Electronic Supplementary Information

Inorganic $AlCl_3$–alkali metal thiocyanate ionic liquids as electrolytes for electrochemical Al technologies

Chih-Yao Chen,[a,b] Tetsuya Tsuda*[a] and Susumu Kuwabata*[a]

[a] *Department of Applied Chemistry, Graduate School of Engineering,*
Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
[b] *AIST-Kyoto University Chemical Energy Materials Open Innovation Laboratory (ChEM-OIL),*
National Institute of Advanced Industrial Science and Technology (AIST), Sakyo-ku, Kyoto 606-8501, Japan

*Corresponding authors: Tetsuya Tsuda and Susumu Kuwabata

E-mail addresses: ttsuda@chem.eng.osaka-u.ac.jp and kuwabata@chem.eng.osaka-u.ac.jp

Experimental

Ionic liquid (IL) preparation

Anhydrous $AlCl_3$ (Nippon Light Metal Company, specially-manufactured ultra-high purity grade (> 99.999 %)) was used as received. High-purity (> 99.0 %) alkali metal thiocyanates purchased from Sigma-Aldrich were vacuum dried at 393 K for 48 h prior to use. The inorganic ILs were prepared by slow addition of $AlCl_3$ into A_MSCN (A_M = Li, Na, K) to the predetermined molar ratio. The reaction between the reagents is highly exothermic. The heat generated from the mixing is enough to partially melt the starting materials. The resulting melts were further purified by leaving high purity Al wires (99.999 % purity, Nilaco Corp.) in the reagent container for 72 h at 393 K. All preparation processes were conducted in an Ar-filled glovebox (Vacuum Atmospheres Co., NEXUS II system) with O_2 and H_2O contents maintained below 1 ppm.

Characterizations

The glass transition temperature of the electrolytes was determined with a differential scanning calorimetry (DSC) using a Bruker DSC3100SA by sealing the samples in Al hermetic pans and lids. The sealed pans were first cooled at 273 K with liquid nitrogen for 2 h and then heated/cooled between 173 K and 373 K at a rate of 5 K min^{-1}. The ionic conductivity of the electrolytes was measured with a Mettler Toledo S230 SevenCompact conductivity meter paired with an InLab 751 probe. The ILs were thermally equilibrated at each temperature for at least 30 min prior to measurement. Viscosity measurements were conducted using a Kyoto Electronics Manufacturing EMS-1000 electromagnetically spinning viscometer. Transmission electron microscope (TEM) images and electron diffraction patterns of the electrodeposits were analyzed with a Hitachi H-7650 microscope at an accelerating voltage of 100 kV.

Electrochemical measurements

A three-electrode cell was used to perform the cyclic voltammetry (CV) and potentiostatic electrolysis at 303–393 K. Al wires (99.999 % purity, Nilaco Corp.) were used as counter and reference electrodes. For CV, Pt wire was used as the working electrode. Before each electrochemical measurement, Pt wire was washed by dilute HNO_3, followed by thoroughly cleaned by ultrapure water and vacuum dried. For potentiostatic electrodeposition, Cu plates were used as the working electrode and were electropolished prior to use. After electrodeposition, the samples were thoroughly rinsed with anhydrous tetrahydrofuran (THF) to remove residual electrolytes adhered to the electrode surface and then dried in the glovebox before characterization. All electrochemical measurements were carried out with a Princeton Applied Research VersaSTAT 4 potentiostat/galvanostat in the glovebox.

Al-anion rechargeable battery (AARB) assembly and testing

A two-electrode cell was constructed to assess the feasibility of $AlCl_3$–LiSCN (67 : 33 mol%) and $AlCl_3$–NaSCN–KSCN (61 : 26 : 13 mol%) ILs as electrolytes for Al secondary batteries. A graphite sheet (Grafoil®, GrafTech Co.) made from thermal expansion of chemically treated natural graphite flakes was used as the cathode material. The loading per electrode area is approximately 15 mg cm^{-2}. An Al foil (99.999 % purity, Nilaco Corp.) was used as the counter electrode. Two sheets of glass fiber (Whatman, GF/A) soaked in the electrolyte were used as the separator. A glass container and a molybdenum (Mo) plate (99.95 % purity, Nilaco Corp.) current collector were used in the cell assembly. Additional cell details can be found in our previous reports.[1,2] The Al/graphite cells were charging to a constant capacity of 100 mAh g^{-1}, followed by discharging to 0.05 V. Galvanostatic charge–discharge test was controlled by a Princeton Applied Research VersaSTAT 4 or a Bio-Logic Science Instruments VSP-300 potentiostat/galvanostat.

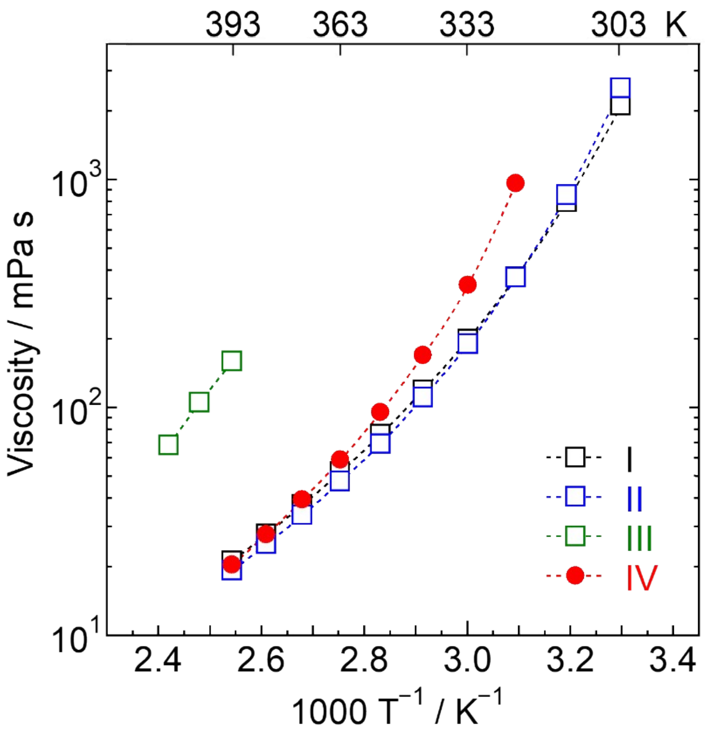

Fig. S1 Arrhenius plots of the viscosity of $AlCl_3$–A_MSCN melts: (I) $AlCl_3$–LiSCN (67 : 33 mol%), (II) $AlCl_3$–NaSCN (67 : 33 mol%), (III) $AlCl_3$–KSCN (67 : 33 mol%), and (IV) $AlCl_3$–NaSCN–KSCN (61 : 26 : 13 mol%).

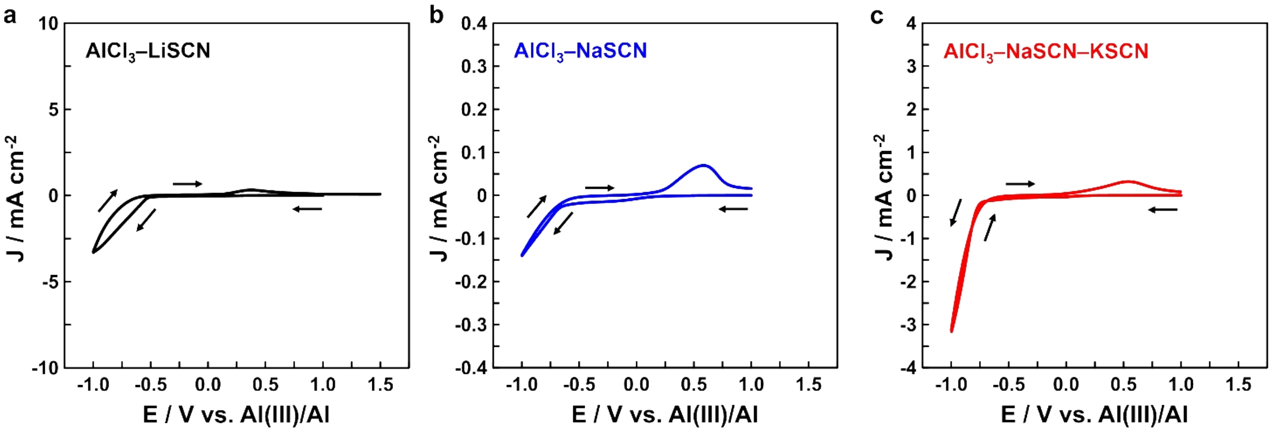

Fig. S2 Cyclic voltammograms of Al deposition–stripping in (a) $AlCl_3$–LiSCN (67 : 33 mol%), (b) $AlCl_3$–NaSCN (67 : 33 mol%), and (c) $AlCl_3$–NaSCN–KSCN (61 : 26 : 13 mol%) ILs in a three-electrode cell using a Pt wire as the working electrode and Al wires as the reference and counter electrodes. The scan rates were 10 mV s^{-1}. The temperature was 303 K. Note that different scales have been used for each voltammogram for clarity.

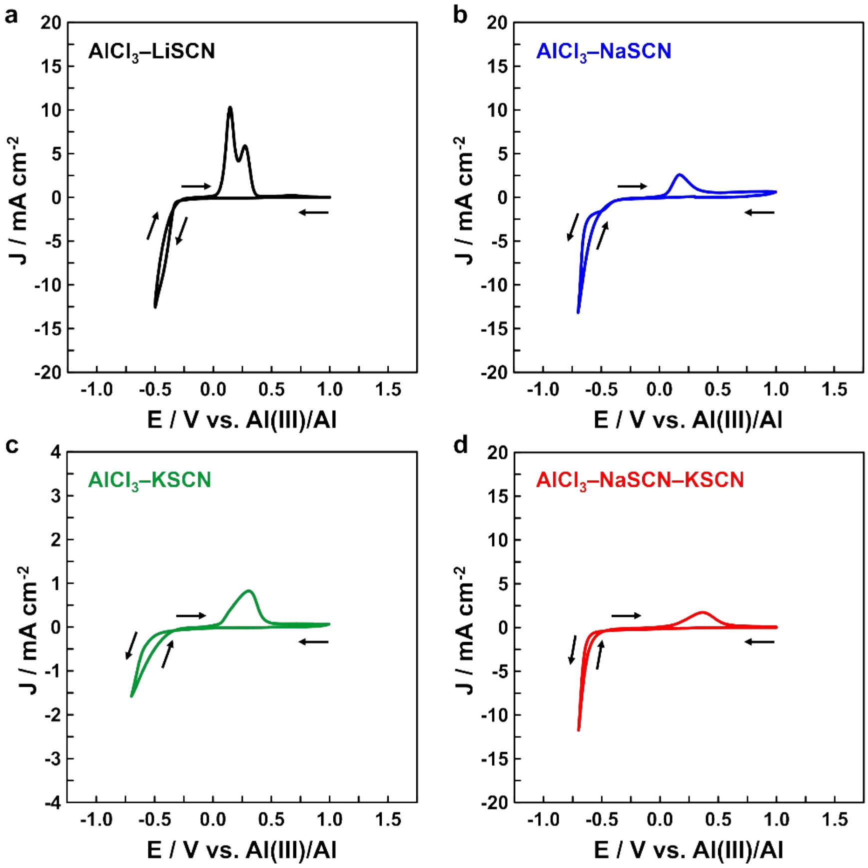

Fig. S3 Cyclic voltammograms of Al deposition–stripping in (a) $AlCl_3$–LiSCN (67 : 33 mol%), (b) $AlCl_3$–NaSCN (67 : 33 mol%), (c) $AlCl_3$–KSCN (67 : 33 mol%), and (d) $AlCl_3$–NaSCN–KSCN (61 : 26 : 13 mol%) ILs in a three-electrode cell using a Pt wire as the working electrode and Al wires as the reference and counter electrodes. The scan rates were 10 mV s^{-1}. The temperature was 363 K. Note that different scales have been used for clarity.

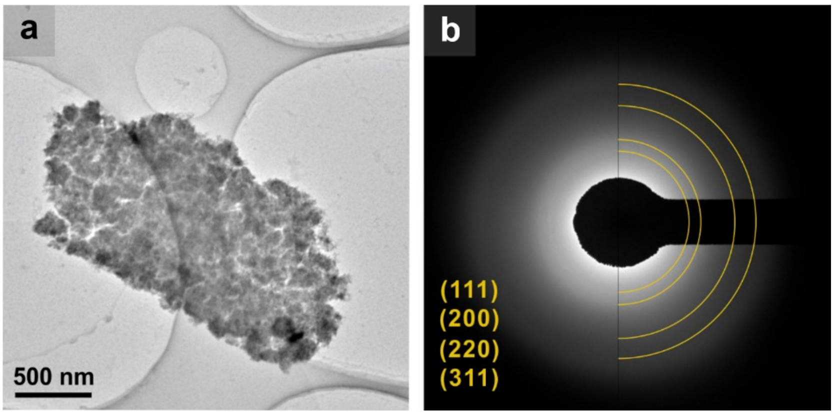

Fig. S4 (a) TEM micrographs and (b) corresponding selected area electron diffraction (SAED) pattern of Al deposits obtained in $AlCl_3$–KSCN (67 : 33 mol%) IL. The electrodeposition was performed by the potentiostatic electrolysis at –0.70 V (vs. Al(III)/Al) for 30 min at 333 K.

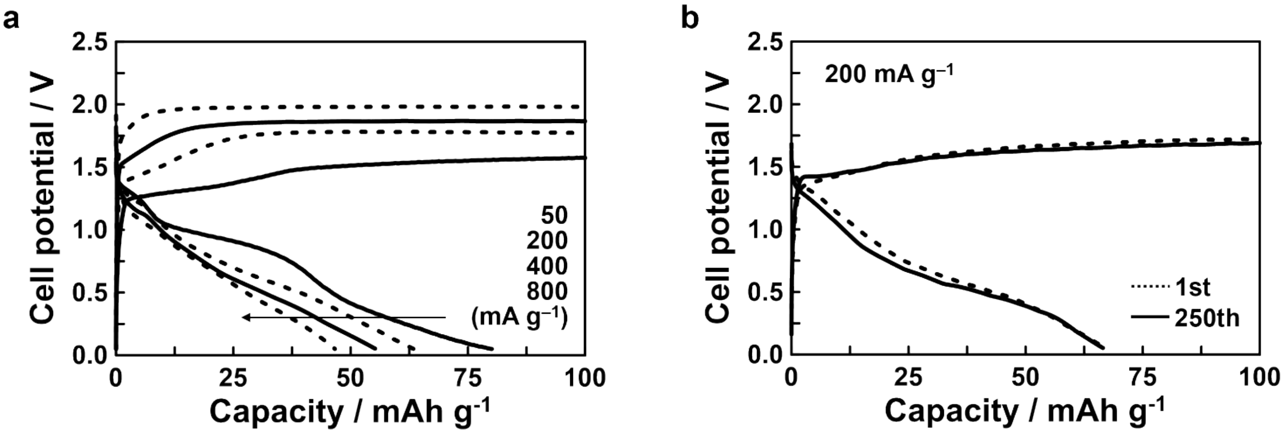

Fig. S5 (a) Galvanostatic charge-discharge curves of the Al | $AlCl_3$–LiSCN (67 : 33 mol%) | graphite cell at various current densities ranging from 50 to 800 mA g^{-1} at 363 K. (b) The 1st and 250th charge–discharge curves of the Al | $AlCl_3$–LiSCN (67 : 33 mol%) | graphite cell at a current density of 200 mA g^{-1} at 363 K.

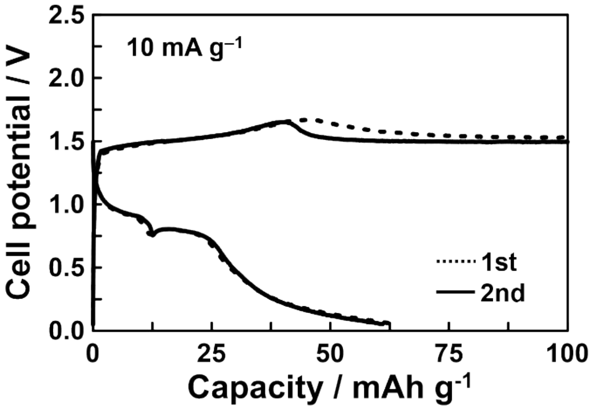

Fig. S6 Galvanostatic charge–discharge curves of the Al | $AlCl_3$–NaSCN–KSCN (61 : 26 : 13 mol%) | graphite cell at a current density of 10 mA g^{-1} at 363 K.

References

1 C. Y. Chen, T. Tsuda, S. Kuwabata and C. L. Hussey, *Chem. Commun*., 2018, **54**, 4164.

2 Y. Uemura, C. Y. Chen, Y. Hashimoto, T. Tsuda, H. Matsumoto and S. Kuwabata, *ACS Appl. Energy Mater*., 2018, **1**, 2269.