Electrochemical Study on Aluminum Speciation in Lewis Acidic Chlooroaluminate-Bis(trifluoromethylsulfonyl)amide Mixed Ionic Liquids

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ABSTRACT

Aluminum species forming in Lewis acidic chlooroaluminate and bis(trifluoromethylsulfonyl)amide (TFSA⁻) mixed ionic liquids having 1-butyl-3-methylimidazolium (BMI⁺) was investigated by potentiometry and Raman spectroscopy. A decrease in the concentration of [Al₂Cl₇⁻] and an increase in that of [AlCl₄⁻] with addition of BMITFSA into acidic BMICl-AlCl₃ were observed by Raman spectroscopy. The redox potential of Al(III)/Al in BMICl-AlCl₃ (1:2 in molar ratio) was found to be −0.68 V vs. an Ag|Ag(I) reference electrode, which was corresponding to −0.25 V vs. the ferrocene/ferrocenium couple at 25°C. The potentiometry of an Al electrode in the mixed ionic liquids with different compositions using the Ag|Ag(I) reference electrode suggested formation of a mixed ligand aluminum complex, Al(TFSA)Cl₂, indicating the instability of [Al₂Cl₇⁻] against TFSA⁻.

Keywords: Lewis Acidic Chlooroaluminate Ionic Liquid, Bis(trifluoromethylsulfonyl)amide Liquid, Aluminum Speciation, Raman Spectroscopy

1. Introduction

Aluminum is impossible to deposit in protic electrolytes because the electrode potential of Al(III)/Al is more negative than that of hydrogen evolution. Electrodeposition of Al has been investigated extensively in the chlooroaluminate ionic liquids, which are composed of aluminum trichloride (AlCl₃) and chloride salts of metal or organic cations. It is possible to obtain the chlooroaluminate ions having the melting temperature below room-temperature by using 1-butylpyridinium (BP⁺) and 1-ethyl-3-methylimidazolium chlorides. The chlooroaluminate ionic liquids contain several kinds of chlooroaluminate ions denoted as [AlₙCl₄₋ₙ]⁻. When the composition of AlCl₃ in the chlooroaluminate ionic liquid is less than 50 mol%, there exists [AlCl₄⁻] which is not reducible within its electrochemical potential window at ambient temperatures. In the case of the Lewis acidic chlooroaluminate ionic liquid with the composition of AlCl₃ greater than 50 mol%, polymeric chlooroaluminate anions like [Al₂Cl₇⁻] and [Al₃Cl₁₀⁻] are known to form depending on the composition. Electrodeposition of Al is reported to occur by reduction of [Al₂Cl₇⁻] in the acidic chlooroaluminate ionic liquids according to the following reaction.

\[ 4[Al₂Cl₇⁻] + 3e^- = Al + 7[AlCl₄⁻] \]  (1)

On the other hand, it has been reported that electrodeposition of Al is possible in the ionic liquid consisting of bis(trifluoromethylsulfonyl)amide (TFSA⁻) with addition of excess amount of AlCl₃. Although formation of several aluminum species like Al(TFSA)₃, [Al(TFSA)₂Cl]⁻ and [Al(TFSA)Cl]⁻ has been proposed by Raman and ²⁷Al nuclear magnetic resonance (NMR) spectroscopies with the aid of quantum chemical calculation, the electroactive species and their electrode reactions have not been clarified in this system. When [Al₃Cl₄⁻] is assumed to form in the TFSA⁻-based ionic liquids, electrodeposition of Al is expected to occur according to Eq. (1). However, there is no report on electrodeposition of Al from the TFSA⁻-based ionic liquids containing [Al₂Cl₇⁻]. In the present study, the stability of [Al₂Cl₇⁻] was evaluated in the mixed ionic liquids of acidic BMICl-AlCl₃ and BMITFSA (BMI⁺ = 1-butyl-3-methylimidazolium) at different compositions.

2. Experimental

AlCl₃ (Wako Chemical Industries) was purified by vacuum sublimation at 140°C for two times before use. AlCl₃ was mixed with BMICl (Kanto Chemical) slowly to form BMICl-AlCl₃ with different compositions. BMITFSA was prepared by the metathesis reaction of BMICl and LiTFSA (Solvay) in deionized water, followed by extraction into dichloromethane, evaporation and vacuum drying at 100°C for 24 hours. The water content in the prepared BMITFSA was less than 10 ppm, which was checked by Karl Fischer titration (Metrohm, 831KF). BMITFSA was added to BMICl-AlCl₃ to prepare the mixed ionic liquids with different compositions. All the hygroscopic reagents were handled and stored in an Ar-filled glovebox with a continuous gas purification apparatus (Miwu MFG, DBO-1K-SH). The concentrations of water and oxygen in the atmosphere were kept below 1 ppm. Electrochemical measurements were performed using an air-tight three-electrode cell made of tetrafluoroethylene-perfluorooalkylvinylether copolymer (PFA). Cu (Nilaco) was used as the working electrode (3 mm, 7.07 × 10⁻² cm²). Al wire (Nilaco, 0.5 mm) was used as the working and counter electrode. The reference electrode consisted of Ag wire (Sanwa Kinzoku, 0.3 mm) immersed in an inner electrolyte of BMPTFSA (Kanto Chemical, BMPI⁺ = 1-butyl-1-methylpyrrolidinium) containing 0.1 M AgCl₂SO₄ (Aldrich). The inner electrolyte was isolated from the test electrolyte by a porous glass (Vycor). The potential of this reference electrode is +0.43 V against the redox potential of ferrocene (Fc)/ferrocenium (Fc⁺) couple. Cyclic voltammetry and open circuit potential measurement were conducted using a potenti/galvanostat (Hokuto Denko, HSV-110 or HZ-7000). The electrodeposits were characterized by a scanning electron microscope (SEM, Keyence, VE-9800) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford.
The composition of BMITFSA is given by the molar ratio of BMITFSA to BMICl-AlCl₃ (67 mol% AlCl₃). Scan rate: 10 mV s⁻¹. Temperature: 25°C.

Figure 1. Cyclic voltammograms of a Cu electrode in (a) BMICl-AlCl₃ (67 mol% AlCl₃) and (b) BMICl-AlCl₃ (67 mol% AlCl₃) mixed with BMITFSA at various composition. The composition of BMITFSA is varied by addition of BMITFSA to BMICl-AlCl₃ (67 mol% AlCl₃). Scan rate: 10 mV s⁻¹. Temperature: 25°C.

Instruments, INCA-E250X3K). Raman spectra of the ionic liquids sealed in a quartz glass cell were obtained by a Raman spectrometer (Renishaw, inVia StreamLine Plus B) using an exciting wavelength of 785 nm.

3. Results and Discussion

Figure 1(a) shows the cyclic voltammogram of a Cu electrode in BMICl-AlCl₃ (67 mol% AlCl₃). A cathodic current observed at the potentials more negative than −0.75 V during the cathodic potential sweep was assigned to deposition of Al according to Eq. (1) because potentiostatic cathodic reduction on a Cu electrode at −0.78 V resulted in deposition of Al, which was confirmed by the SEM image and EDS spectrum of the deposits on the electrode. Consequently, an anodic current peak around −0.62 V during the successive anodic potential sweep was ascribed to anodic dissolution of Al deposited on the Cu electrode. The open circuit potential of an Al electrode in BMICl-AlCl₃ (67 mol% AlCl₃) was −0.68 V, which was corresponding to −0.25 V vs. Fe|Fe⁺. This potential was in good agreement with that reported in BPCI-AlCl₃ (67 mol% AlCl₃), −0.27 V vs. Fe|Fe⁺ at 40°C. When BMITFSA was added to BMICl-AlCl₃ (67 mol% AlCl₃), the redox potential for deposition and dissolution of Al shifted to the more negative side with an increase in the molar ratio of BMITFSA to BMICl-AlCl₃, as shown in Fig. 1(b). The negative shift of the redox potential suggested a decrease in the molar fraction of [Al₂Cl₇]⁻, X([Al₂Cl₇]⁻), and/or an increase in that of [AlCl₄]⁻, X([AlCl₄]⁻), because the equilibrium potential of [Al₂Cl₇]⁻/Al depends on X([Al₂Cl₇]⁻) and X([AlCl₄]⁻), as given by the following equation according to Eq. (1).

\[ E = E^\circ + \frac{2.303RT}{3F} \log \frac{X([Al₂Cl₇]^-)^2}{X([AlCl₄]^-)} \]  

The species existing in the mixed ionic liquids of BMICl-AlCl₃ (67 mol% AlCl₃) and BMITFSA were investigated by Raman spectroscopy, as shown in Fig. 2. In the case of BMICl-AlCl₃ without BMITFSA, a peak assignable to v₁(A₁g) of [Al₂Cl₇]⁻ was observed at 312 cm⁻¹, as shown in Fig. 2(a). In addition, no peak was observed in the wavenumber region from 700 to 800 cm⁻¹, where the peaks related to v₁(N-S-S) of TFSA⁻ are observed. When BMITFSA was added to BMICl-AlCl₃, peaks assignable to v₁(A₁g) of [Al₂Cl₇]⁻ and v₁(N-S-S) of TFSA⁻ were observed at 349 and 752 cm⁻¹, respectively, in addition to that of [AlCl₄]⁻, as seen in Figs. 2(b)-(e), indicating formation of [AlCl₄]⁻ by addition of BMITFSA. The wavenumber of the peak assigned to v₁(N-S-S) of TFSA⁻ was greater than that assigned to unbound (or liberated) TFSA⁻, which typically gives the peak at 742 cm⁻¹, indicating TFSA⁻ was bound to Al⁺. An increase in the molar fraction of BMITFSA resulted in a decrease in the peak intensity of [Al₂Cl₇]⁻ and an increase in the peak intensities of [AlCl₄]⁻ and bound TFSA⁻, suggesting that [Al₂Cl₇]⁻ reacted with TFSA⁻ to form [AlCl₄]⁻ and the species consisting of AlCl₃⁻ and TFSA⁻. These results are consistent with the negative shift of the redox potential, as shown in Fig. 1(b).

Although there are several possible Al species with both Cl⁻ and TFSA⁻, we assumed formation of neutral and monovalent anionic species formed by the following reactions.

\[(n + 1)[Al₂Cl₇]^- + nTFSA^- \rightarrow Al(TFSA)ₙCl₃₋ₙ + (2n + 1)[AlCl₄]^- \]  

(3)  

\[n[Al₂Cl₇]^- + nTFSA^- \rightarrow [Al(TFSA)ₙCl₄₋ₙ]^- + (2n - 1)[AlCl₄]^- \]  

(4)

When [Al₂Cl₇]⁻ is assumed to be the electroactive species in the mixed ionic liquid, the open circuit potential of an Al electrode in the mixed ionic liquid is expected to be determined by the molar fractions of [Al₂Cl₇]⁻ and [AlCl₄]⁻ according to Eq. (2). In order to
estimate the value of $\log(\frac{X[AlCl_4]^{-}}{X[AlCl_3]})$ for the mixed ionic liquid of BMICl-AlCl$_3$ and BMITFSA, the open circuit potential of an Al electrode was measured in acidic BMICl-AlCl$_3$ with different molar fractions of AlCl$_3$ at 27°C, as shown in Fig. 3. The open circuit potential was dependent linearly on the value of $\log(\frac{X[AlCl_4]^{-}}{X[AlCl_3]})$, as expected from Eq. (2). However, the slope of the regression line was $15 \text{ mV decade}^{-1}$, which was smaller than the theoretical value at 27°C ($20 \text{ mV decade}^{-1}$), presumably due to the errors derived from repeated multiplication in the calculation of $\log(\frac{X[AlCl_4]^{-}}{X[AlCl_3]})$. Then, the values of $\log(\frac{X[AlCl_4]^{-}}{X[AlCl_3]})$ in the mixed ionic liquids of BMICl-AlCl$_3$ and BMITFSA were estimated using the regression line from the open circuit potentials of an Al electrode in the mixed ionic liquids, as listed in Table 1. Figure 4 shows the correlation plots between the values of $\log(X[AlCl_4]^{-}/X[AlCl_3])$ estimated from the open circuit potentials and those calculated from the compositions of the mixed ionic liquids assuming formation of $\text{Al(TFSA)}_2\text{Cl}$ and $\text{Al(TFSA)}_3\text{Cl}$ according to Eqs. (3) and (4). As can be seen in the correlation plots, the neutral species, $\text{Al(TFSA)}_2\text{Cl}$ ($n = 1$ in Eq. (3)), was considered the most probable species among these seven species because of the best correspondence between the observed and calculated values of $\log(X[AlCl_4]^{-}/X[AlCl_3])$. Formation of some neutral species in the transparent phase of the mixture of BMITFSA and AlCl$_3$ has also been suggested by $^{13}$C-NMR spectroscopy. In the case of addition of AlCl$_3$ to TFSA$^-$-based ionic liquids, the most probable neutral species was considered to be $\text{Al(TFSA)}_2\text{Cl}$, which was not reducible. Assuming AlCl$_3$ is liberated from $[\text{Al}_2\text{Cl}_7]^{-}$ in the present study, formation of $\text{Al(TFSA)}_2\text{Cl}$ may be explained by the stepwise formation of $\text{Al(TFSA)}_2\text{Cl}$ from AlCl$_3$ and TFSA$^-$ as represented below.

**Table 1.** Open circuit potentials of an Al electrode in the mixed ionic liquids with different compositions given by the molar ratios of BMITFSA to BMICl-AlCl$_3$ (67 mol% AlCl$_3$).  

| BMITFSA/BMICl-AlCl$_3$ | OCP/V   |
|-------------------------|---------|
| 0.10                    | -0.768  |
| 0.20                    | -0.804  |
| 0.25                    | -0.837  |
| 0.33                    | -0.850  |
the concentrations of $[\text{Al}_2\text{Cl}_7]^{-}$ and $[\text{AlCl}_4]^{-}$ from the electrode potentials of an Al electrode in acidic BMICl-AlCl$_3$ with different molar fractions of BMITFSA. In contrast to addition of AlCl$_3$ to TFSA$^-$-based ionic liquids, Al(TFSA)$_3$ does not form because formation of Al(TFSA)$_3$ requires an enough amount of Lewis acid, AlCl$_3$. $[\text{Al}_2\text{Cl}_7]^{-}$ has been found to be unstable in TFSA$^-$-based ionic liquids. The electroactive species in the mixture of TFSA$^-$-based ionic liquids and AlCl$_3$ are considered not $[\text{Al}_2\text{Cl}_7]^{-}$ but some mixed ligand complexes of aluminum with TFSA$^-$ and Cl$^-$. 

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