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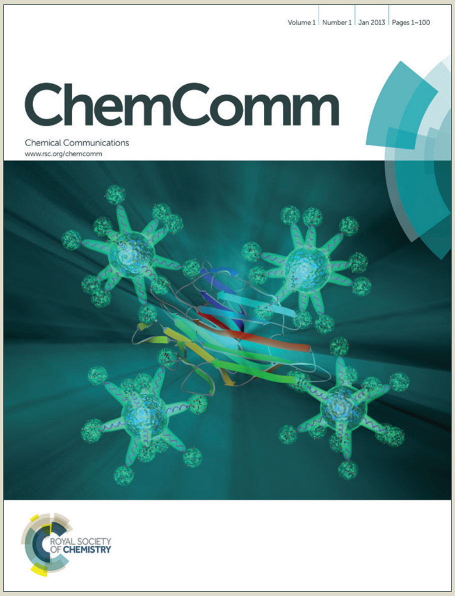

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ARTICLE TYPE

New ionic liquids based on complexation of dipropylsulfide and $AlCl_3$ for electrodeposition of aluminum

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A new kind of ionic liquid based on complexation of dipropyl sulfide (DPS) and $AlCl_3$ has been prepared. The equivalent concentration of $AlCl_3$ in the ionic liquid is as high as 2.3 M. More importantly, it is highly fluidic and exhibits an ambient ionic conductivity of 1.25 x 10^{-4} S cm^{-1}. This new ionic liquid can be successfully used as an electrolyte for electrodeposition of aluminum.

Introduction

Al containing room temperature ionic liquids (Al-RTILs) have attracted great attentions in science and technology field owing to their wide applications in catalysis,[1] electrochemistry,[2-4] biotechnology[5] and material processing.[6] Typically, $AlCl_3$ based ILs are prepared by mixing anhydrous $AlCl_3$ with organic halide salts such as N-(1-butyl)pyridinium chloride 1-ethyl-3-methylimidazolium chloride. [7, 8] It has been shown that these ILs contain the quaternary ammonium cations and chloroaluminate anions, among which the electroactive species in the acidic mixture is believed to be $Al_2Cl_7^-$. Recently, it has been shown that N containing "neutral" ligands could generate new room temperature ionic liquids when mixed with $AlCl_3$. The reaction between $AlCl_3$ and neutral ligands forms both Al containing anionic and cationic species according to the following equation:

$$x\mathrm{AlCl_3} + y\ \mathrm{base} \leftrightarrow [\mathrm{Al}x_{-1}\mathrm{Cl}_{3x-4}(\mathrm{base})_y]^+ + \mathrm{AlCl_4}^- \qquad (1)$$

Based on a similar reaction scheme, few ILs based on $AlCl_3$ and neutral ligands such as acetamide,[9] urea, [9] 1,3-dimethyl-2-imidazolidinone,[10] and 4-propylpyridine[11] have been reported.

Aluminum coatings have been routinely used for corrosion protection in electronics, buildings, architecture, automotive components, the marine industry, aviation, and aerospace. Among different technique for aluminum coating, electrodeposition is considered to be more efficient. Unfortunately, aluminum cannot be electrodeposited from aqueous solutions because hydrogen is evolved before aluminum is plated. So far, three kinds of non-aqueous baths have been used for Al electrodeposition: 1) organic solvents 2) inorganic molten salts, and 3) organic molten salts (Al-RTILs).[10] Organic solvent bath generally contains volatile organic solvents and highly flammable Al sources such as $LiAlH_4$ and alkylaluminum, which demands stringent environment for practical applications. [7] As for inorganic molten salts, relatively high temperature is required, which can lead to not only high energy consumption but also the sublimation of corrosive $AlCl_3$. Comparatively, Al-RTILs can be used at much lower temperatures with less safety concerns. However, the high cost of quaternary ammonium halide salts and their hygroscopic nature limit the application of Al-RTILs for aluminum deposition. Therefore, development of ILs from readily available and relatively hydrophobic "neutral" ligands is of great interest for practical electroplating of Al.

Currently, most of the neutral ligands based ILs have been prepared using group V nitrogen based ligands. Even though group VI elements also possess the lone pair electrons, Al-RTILs based on ligands from group VI elements such as O and S have hardly been investigated. We have preliminarily examined ethers such as diethyl ether and tetrahydrofuran as the potential ligands to form Al-RTILs, unfortunately, only little $AlCl_3$ can be dissolved in those solvents. Therefore, they are dilute solutions rather than ionic liquids (data not shown). Herein, we report a new Al-RTIL based on $AlCl_3$ and an alkyl sulfide, dipropyl sulfide (DPS). DPS interacts with $AlCl_3$ to produce both Al-containing cation and anion by the asymmetric cleavage of $AlCl_3$, which is characterized by mass spectrometry (MS) and infrared spectroscopy. The new IL possesses low viscosity and high ionic conductivity. Gray-white Al has been successfully electroplated in the new IL at 50 °C, indicating the suitability of this new IL for electrodeposition of Al.

The DPS/$AlCl_3$ ILs were prepared by adding calculated amount of $AlCl_3$ into DPS with stirring in an Ar-filled glove box. External heat might be needed to get more $AlCl_3$ reacted A high molar ratio of 1:1.05 between DPS and $AlCl_3$ can be readily obtained, producing a near colorless (slightly yellow) liquid with a low viscosity of 6.87 mPa•s at room temperature (Fig. 1).

Direct analysis in real time mass spectrometry (DART-MS) was used to identify the cations and anions produced by the reaction between DPS and $AlCl_3$. As shown in Fig. 2, both cationic species $[AlCl_2(DPS)_2]^+$ and anionic species $AlCl_4^-$ are directly observed, however, $Al_2Cl_7^-$ is not found in the MS spectrum. This result is similar to those previously reported for the ILs based on the complexation of "neutral" ligands and $AlCl_3$. [9, 11] It is assumed that the asymmetric cleavage of $AlCl_3$ generates $AlCl_2^+$ and $AlCl_4^-$, with the former being coordinated with DPS, according to the following equation:

$$2\mathrm{AlCl_3} + 2\ \mathrm{DPS} \leftrightarrow [\mathrm{AlCl_2(DPS)_2}]^+ + \mathrm{AlCl_4}^- \qquad (2)$$

Fig. 1 Digital photo of DPS/AlCl$_3$ (1:1.05, molar ratio) IL.

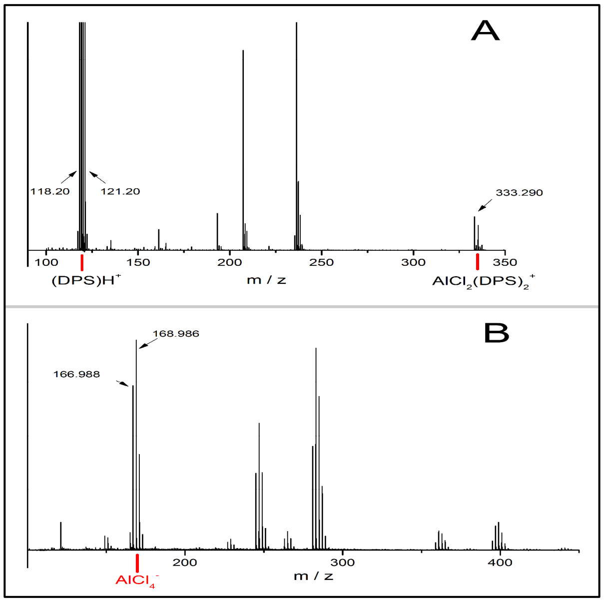

Fig. 2 MS spectrum of DPS/AlCl$_3$ (1:1.05) (DPS= dipropyl sulfide, A: cationic species; B: anionic species).

It should be noted that some intense peaks are difficult to identify, which might be due to the fragments produced during the ionization and recombination processes.

The ionic conductivities of DPS/AlCl$_3$ ILs were measured by electrochemical impedance spectroscopy with a self-made two-platinum-electrode cell calibrated with a 0.1 M KCl aqueous solution.[12] Fig. 3 shows the temperature dependence of the ionic conductivities of the ILs. Generally, the ionic conductivity can be described by the Arrhenius equation $\sigma = Ae^{-Ea(\sigma)/(RT)}$, where T is temperature, A is a coefficient, E$_a$ is the activation energy and R is the universal gas constant. A calculated average E$_a$ of the DPS/AlCl$_3$ ILs is 33.80 kJ/mol. It is interesting to note that the ionic conductivities can be obviously divided into two segments with 50 °C as a transition point. This might be related to the solid like transition around 40 °C observed in the DSC scan (Fig. S1, ESI). However, the source of the transition is unknown, which could be related to the impurity of DPS. For the ionic conductivity above 50 °C, a clear trend can be observed. For example, the ionic conductivity increases with increasing the molar ratio of AlCl$_3$ from 0.8 to 1.0, which can be attributed to the equilibrium of reaction (2) shifting to the right, that is, more ionic species are generated. However, the ionic conductivity decreases when the molar ratio of AlCl$_3$ is further increased to 1.05, which might be due to the increased viscosity of the ionic liquid. [11]

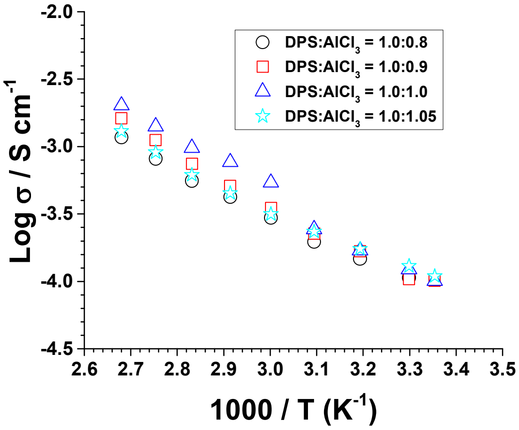

Fig. 3. Temperature (from 25 to 100 °C) dependence of ionic conductivities of ionic liquids on different molar ratios of DPS:AlCl$_3$.

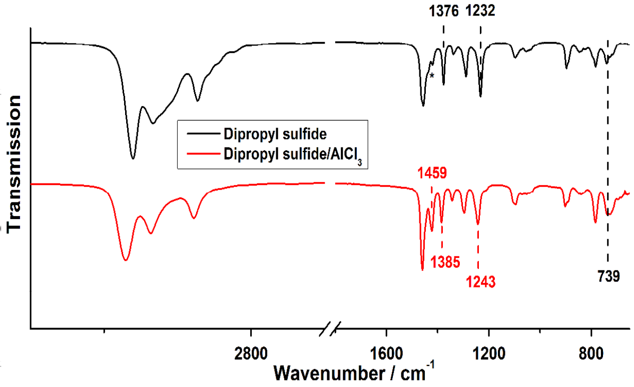

Fig. 4. FT-IR spectrum of DPS and DPS/AlCl$_3$ (1:1).

The reaction between DPS and AlCl$_3$ was also investigated by IR spectra in order to examine the effect of AlCl$_3$ complexation.[13] As shown in Fig. 4, the peak at 739 cm^{-1} can be attributed to C-S stretching vibration of DPS (black), which becomes broader after complexation with AlCl$_3$. The C-H wagging and twisting vibration peaks shift from 1232 and 1376 for neat DPS to 1243 and 1385 cm^{-1} after complexation with AlCl$_3$, respectively. Similar peak shifts were also observed for the complexation between pyridine and AlCl$_3$.[11] It was also observed that the characteristic peaks gradually shifted to higher wavenumbers with increasing the acidity of the IL.[14] The above observed IR spectra shifts further confirm that new IL is generated from the complexation of AlCl$_3$ and DPS *via* Al-S coordination interaction.

Fig. 5 shows the cyclic voltammogram of the ILs on a platinum working electrode under a scan rate of 100 mV/s at room temperature. Apparent aluminum deposition/stripping are observed for the IL with a molar ratio of 1:1.05 between DPS and AlCl$_3$ (black line). [4, 15] A characteristic "nucleation loop" is also noted for the above IL. [16] However, no reversible aluminum deposition/stripping can be observed for the ILs with lower AlCl$_3$ contents. It has been reported for the ILs based on quaternary ammonium halide salts and AlCl$_3$ that only the acidic ones support reversible Al deposition/stripping. [17, 18] However, for "neutral" ligands based ILs, this may be different for the following reasons: 1) Al deposition is possible for acetamide/$AlCl_3$ based IL with equal molar ratio of the two components;[9] 2) anionic species $Al_2Cl_7^-$ cannot be observed in the MS spectra for neutral ligand based ILs. [9, 11, 19] Unfortunately, the detailed reduction mechanism is still not clear, and we speculate that the Al-containing cations are the electroactive species. To check the possibility of electroplating Al using this IL, a constant current density of 4 mA/cm^2 was applied at 50 °C for 2 h with copper plate as the working electrode and Al as the counter electrode. Fig. 6A shows that the Cu substrate is covered by a white-gray deposit after the electrodeposition. A SEM image also shows fine grain-like Al crystals (Fig. 6B), which are similar to our previous results using pyridine based ILs.[11] EDS (Energy-dispersive X-ray spectroscopy) analysis is also used to identify the composition of the electrodeposited film. As shown in Fig. 6C that the deposition film is composed of pure Al without sulfur contamination. The ability to electrodeposit aluminum from this IL suggests the new sulfide/$AlCl_3$ IL indeed can be used for electrodeposition of aluminum.

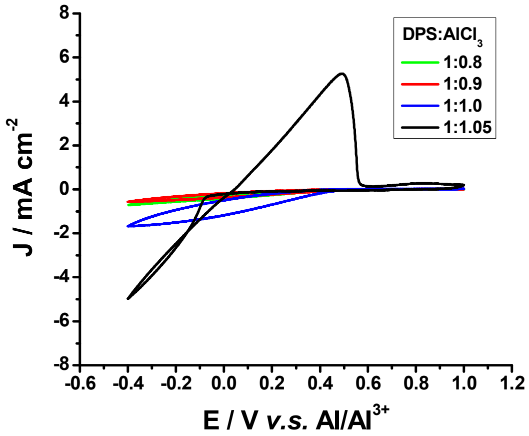

Fig. 5. Cyclic voltammogram of DPS:$AlCl_3$ at different molar ratios on a platinum working electrode with aluminum wire as both counter and reference electrode. Start potential: 1.0 V. Scan rate: 100 mV/s.

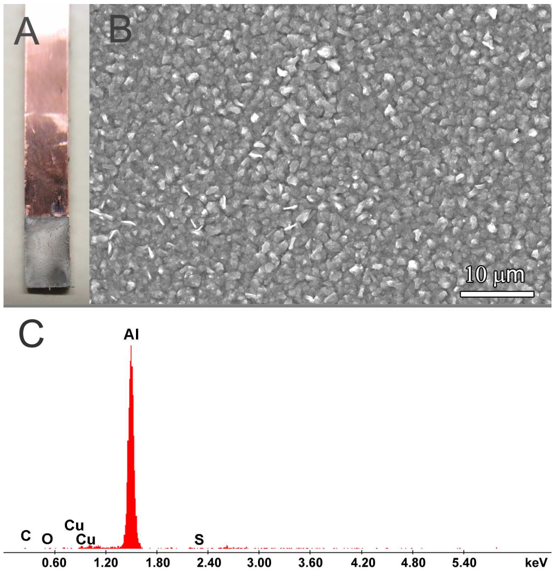

Fig. 6. Digital image (A) and scanning electron micrograph (B) and Energy-dispersive X-ray spectroscopy analysis (C) of electrodeposited aluminum on copper substrates.

Conclusion

A new kind of IL is obtained by reacting $AlCl_3$ and dipropylsulfide. The asymmetric cleavage of $AlCl_3$ produces both Al-containing cations and anions, as confirmed by MS measurements. The resulted ILs have low viscosity, low melting point and high ionic conductivity. The new ILs can be successfully used for electrodeposition of aluminum. The discovery of alkyl sulfide ligand/$AlCl_3$ based ILs not only can extend the family of "neutral" ligands based ILs but also can inspire those interested to discover and design novel alkyl or other neutral ligands with desired properties for practical applications in various fields.

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Notes and references

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