Novel applications of ionic liquids in materials processing

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Abstract. Ionic liquids are mixtures of organic and inorganic salts which are liquids at room temperature. Several potential applications of ionic liquids in the field of materials processing are electrowinning and electrodeposition of metals and alloys, electrolysis of active metals at low temperature, liquid-liquid extraction of metals. Results using 1-butyl-3-methylimidazolium chloride with AlCl₃ at low temperatures yielded high purity aluminium deposits (>99.9% pure) and current efficiencies >98%. Titanium and aluminium were co-deposited with/without the addition of TiCl₄ with up to 27 wt% Ti in the deposit with current efficiencies in the range of 78-85%. Certain ionic liquids are potential replacements for thermal oils and molten salts as heat transfer fluids in solar energy applications due to high thermal stability, very low corrosivity and substantial sensible heat retentivity. The calculated storage densities for several chloride and fluoride ionic liquids are in the range of 160-210 MJ/m³. A 3-D mathematical model was developed to simulate the large scale electrowinning of aluminium. Since ionic liquids processing results in their low energy consumption, low pollutant emissions many more materials processing applications are expected in future.

1. Introduction
Ionic liquids are mixtures of organic and inorganic salts and at room temperature they are in liquid state. They are comprised entirely of cations and anions and hence the name ionic liquids. A range of ionic liquids can be synthesized by mixing various salts containing different anions and cations. It is possible to obtain ionic liquids with a variety of physical and chemical properties for specific applications. Many room temperature ionic liquids based on imidazolium cations have been extensively explored in the recent years. Ionic liquids have a very low melting point, normally below room temperature. They have emerged as the next generation solvents which are capable of replacing traditionally used volatile organic compounds as industrial solvents. They have several unique properties such as wide electrochemical potential window for electrochemical processing, high chemical and thermal stability, very low vapor pressure, non-inflammability, high ionic conductivity, high solvating capability, and very low corrosivity. They are environmentally benign with no organic emissions. These characteristics make ionic liquids excellent candidates for a range of potential applications, including batteries, catalysis, supercapacitors, photovoltaics, solvents, and heat-transfer fluids. Due to their unique properties ionic liquids can be used as electrolytes in the extraction and refining of metals such as aluminum, titanium, copper, magnesium, at ambient temperature that are otherwise refined at high temperatures [1-3].

Ionic liquids are synthesized using the standard procedure [4]. Most popular and extensively studied ionic liquids are imidazolium cation based salts. Ionic liquids are characterized using nuclear
magnetic resonance (NMR) spectrometer, differential thermal analysis (DTA) and differential Scanning Calorimeter (DSC). The properties of these liquids such as thermal stability, heat capacities, and thermodynamic properties are measured [5, 6]. We present here the results obtained in our research group on the electrochemical processing of aluminum, titanium and Al-Ti alloy, thermal storage and heat-transfer capabilities of some ionic liquids, and a 3-D mathematical model to simulate the electrowinning of aluminum in a batch reactor.

2. Electrochemical Processing of Metals and Alloys using Ionic Liquids

Recent advancements in the area of ionic liquids for electrochemical extraction and refining of metals had proved that electrolysis in ionic liquids electrolytes is the future direction of energy-efficient, environmentally benign metal extraction/ refining technology. Physicochemical properties of ionic liquids are critical for considering them as alternatives to organic solvents or molten salts. However, not all the physical properties are important for the metals extraction applications. Liquid temperature range, thermal stability, and electrolytic conductivity have the highest priority in determining the operating temperature range and electrical parameters. One of the most important and attractive features of ionic liquids is the extended temperature range of liquid state. The wide liquidus temperature range is manifested in their low melting points and high thermal decomposition temperatures that have been reported [7, 8]. Liquid state of the ionic liquids at or below room temperature is a unique feature that facilitates several chemical reactions that are otherwise impossible at these temperatures using molten salts. We will now look at the use of ionic liquids in the electrowinning and electorefining of aluminum and titanium and also electrodeposition of Ti-Al alloys.

2.1. Extraction of Aluminum

The use of ionic liquids in the electrowinning of aluminum has several advantages such as low consumption of energy and electrode materials, no pollutant emissions, and low operating costs. The electrochemical processing of aluminum in ionic liquids media saves up to 85% of electrical energy, prevents any gaseous pollutant emission (CO, CF₄, etc.) and avoids any solid waste (e.g., aluminum dross and spent potliner) [7]. Electrowinning of aluminum from a solution containing 1-butyl-3-methyl imidazolium chloride and anhydrous AlCl₃ at ambient temperature were reported [3]. Experiments were performed using an electrolytic cell consisting of a graphite anode and copper cathode. The electrochemical reactions for the process are as follows:

Anodic: \[ \text{AlCl}_3 + 7\text{AlCl}_4^- \rightarrow 4\text{Al}_2\text{Cl}_7^- + 1.5\text{Cl}_2 + 3e^- \]

Cathodic: \[ 4\text{Al}_2\text{Cl}_7^- + 3e^- \rightarrow \text{Al} + 7\text{AlCl}_4^- \]

Overall reaction: \[ \text{AlCl}_3 \rightarrow \text{Al} + 1.5\text{Cl}_2 \]

During the electrolysis, chlorine was released on the anode and aluminum was deposited on the cathode. After the electrolysis, the anode and cathode were taken out from the cell, washed with water, and weight changes were determined. The morphologies of the deposited aluminum were dependant on experimental conditions. Dense deposition of aluminum on the cathode was obtained which was characterized by XRD.

The cathode current density and efficiency change with temperature, cell voltage, and molar ratio of AlCl₃ and C₄mimCl. The cathode efficiencies of greater than 99 pct were obtained with a cell voltage of 3.1 V, temperature of 105 °C and molar ratio of AlCl₃ to C₄mimCl above 1.7. The experimental conditions such as cell voltage and energy consumption are much lower than those of the current industrial method. Aluminum electrodeposition in an analogous system that comprised of 1-hexyl-3-methyl imidazolium chloride and anhydrous AlCl₃ was studied [9, 10].
Figure 1. Thickness of aluminum deposition on copper cathode with change of current density (a) Current density: 460A/m², 105°C; (b) Current density: 460A/m², 130°C (c) Current density: 160A/m², 105°C; (d) Current density: 160A/m², 130°C [2].

Process parameters influencing current density, current efficiency and morphology of aluminium deposition were investigated. Aluminum was electrowon from C₆mimCl-AlCl₃ melts with molar ratio from 1:1 to 1:2 at temperature range of 90 º to 140 ºC and with cell voltages from 2.5 to 3.4 V. It is established that the current density and current efficiency increase with temperature and applied cell voltage. The thickness of deposited aluminum increased with increase in current density and temperature, as shown in figure 1. The optimum electrowinning parameters under laboratory conditions were determined to be 110 ºC, 3.5 V and electrolyte molar ratio (C₆mimCl-AlCl₃) of 1:1.7. Large scale aluminium electrowinning experiments in ionic liquid electrolyte were carried out in a batch recirculation type of electrolytic cell [11]. Recycling of aluminum scrap and refining aluminium alloys was successfully carried out using AlCl₃-C₄minCl and AlCl₃-C₆mimCl ionic liquids [12-14].

2.2 Modeling of the Electrowinning Process
A 3-D mathematical model was developed for the batch reactor of low temperature aluminium electrowinning using ionic liquid electrolytes [15]. This model solves the Poisson equation which describes the potential distribution within the bulk electrolyte. The electrical double layer at the electrode caused due to the charge of each species is also taken into consideration while solving the Poisson equation in order to calculate the cathode current density and current efficiency. The model describes the deposition process taking into account the mass transport of participating ionic specie, homogeneous chemical reactions within the diffusion layer, and the associated electrochemical kinetics. Processing parameters for the optimal reactor performance have been assessed in this research. Aluminum electrowinning experiments were conducted in a batch recirculation cell using C₆mimCl-AlCl₃ as electrolyte with AlCl₃ concentration of 5ml/L, graphite as anode and copper plate as cathode. The conditions used in the cell were: temperature: 80 ºC, electrolyte flow rate between 5 to 20 ml/min, and an applied cell voltage of 3 to 3.5 V. The results are shown in figure 2 where the model results are in good agreement with the experimental data.
2.3 Electrochemical Processing of Titanium-Aluminum Alloys

The electrochemical production of Ti and Ti-Al alloys is complicated due to the variable oxidation states of titanium (Ti$^{2+}$, Ti$^{3+}$, and Ti$^{4+}$). Electrochemical processing of Ti and Ti-Al alloys in ionic liquids was investigated by several authors [16-20]. In our research group we have studied the electrodeposition of Ti-Al alloy from the AlCl$_3$-1-butyl-3-methyl imidazolium chloride(BmimCl) mixture in the temperature range of 70 ºC to 125 ºC [21].

The bulk electrodeposition of Ti-Al alloy was carried out at different applied potentials in the range of 1.5 – 3.0 V with an electrolyte having a molar ratio of AlCl$_3$-BmimCl of 2:1 in the temperature range of 70 ºC to 125 ºC.

The cathodic reactions are:

$$\text{Ti(Anode)} + 4\text{(Al}_{2}\text{Cl}_{7})^{-} = \text{Ti(Cathode)} + 4\text{(Al}_{2}\text{Cl}_{7})^{-} + 2\text{e}^{-}$$

$$4\text{Al}_{2}\text{Cl}_{7}^{-} + 3\text{e}^{-} = \text{Al(Cathode)} + 7\text{AlCl}_{4}^{-}$$

The anodic reactions are:

$$\text{Ti(Anode)} + 4\text{(Al}_{2}\text{Cl}_{7})^{-} = \text{Ti(Anode)} + 4\text{(Al}_{2}\text{Cl}_{7})^{-} + 2\text{e}^{-}$$

$$\text{AlCl}_{3} + 7\text{AlCl}_{4}^{-} = 4\text{Al}_{2}\text{Cl}_{7}^{-} + 1.5\text{Cl}_{2} + 3\text{e}^{-}$$

Figure 2. Effect of cell voltage on the current densities for large scale aluminium electrowinning. Comparison of modelling results with the experimental data [15].

The effect of applied cell voltage on the cathodic current density, current efficiency and deposit morphology of Ti-Al alloy was investigated in the range of 1.5-3.0V at constant experimental temperature of 100 ºC. The average compositions of the deposits obtained during the experiments as a function of applied voltage were in the range of 17-27 wt% Ti and 72-82 wt% Al. The cathodic current density increased linearly with applied voltage in the range of 36-187 A/m$^2$ [21].

The current densities varied linearly with applied cell voltage. Increase in cell voltage also enhances the cathodic reduction reaction, hence increase the current density. Current efficiencies did not vary much as a function of applied cell voltage and were within the range of 78-85%. Figure 3 shows the SEM micrographs of the deposits obtained at 100 ºC with applied cell voltages of 1.5V and 3.0V. At low voltage (1.5V) a uniform spherical microstructure of the deposit was observed and the deposit tends to preferentially agglomerate at various sites with increase in applied cell voltage. A uniform spherical microstructure of Ti-Al particles in a very narrow size range between 5-20 µm was
obtained. A similar trend was observed with the deposits with increase in temperature at a fixed applied cell voltage of 2.5V. At low temperatures the microstructure had even distribution of uniform spherical particles with a narrow size range between (50-70 µm). Aluminum and titanium were co-deposited and the compositional analysis confirms the formation of Al₃Ti. The deposit tends to agglomerate with increase in temperature and applied voltage.

![Figure 3](image)

**Figure 3.** SEM micrographs of the Ti-Al deposits obtained at 100 ºC (A) 3.0V, (B) 1.5V [21]

The feasibility of obtaining a Ti-Al alloy deposit by electrochemical method using an AlCl₃-BmimCl electrolyte (molar ratio 2:1) at low temperatures (75-125ºC) and low applied cell voltages (1.5-2.5V) was successfully demonstrated. The electrodeposited alloy containing up to 27 wt% of Ti was produced. High current efficiency of up to 85% was achieved [21].

### 3. Ionic Liquids as Thermal Storage Fluids

Ionic liquids have been proposed as thermal storage and heat transfer media due to their several advantages over thermal oils, liquid metals and molten salts traditionally used in thermal power plants. These advantages include wide liquid temperature range, high thermal/chemical stability, and low vapor pressure. Several researchers have evaluated certain ionic liquids as thermal storage fluids and their general aspects of application in terms of physic-chemical properties. Reddy et al. [6] have studied the thermal stability and corrosivity of a series of ionic liquids and compared them with thermal storage molten salts. Thermal stability and thermodynamic properties of [C₄mim][Tf₂N] ionic liquids were studied [22]. It is found that [C₄mim][Tf₂N] has several advantages over other ILs such as wider liquid temperature range, lower viscosity, higher chemical stability, moderate heat capacity and storage density. The calculated sensible heat storage density for [C₄mim][Tf₂N] was more than 170 MJ/m³ when the inlet and outlet field temperature were 210°C and 310°C. It is concluded that the evaluated ionic liquids are suitable for use as heat-transfer fluids and they are superior to present commercial heat-transfer fluids in terms of wide liquidus temperature range, low vapor pressure and ability to store substantial sensible heat [23].

In our research group we evaluated the thermal stability and thermodynamic properties of several ionic liquids and then assessed their viability as thermal storage and heat transfer media. The ionic liquids chosen for this study are widely used imidazolium-based ionic liquids due to their relatively low viscosities and high thermal stabilities. To achieve high thermal conversion efficiency, sensible thermal storage systems require the heat transfer fluid possess several important characteristics, such as wide liquid temperature range, high thermal stability and storage density. In particular the operating temperature higher than 400°C in a parabolic trough system would greatly enhance the thermal cycle efficiency.
4. Conclusions
Some of the novel applications of ionic liquids in materials processing have been presented in this paper. Aluminum was electrowon, electrorefined and recycled using C\textsubscript{4}mimCl-AlCl\textsubscript{3} ionic liquid. High purity deposits (>99.9%) were obtained with very high current efficiency (>98%). Ti-Al alloys were deposited with or without TiCl\textsubscript{4} in the electrolyte with Ti content up to 27 wt% and current efficiency in the range of 78-85%. A uniform spherical well dispersed microstructure was obtained. This technique is being extended to other metals such as titanium, magnesium, etc whose industrial processing involves consumption of enormous amount of energy with the emission of pollutants. Heat capacities and densities for several ionic liquids were measured. Sensible heat storage capacities for ionic liquids were determined and compared with those of the existing heat transfer fluids. Sensible heat storage densities of ionic liquids were in the range of 160-210 MJ/m\textsuperscript{3}. The 3-D mathematical model developed to simulate the large scale electrowinning of aluminum showed good agreement with the experimental data. The novel electrochemical technique of extraction, processing and refining of metals such as aluminum and titanium is fast realized as an alternate route in the field of metals processing technology. Ionic liquids are realized as alternatives to heat transfer fluids in solar energy applications.

Acknowledgments
The author gratefully acknowledges the financial support from The U.S. Department of Energy, National Science Foundation, ACIPCO, and The University of Alabama.

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