solution are absolutely identical.



- a) 2970 cm⁻¹: CH₃ asym. stretch^{[1][4]}
- b) 2882 cm⁻¹: CH₂ asym. stretch^{[1][4]}
- c) 1467 cm⁻¹: CH₂ scissoring^{[1][4]}, CH bend^[2]
- d) 1433 cm⁻¹: CH₂ scissoring^{[1][4]}
- e) 1347 cm⁻¹: CH₂ wag^{[1][4]}
- f) 1330 cm⁻¹: CH₃ deformation^[1], Cis-trans TFSI^[2]
- g) 1226 cm⁻¹: CH₃ sym. stretch^[1], SO₂ asym. stretch^[4]
- h) 1175 cm⁻¹: SO₂ asym. stretch^[4], CF stretch^[1]
- i) 1132 cm⁻¹: CF₂ sym. stretch^{[1][4]},
- j) 1051 cm⁻¹: SO₂ sym. stretch^[4]
- k) 1005 cm⁻¹: CC stretch^[1], C₃ rock^[4],
- l) 965 cm⁻¹: SNS asym. stretch^{[1][4]},
- m) 928 cm⁻¹: Possible CH₂ rock from pyrrolidinium^[1]
- n) 788 cm⁻¹: CF stretch^[1], Cis-Trans TFSI^[3]
- o) 762 cm⁻¹: Cis-Trans TFSI^[3]
- p) 740 cm⁻¹: SNS pseudo-sym. stretch^{[3][4]}, Cis-Trans TFSI^[2]
- q) 653 cm⁻¹: Cis TFSI-Trans TFSI^[2]
- r) 3336.9 cm⁻¹: OH asym. stretch^[1]
- s) 3241.4 cm⁻¹: OH stretch^[1]
- t) 2439.7 cm⁻¹: CH₃ deformation^{[1][5]}
- u) 1657.5 cm⁻¹: H₂O bent^[1]
- v) 1323.7 cm⁻¹: SO₂ asym stretch^[1]
- w) 1181.57 cm⁻¹: (Mixed) Asym. SO₃ vibrations^{[1][5]}
- x) 1027.9 cm⁻¹: (Mixed) Sym. SO₃ vibrations^{[1][5]}
- y) 795.3 cm⁻¹: CF₃ vibrations^[5]

Figure 3: FTIR spectra of Al(OTf)₃ in BMPTFSI vs pure BMPTFSI (Shimanouchi, 2005)^[1] (Vitucci, Trequatrini et al., 2014)^[2] (Nelson, 1971)^[3] (Mao, Nulwala et al., 2012)^[4] (Ramesh, Lu et al., 2013)^[5]

3.2.2 Aluminium electrowinning

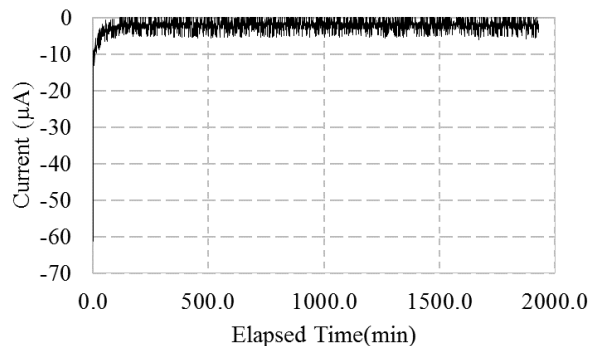


Figure 4: Evolution of cell current during the electrolysis test at cathodic potential of -2.8V vs Ag/Ag⁺ in Acetonitrile and ambient temperature.

The evolution of cell current during the electrolysis test at ambient temperature and under cathodic polarization at -2.8V vs Ag/Ag^+ in Acetonitrile is given in Figure 4. The results show that there is a relevant slow response of the cell to the applied potential. The cell current, upon the cathode polarization, immediately took the value of almost $60\mu\text{A}$ and within a period of around 3 minutes, diminishes rapidly to a value lower than $10\mu\text{A}$. Next, within the duration of 2 hours, the system slowly reaches equilibrium value of $3\mu\text{A}$, followed by constant amplitude until the end of electrolysis. This behavior is typical of intense non-faradaic phenomena at the cathode/solution interface attributed to a relatively thick compact surface layer, due to the high solution viscosity, in which the concentration of the Al electroactive species is very low because of specific speciation of Al in the ionic liquid.

The SEM/EDS analysis (Figure 5) indicates clear Al deposition on the copper electrode surface. At the initial stages of electrowinning (after 5h), trace amounts of Al are deposited as nuclei in the edges of cathodic electrode in Figure 5(a). After 32h, the aluminium metal nucleation has been spread out on the whole cathode surface while concurrently expanding the small nuclei to form islands of deposited Al on the electrode surface (Figure 5(b) & (c)). EDS analysis shows that the metal deposited is pure aluminium. Silicon in small amounts is also found together with Al, as shown in Figure 5(a) and (c). This is an impurity caused by the polishing of cathode surface by SiC abrasive paper during cathode preparation step.

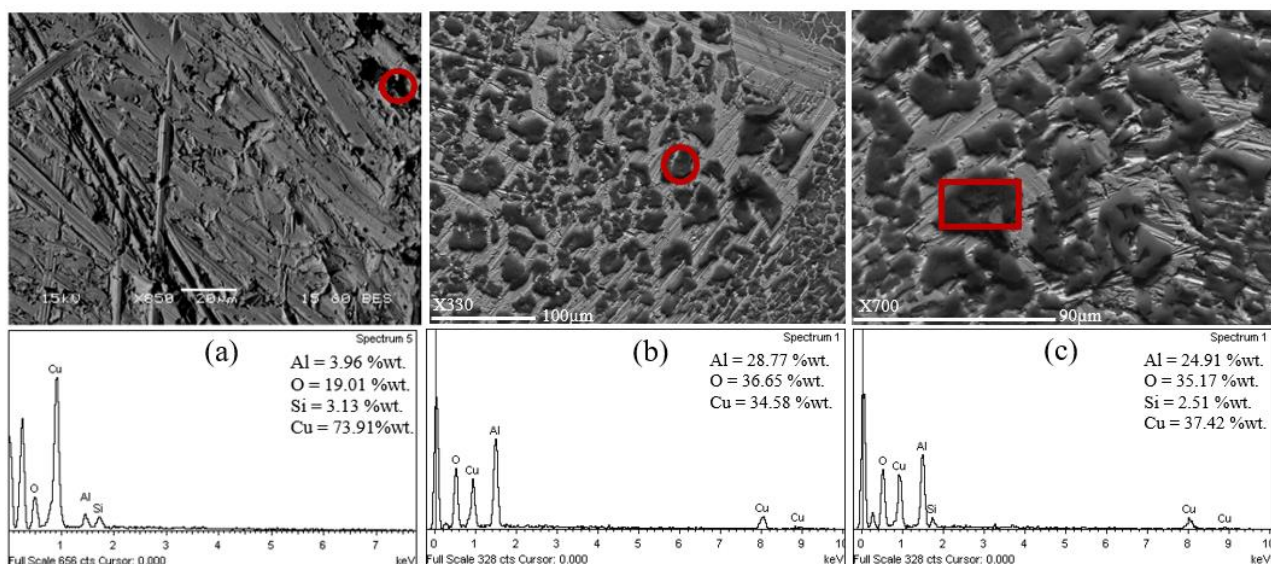


Figure 5: Back-scattered electron image from SEM/EDS surface morphology of (a) 5h CA; (b) and (c) 32 hr CA Al-deposited copper cathode.

4. CONCLUSION

The ionic liquid BMPTFSI has been proven from this study to be an effective electrolyte for the electrowinning of Al metal. It has good electrical conductivity and appropriate electrochemical window to electrowin aluminium despite its high viscosity at ambient temperature. BMPTFSI is not an excellent solvent, but this study proved that the aluminium triflate salt ($\text{Al}(\text{OTf})_3$) can be dissolved in it.

The solution of $\sim 0.1\text{M}$ $\text{Al}(\text{OTf})_3$ in BMPTFSI has higher viscosity and lower electrical conductivity compared to the pure BMPTFSI. Nevertheless, the values of viscosity and conductivity of $\text{Al}(\text{OTf})_3/\text{BMPTFSI}$ solution at ambient temperature are inferior, and substantially in the case of viscosity, when compared to strong aqueous electrolyte solutions with same metal concentrations.

The aluminium electrowinning test proved that pure aluminium can be deposited on the cathode. However, it also gave evidences on inhibitions attributed to the high solution viscosity, thus limiting the concentration of the aluminium electroactive species on the surface of the cathode.

By taking into consideration the results of this paper, a possible proposed route of the aluminium recovery process from bauxite residue is shown in Figure 6, and is currently being researched as part of the MSCA-ETN REDMUD Project in coalition with NTUA and AoG efforts.

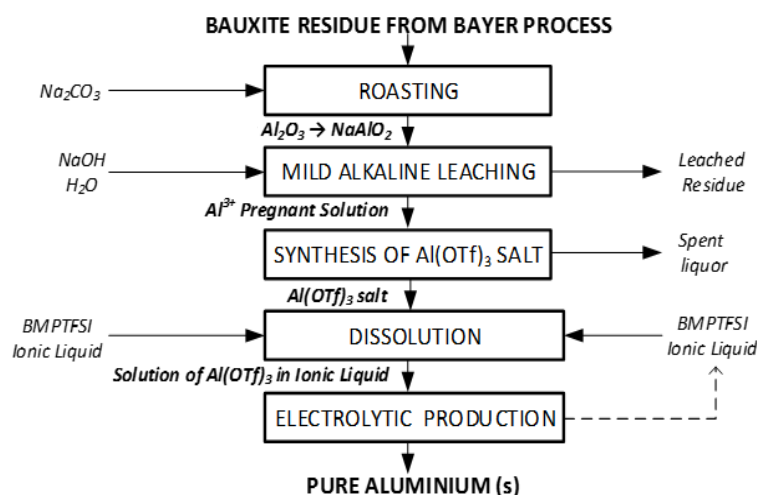


Figure 6: Proposed flowsheet of aluminium recovery from bauxite residue.

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