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Electrodeposition of aluminium and aluminium-copper alloys from a room temperature ionic liquid electrolyte containing aluminium chloride and triethylamine hydrochloride

P.V. Suneesh, T.G. Satheesh Babu, and T. Ramachandran

Department of Sciences, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Amritanagar P. O., Coimbatore - 641112, India

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Abstract: The electrodeposition of Al and Al-Cu binary alloys on to gold substrates from a room temperature ionic liquid electrolyte containing $AlCl_3$-Et_3NHCl was studied. The electrochemical behavior of the electrolyte and the mechanism of deposition were investigated through cyclic voltammetry (CV), and the properties of deposits obtained were assessed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffraction (XRD). Al of 70 μm in thickness and an Al-Cu alloy of 30 μm in thickness with 8at% copper were deposited from the electrolyte. SEM images of the deposits indicate that the Al deposit was smooth and uniform, whereas the Al-Cu deposit was nodular. The average crystalline size, as determined by XRD patterns, was found to be (30 ± 5) and (29 ± 5) nm, respectively, for Al and Al-Cu alloys. Potentiodynamic polarization (Tafel plots) and electrochemical impedance spectroscopic (EIS) measurements showed that Al-Cu alloys are more corrosion resistant than Al.

Keywords: electrodeposition; aluminium copper alloys; ionic liquids; triethylamine hydrochloride; copper acetylacetonate

1. Introduction

Aluminium and its alloys with transition metals, such as copper, zinc, and zirconium have been extensively used for aerospace applications, owing to their good strength, light weight, and high corrosion resistance [1-2]. The regular methods used for Al coatings include hot dipping, thermal spraying, sputter deposition, and vapour deposition [3]. Copper has been the most commonly used alloying element almost since the beginning of the aluminium industry, and such alloys are grouped as cast alloys, durals, and wrought alloys [4].

Among the various methods for metal coating, electrodeposition is one of the most promising techniques, since the properties of deposits can be easily tuned by varying the parameters, such as electrolyte composition, current density, and deposition potential. Furthermore, electroplating techniques are convenient as well as inexpensive and also feasible for room temperature operation [3]. However, aluminium and its alloys cannot be electrodeposited from aqueous or protic electrolytes because of hydrogen evolution. In order to overcome this difficulty, aprotic organic electrolytes based on common organic solvents and ionic melts have been used for the electrodeposition of aluminium and its alloys [3, 5-10]. The electrolytes that are based on organic solvents have comparatively less electrochemical potential window and high flammability restricting their application in the electrodeposition process [3, 5].

A number of highly electropositive metals and semiconductors have been successfully deposited from Lewis acidic ionic melts [11-13], which possess good ionic conductivity, wide electrochemical window, adjustable Lewis acidity, and low flammability [3, 5]. Pyridinium- and imidazolium-based electrolytes are most commonly employed for the electrodeposition of aluminium, aluminium alloys, and semiconductors. Recently, electrodeposition of microcrystalline and nanocrystalline aluminium as well as the nanopillars of aluminium were reported from 'room-temperature imidazolium-based ionic liquid electrolytes' [3, 13-14]. In spite of their advantages, they are costly and

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Corresponding author: T.G. Satheesh Babu E-mail: tgsatheesh@gmail.com

difficult to handle in normal atmosphere. Pyridinium electrolytes are cheaper than imidazolium, but their electrochemical window is comparatively less due to the reduction of pyridinium ions [15-16]. Trimethyl phenyl ammonium chloride (TMPAC)-based electrolytes are cheaper and have almost the same electrochemical window of imidazolium-based ionic liquids [9, 17]. The electrodeposition of aluminium from triethylamine hydrochloride (Et_3NHCl) on aluminium substrates was reported by Gao *et al.* [10].

The deposition potential of aluminium and other alloying metals falls closer in ionic melt containing $AlCl_3$-dimethylethylphenylammonium bromide and acetylacetonate of the alloying metals [18]. The formation of aluminium alloys, like Al-Cr [19], Al-Zn [20], Al-Ti [21], Al-Mn [22], Al-Zr [23], Al-Ag [24], Al-Co [25], Al-Mo [26], Al-Ce [27], Al-Mo-Mn [28], and Al-Mo-Ti [29], has been reported using different ionic liquids. The electrodeposition of Al-Cu alloys was studied in various ionic liquids [30-31] using copper or Al-Cu alloys as the anode. The codeposition of copper with aluminium is difficult as copper can displace aluminium from the deposit together with the thermodynamic instability of the alloys in the plating bath [30]. The authors have not come across any report on the electrodeposition of Al-Cu alloys from Et_3NHCl ionic liquid based electrolytes.

The present work aimed at developing an electrolyte for the deposition of aluminium (Al) and aluminium-copper (Al-Cu) alloys. Cyclic voltammetry (CV) was used to investigate the deposition process. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) analyses of the deposited Al and Al-Cu alloys were performed to determine their morphology, composition, and phase composition respectively. The chloride pitting corrosion behavior of the deposits was investigated by Tafel polarization and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Chemicals

Anhydrous aluminium chloride (Lobachemie, India), copper acetylacetonate (Aldrich, 97% pure), and triethylamine hydrochloride (Fluka, 99% pure) were purchased and used without further purification. All other chemicals were of analytical grade and used as received. Chemicals were handled under inert atmosphere of dry nitrogen in an indigenously fabricated glove box.

2.2. Electrodes and instruments

All electrochemical experiments were performed at room temperature using CHI660C electrochemical workstation (CH Instruments, TX, USA) by continuous purging of dry nitrogen through the electrolyte. A gold disc electrode of 2 mm in diameter was used as the working electrode, a platinum disc as the counter electrode, and another platinum wire as the pseudo reference electrode for electrochemical studies. Gold and platinum plates of 5 mm × 5 mm area and a platinum wire were used as the working, counter, and pseudo reference electrodes, respectively, for the bulk electrodeposition. One side of the working and counter electrodes were masked with Teflon. All electrodes were cleaned with a hot acidic mixture of 2 N $H_2SO_4$and 30vol% H_2O_2 (1:1 in volume ratio), polished with 0.05 μm alumina, ultrasonicated with water, acetone, and finally dried.

The surface morphology and the average composition of the deposits were analyzed using a Hitachi SU6600 variable pressure field emission scanning electron microscope (FESEM) coupled with energy dispersive spectroscopy (EDS) (Horiba, EMAX, 137 eV). The crystal structure of the electrodeposits was examined with standard X-ray diffraction techniques by using powder XRD (Bruker AXS D8 Advance) that operates with a Cu K_α radiation of the 0.15406 nm wavelength. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Electron IRIS INTREPID II XSP DUO) measurements were performed for the quantitative analysis of the alloys. Thickness of the deposits was determined using a video measuring system (ARCS Precision Technology Co. Ltd., China Taipei) by making a scratch on the deposit and measuring the displacement in the z-direction.

2.3. Preparation of the ionic liquid electrolyte

An $AlCl_3$-Et_3NHCl ionic liquid of 2:1 (weight ratio) was prepared by slow addition of $AlCl_3$ to Et_3NHCl with continuous stirring for 2 h at 80°C. The light brown solution thus formed was cooled to room temperature and pre-electrolyzed at –0.9 V for 15 h, and the resulting clear melt was used for the electrodeposition of aluminium. For Al-Cu alloy deposition weighed amount of copper acetylacetonate was added to the pre-electrolyzed $AlCl_3$-Et_3NHCl ionic melt to make copper to aluminium ionic ratios of 0.25wt%, 0.5wt%, and 1.0wt% and was heated at 80°C with continuous stirring for 1 h. The brown coloured electrolyte thus formed was cooled to room temperature and used for electrodeposition without any further treatment.

2.4. Electrochemical measurements

All electrochemical experiments were carried out at room temperature and under inert atmosphere of nitrogen. In order to determine the deposition potentials and the mechanism of deposition, CV was conducted at different potential windows and at different scan rates in the ionic electrolytes. Bulk deposition of Al was carried out galvanostatically at various current densities (0.5, 1.0, and 1.5 A/dm^2), and electrodeposition of Al-Cu alloys was performed on the gold plate electrode at constant potentials predetermined by CV. Potentiodynamic polarization and EIS measurements were performed with as-deposited Al-Cu alloys and Al on the gold working electrode keeping

Ag/AgCl (3 M KCl) as the reference electrode and 0.5 M NaCl as the electrolyte in either case.

3. Results and discussion

3.1. Cyclic voltammetry

The shape and nature of the cyclic voltammogram obtained at a scan rate of 20 mV/s (Fig. 1(A)) is similar to that reported for electrodeposition of aluminium from other ionic liquids [3, 9, 14]. During the cathodic scan, two small peaks 'a' and 'b' were observed, respectively, at –1.4 and –1.8 V. The former is due to the underpotential deposition (UPD) of aluminium and the latter may be due to the formation of intermetallic alloys between aluminium and gold [3]. The intense peak 'c' observed at –2.4 V can be attributed to the bulk deposition of aluminium. The nucleation loop reported by Gao *et al.* [10] on the aluminium surface was not observed on the gold surface, which indicates that the deposition of aluminium on the gold substrate does not require overpotential to initiate the nucleation and growth of deposits [3]. During the anodic scan, two peaks were observed; the peak at 'd' is caused by bulk aluminium deposition, whereas the peak at 'e' is due to the UPD aluminium, which both resulted from oxidation [9]. A systematic study of aluminium UPD current with scan rate (20-100 mV/s) shows that the deposition current is linearly increasing with the square root of scan rate with a regression coefficient $r = 0.9992$ (Fig. 1(B)). This study establishes that the UPD of aluminium on the gold substrate follows a diffusion controlled growth process; similar reports are reported for Al deposition on some other substrates [29]. The cathodic current for bulk deposition of aluminium does not show much change at lower scan rates (20-120 mV/s), but at higher scan rates (above 120 mV/s), there is a decrease in the reduction current, which may be due to insufficient time for nucleation of aluminium to occur [9]. ICP-AES analysis of the stripped solution of the deposit shows the presence of gold which serves as supporting evidence for the formation of Al-Au intermetallic compounds as evidenced by CV.

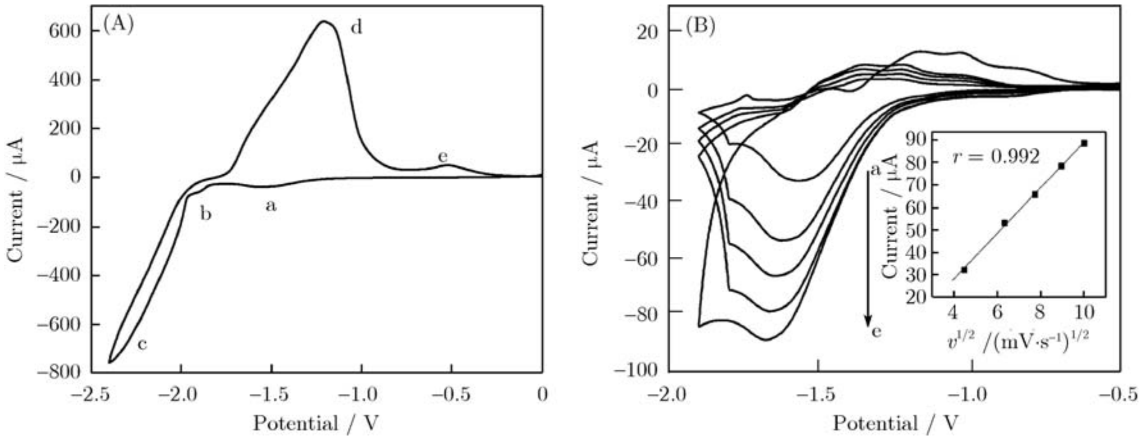

Fig. 1. Cyclic voltammogram recorded for the electrodeposition of aluminium in the 2:1 (weight ratio) $AlCl_3$-Et_3NHCl ionic liquid at a scan rate of 20 mV/s (A) and the underpotential deposition (UPD) of aluminium at different scan rates (B). Inset shows the plot of UPD current against the square root of scan rate on the gold electrode at room temperature.

A cyclic voltammogram of the gold disc electrode in the $AlCl_3$-Et_3NHCl electrolyte with a copper to aluminium ionic ratio of 0.5wt% is shown in Fig. 2(A). During cathodic scan, a small peak 'a' appears at –1.2 V, which corresponds to the deposition of copper; and another small peak 'b' at –1.6 V may be attributed to Al-Cu alloy formation [31]. A considerable increase in reduction current after –2.0 V indicates the bulk deposition of aluminium. During the reverse scan, the peaks 'd', 'e', and 'f ' obtained may be due to the oxidation of aluminium, Al-Cu alloys, and copper, respectively [31]. As observed in Al deposition, no nucleation loop was obtained for the Al-Cu alloy deposition, which suggests that the electrodeposition of Al and Cu on the gold electrode does not require an overpotential for nucleation [3]. While decreasing the potential window to less negative values (–2.6 to –1.6 V), the oxidation peak current of aluminium decreases, as shown in Fig. 2(B). The copper dissolution peak current also decreases but at a lesser rate. The cyclic voltammogram in Fig. 2(C) shows that the cathodic peak current for copper reduction is linearly related to the square root of scan rate with a regression coefficient $r = 0.9992$, indicating that the reduction of copper from this ionic liquid follows diffusion controlled growth on the gold substrate. The copper oxidation peak is sharp, which is characteristic of the oxidation of bulk deposited copper

[31].

3.2. Surface characterization

The EDS spectrum of the Al deposit (Fig. 3(a)) shows a strong peak corresponding to Al (72.39at %). Since the deposit was thick, no peak for gold was observed, as expected [3]. Small percentage of chlorine (2.58at%) may be due to the incorporation of traces of molten salts in the deposit from the bath or entrapped $AlCl_3$ or some chloroaluminate species [30]. The spectrum also shows reasonably high amount of oxygen content, which is due to the presence of aluminium oxide. The thickness of the deposit was found to be 70 μm.

The deposit obtained from the electrolyte with a copper to aluminium ionic ratio of 0.5wt% showed good adherence and uniformity on the gold electrode compared with the deposits obtained at other compositions. A copper concentration of 8at% to aluminium was obtained by depositing the Al-Cu alloy at –2.2 V (Fig. 3(b)). The chlorine content was found to be about 2.5at%, which is comparable to that observed for other aluminium depositions from ionic liquids [30]. Table 1 shows the effect of applied potential on the composition of the Al-Cu alloy and elucidates that the copper content in the alloy increases with a decrease in applied potential. The results of ICP-AES analyses of the stripped samples establishes the codeposition of copper with aluminium and also shows that the copper content in the alloy increases with an increase in the copper concentrations in the bath.

The Al deposits obtained at 1 A/dm^2 are uniform in texture and adherent, as shown in Fig. 4(a) and (b), whereas the deposit obtained at 1.25 A/dm^2 shows a slightly porous morphology. The irregular shapes on the surface maybe due to the tenacious oxide film formed by

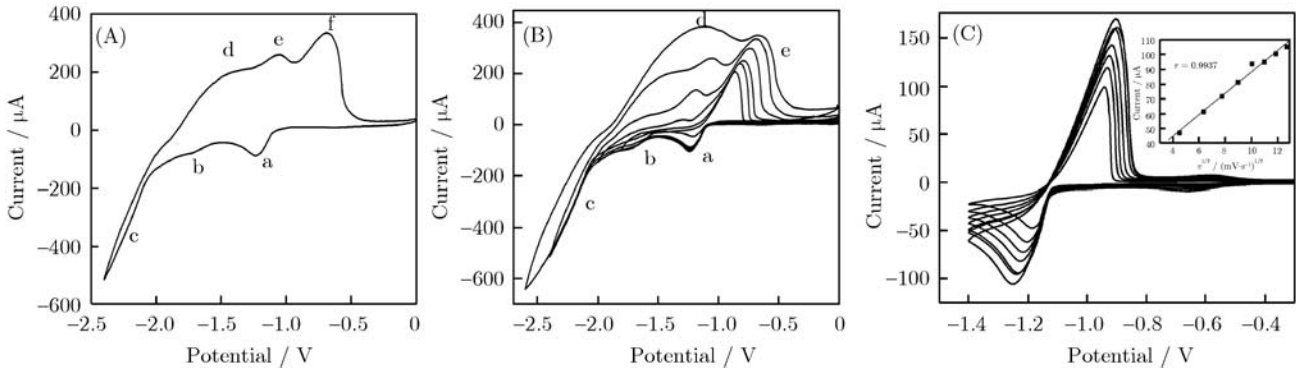

Fig. 2. Cyclic voltammogram obtained on the gold disc electrode at room temperature in a 2:1 (weight ratio) $AlCl_3$-Et_3NHCl ionic liquid with a copper to aluminium ionic ratio of 0.5wt% at a scan rate of 20 mV/s (A), at different potential windows (B) and variation of cathodic current for copper reduction with scan rate (C). The inset shows the plot of copper reduction current with the square root of scan rate.

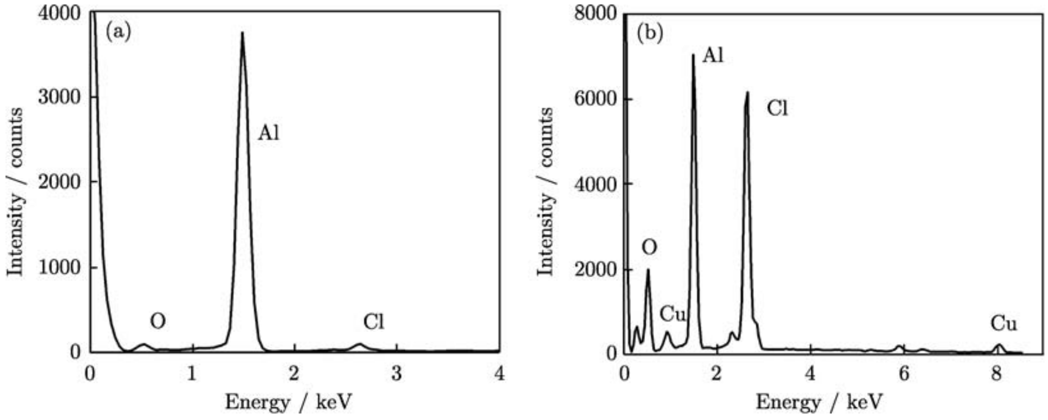

Fig. 3. EDS spectra of the deposited aluminium obtained from $AlCl_3$-Et_3NHCl (2:1 in weight ratio) ionic melt (a) and Al-Cu deposit obtained from the ionic liquid containing copper acetylacetonate (b).

Table 1. Variation of copper composition with potential in Al-Cu alloys electrodeposited from a 2:1 (weight ratio) $AlCl_3$-Et_3NHCl ionic liquid with a copper to aluminium ionic ratio of 0.5wt% at room temperature on the gold electrode

Electrodeposition potential / V	Copper / at%
–2.0	12
–2.2	8
–2.4	5

atmospheric oxidation. A scratch test ascertained that the Al-Cu deposit obtained was highly adherent on the substrate. The deposits possess an average thickness of 30 μm. Fig. 4(c) shows the FESEM image of the electrodeposited Al-Cu alloy on the gold substrate, and its magnified image (Fig. 4(d)) depicts a uniform deposit but has nodular appearance. These observations are similar to those reported earlier [9-10, 30-32].

3.3. Crystallographic analysis by X-ray diffraction

The XRD analysis of electrodeposited Al in Fig. 5(a) shows the characteristic diffraction patterns for crystalline Al [3]. The peaks correspond to different diffraction planes as per the JCPDS data (No. 65-2869), and the interplanar spacing (d_{hkl}) for each plane was calculated and compared with the values obtained from XRD analysis. The broad peaks indicate the presence of small crystalline deposits of aluminium. In spite of the precautions taken to prevent exposure to atmosphere, oxygen interference occurred during the analysis. The deposited aluminium shows a full width half maximum (FWHM) of 0.309° for a 2θ value of 63.77°, from which the grain size was calculated as (30 ± 5) nm using the Scherrer's equation.

The XRD patterns of the Al-Cu alloy in Fig. 5(b) exhibits intense peaks, which indicate high crystalline nature of the deposit. Oxidation of the surface occurs prior to XRD analysis, oxides of Al and Cu were formed, which make the spectra difficult to explain [33]. The peaks obtained are compared with JCPDS data, and the different phases are labeled as shown in the diagram. The aluminium diffraction peaks (JCPDS No. 65-2869) were prominent and diffraction patterns from different phases of crystals containing the oxygenated Al-Cu alloy are observable (JCPDS Nos. 83-1476 and 75-2356). From the observed FWHM of 0.322° at a 2θ value of 64.673°, the crystalline size of the deposit was calculated to be (29 ± 5) nm using the Scherrer's equation.

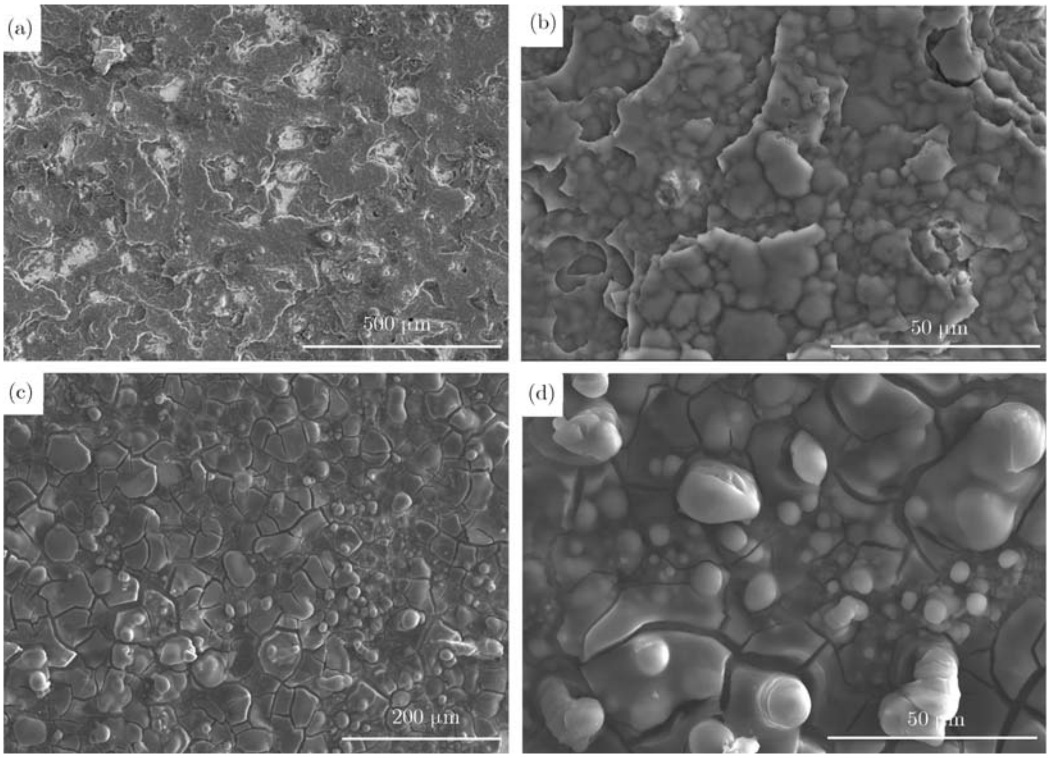

Fig. 4. FESEM images of electrodeposited aluminium on gold from an $AlCl_3$-Et_3NHCl (2:1 in weight ratio) ionic melt at room temperature at 1 A/dm^2 (a, b) and the Al-Cu alloy deposited at –2.2 V (vs. Pt wire) from an $AlCl_3$-Et_3NHCl (2:1 in weight ratio) ionic liquid with a copper to aluminium ionic ratio of 0.5wt% (c, d).

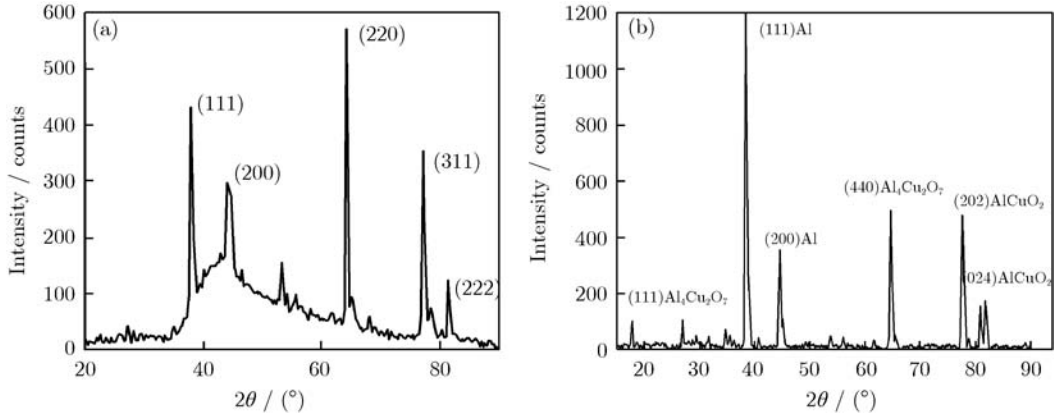

Fig. 5. XRD patterns of electrodeposited aluminium from $AlCl_3$-Et_3NHCl (2:1 weight ratio) ionic liquid (a) and the Al-Cu alloy deposited from a room temperature ionic liquid based on the $AlCl_3$-Et_3NHCl (2:1 weight ratio) electrolyte with a copper to aluminium ionic ratio of 0.5wt% on the gold electrode (b).

3.4. Corrosion studies

Results of the potentiodynamic polarization studies (Tafel plots) and EIS measurements of the electrodeposited Al and Al-Cu alloy in 0.5 M NaCl solution are shown in Fig. 6(a). It is difficult to compare the corrosion currents (i_{corr}) of Al and the Al-Cu alloy, because the roughness of the deposit increases with an increase in the amount of the deposit and, hence, the surface area. Similar results were reported by Caporali *et al.* [34]. Tafel plots show a shift in corrosion potential of the Al-Cu alloy towards more positive values compared with Al, which indicates that the alloy is more corrosion resistant than Al deposited. Further, the calculated values of anodic transfer coefficients (α_a) for the alloy and Al deposits are 0.326 and 0.728, respectively, indicating that the aluminium deposit is more prone to corrosion than the Al-Cu deposit.

Nyquist plots are semicircular, and the diameter of the curve gives the charge transfer resistance (R_{et}) and in turn corrosion resistance. Higher R_{et} values of the Al-Cu alloy compared with that of Al show that the alloy is more corrosion resistant than Al (Fig. 6(b)). The increase in corrosion resistance of the Al-Cu alloy can be attributed to the mixed oxides of Al and Cu formed on the alloy surface [33].

4. Conclusion

Electrodeposition of metallic Al and Al-Cu alloys were successfully carried out from $AlCl_3$-Et_3NHCl room-temperature ionic liquid with copper acetylacetonate as the source of copper ions. During the course of the study, Al deposits of 70 μm in thickness and Al-Cu alloys of 30 μm in thickness were obtained on the gold electrode. Elemental analysis of Al-Cu alloys showed that a decrease in deposition potential or an increase in copper concentration in the electrolyte leads to an increase in copper concentration in the alloy deposit. Crystallographic analysis established the formation of nanocrystalline Al and Al-Cu deposits. The Al-Cu alloy was found to be more corrosion resistant than the Al deposit obtained from a similar bath.

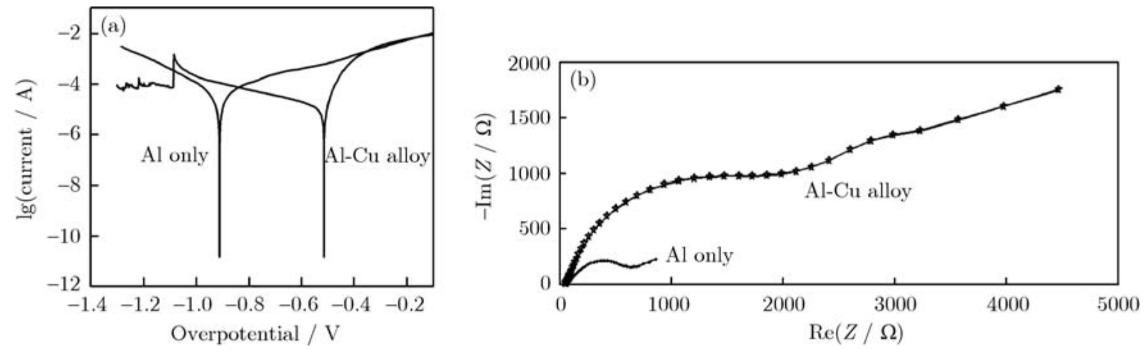

Fig. 6. Potentiodynamic anodic polarization curves (a) and EIS curves (b) for the electrodeposited Al and Al-Cu alloy in 0.5 M NaCl solution.

The ionic liquid used was found to be stable in the experimental potential window for electropositive aluminium. This suggests that the ionic liquid developed can be used as an electrolyte for the electrodeposition of similar electropositive metals and their alloys. Moreover, the bath is cost effective as compared with imidazolium-based ionic liquids, which are commonly employed as electrolytes for the deposition of aluminium and its alloys.

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