Electronic Supplementary Information

Aluminum metal anode rechargeable batteries with sulfur-carbon composite cathodes and inorganic chloroaluminate ionic liquid

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Electrolyte preparation

Anhydrous $AlCl_3$ (Fluka, ≥ 99.0 %) was purified by sublimation from a 99-1 wt% $AlCl_3$−NaCl mixture, with some Al pieces (ca. 5 × 5 × 30 mm), in a thick-walled reaction kettle with a cover, under vacuum conditions at 453 K. Most metal cation impurities, such as iron(II), iron(III), copper(II), etc., were removed by substitution reactions between the impurities and the Al pieces in an $AlCl_3$−NaCl melt formed at the bottom of the kettle. Anhydrous NaCl (Wako Pure Chemical Industries, Ltd.) and KCl (Wako Pure Chemical Industries, Ltd.) were used after vacuum drying at 473 K for 24 h. A Lewis acidic chloroaluminate inorganic ionic liquid (IL) electrolyte, $AlCl_3$−NaCl−KCl (61.0-26.0-13.0 mol%), was prepared by mixing the ternary salt mixtures in the sealed glass tube with some Al pieces (ca. 5 × 5 × 30 mm) at 403 K for more than 48 hours. The final product was a colorless, transparent liquid. All preparation processes were conducted in an Ar-filled glovebox (Vacuum Atmospheres Co., NEXUS II system) with O_2 and H_2O < 1 ppm. Diagrammatic illustrations of the apparatus for $AlCl_3$ sublimation purification and the preparation processes for 61.0-26.0-13.0 mol% $AlCl_3$–NaCl–KCl inorganic IL are given in Fig. S1.

Viscosity measurements

Viscosity of the 61.0-26.0-13.0 mol% $AlCl_3$−NaCl−KCl inorganic IL was measured by a Kyoto Electronics Manufacturing EMS-1000 electromagnetically spinning viscometer in a range of 373–413 K. The measurement was conducted using the inorganic IL in an airtight glass tube filled with dry argon gas. The viscosity data are given in Table S1 along with the ionic conductivity data reported in our previous paper.[S1] Other physicochemical properties, e.g., eutectic point[S2] and density,[S3] of this

inorganic IL systems have already been examined by Midorikawa.

Preparation of SPEG composite electrodes

The procedure used to prepare the sulfurized polyethylene glycol (SPEG) cathode active material was the same as that reported by Kojima, et al. (Fig. S2a).[S4,S5] The sulfur content in the SPEG used in this research was 48.0 wt%, which was determined by elemental analysis. The SEG composite electrodes were fabricated using the following three steps (Fig. S2b): The first step was a mixing process of SPEG and a conduction supporting agent, ketjen black (KB) or multiwalled carbon nanotube (MWCNT), using a planetary centrifugal mixer for 3 min. Subsequently, polytetrafluoroethylene (PTFE) fine power binder (mean particle size: 470 μm) was added to the blended material, and the mixture was mixed again for 3 min. The next step was kneading the mixture using an agate mortar and pestle. After approximately 30 min, it became like a kneaded eraser. The final step was the sheeting process. The eventual SPEG composite sheet had a thickness of ca. 50 μm and was formed into disks by a punching press of 8 mm in diameter. The compositions of the cathodes were SPEG : conduction-supporting agents (KB or MWCNT) : PTFE = 50 : 45 : 5 wt% and 85 : 10 : 5 wt%. The loading per electrode area was roughly 4.8 mg cm^{-2}. Further information on SPEG characterization is available in our previous papers.[S4,S5]

Electrochemical measurements

All electrochemical experiments were conducted using a two-electrode sealed cell assembled in an Ar-filled glovebox. A schematic of the cell setup is presented in Fig. S2c. Aluminum metal foil (99.999 %

purity, 16 mm in diameter) served as both the reference and counter electrodes. A glass fiber sheet (ADVANTEC GB-100R, 25 mm in diameter) soaked in the electrolyte was used as the separator. To prevent any unexpected chemical reactions derived from the Lewis acidic IL electrolyte, a molybdenum container and current collector were used in the cell assembly. Prior to assembling the cell, all components were vacuum dried at 373 K for 24 h to remove residual water. Cyclic voltammetry and charge-discharge tests were carried out with a potentiostat/galvanostat (Bio-Logic Sciences Instruments, VSP-300) and a battery test system (Scribner Associates, 580), respectively. All the charge-discharge tests were initiated from the discharge step.

References

S1 C.-Y. Chen, T. Tsuda, S. Kuwabata and C. L. Hussey, *Chem. Commun.*, 2018, **54**, 4164.

S2 R. Midorikawa, *Denki Kagaku*, 1955, **23**, 127.

S3 R. Midorikawa, *Denki Kagaku*, 1955, **23**, 352.

S4 T. Kojima, H. Ando, N. Takeichi and H. Senoh, *ECS Trans.*, 2017, **75**, 201.

S5 N. Takeichi, T. Kojima, H. Senoh and H. Ando, *Sci. Rep.*, 2020, **10**, 16918.

Table S1 Viscosity and ionic conductivity of the 61.0-26.0-13.0 mol% $AlCl_3$−NaCl−KCl inorganic ionic liquid

Temperature / K	Viscosity / mPa s	Ionic conductivity / mS cm^{-1} S1
373	11.2	-
383	9.09	-
393	7.58	102
398	-	108
403	6.76	115
413	5.76	-

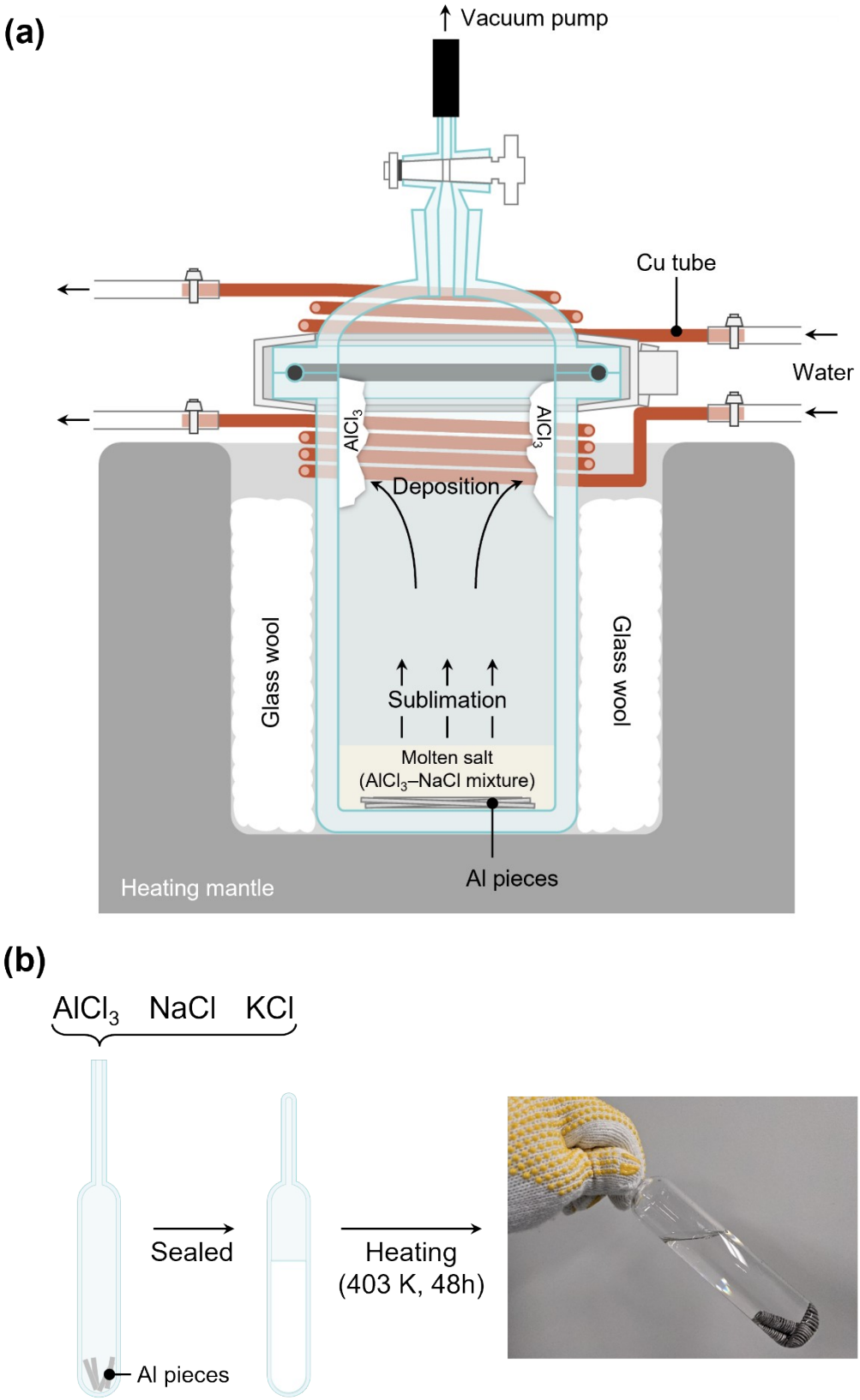

Fig. S1 Diagrammatic illustrations of (a) the apparatus for $AlCl_3$ sublimation purification and (b) the preparation processes for 61.0-26.0-13.0 mol% $AlCl_3$–NaCl–KCl inorganic IL.

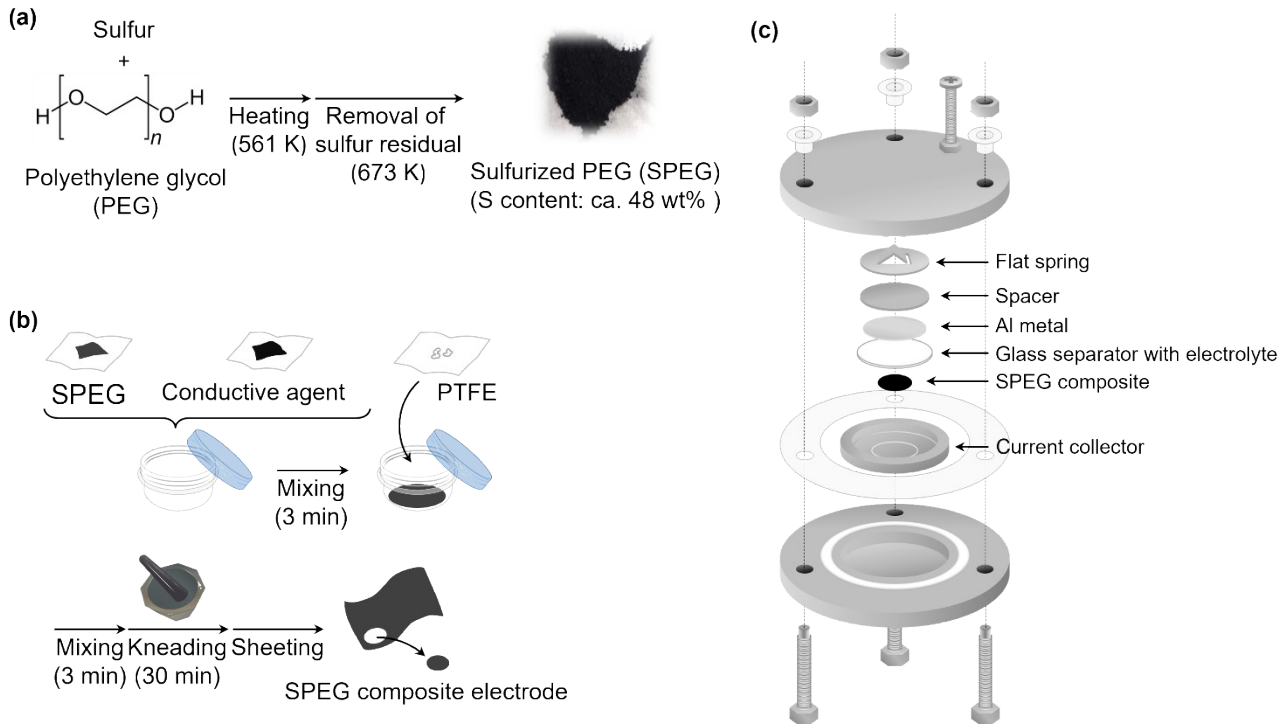

Fig. S2 Diagrammatic illustrations of preparation processes for (a) sulfurized polyethylene glycol (SPEG), (b) SPEG composite electrodes, and (c) the two-electrode cell utilized in this research. The conduction-supporting agents were ketjen black (KB) or multi-walled carbon nanotube (MWCNT). The compositions were SPEG : conduction-supporting agents (KB or MWCNT) : PTFE = 50 : 45 : 5 wt% and 85 : 10 : 5 wt%. The electrolyte was 61.0-26.0-13.0 mol% $AlCl_3$–NaCl–KCl inorganic IL.

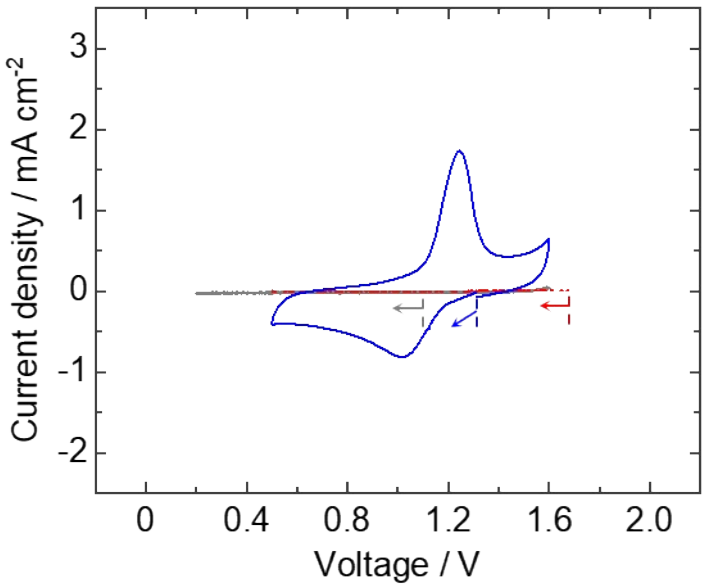

Fig. S3 Cyclic voltammograms recorded at (—) Mo and SPEG composite electrodes with (—) KB (10 wt%) + PTFE (5 wt%) and (—) MWCNT (10 wt%) + PTFE (5 wt%) in a 61.0-26.0-13.0 mol% $AlCl_3$–NaCl–KCl inorganic IL electrolyte at 393 K. The scan rates were 1 mV s^{-1}.

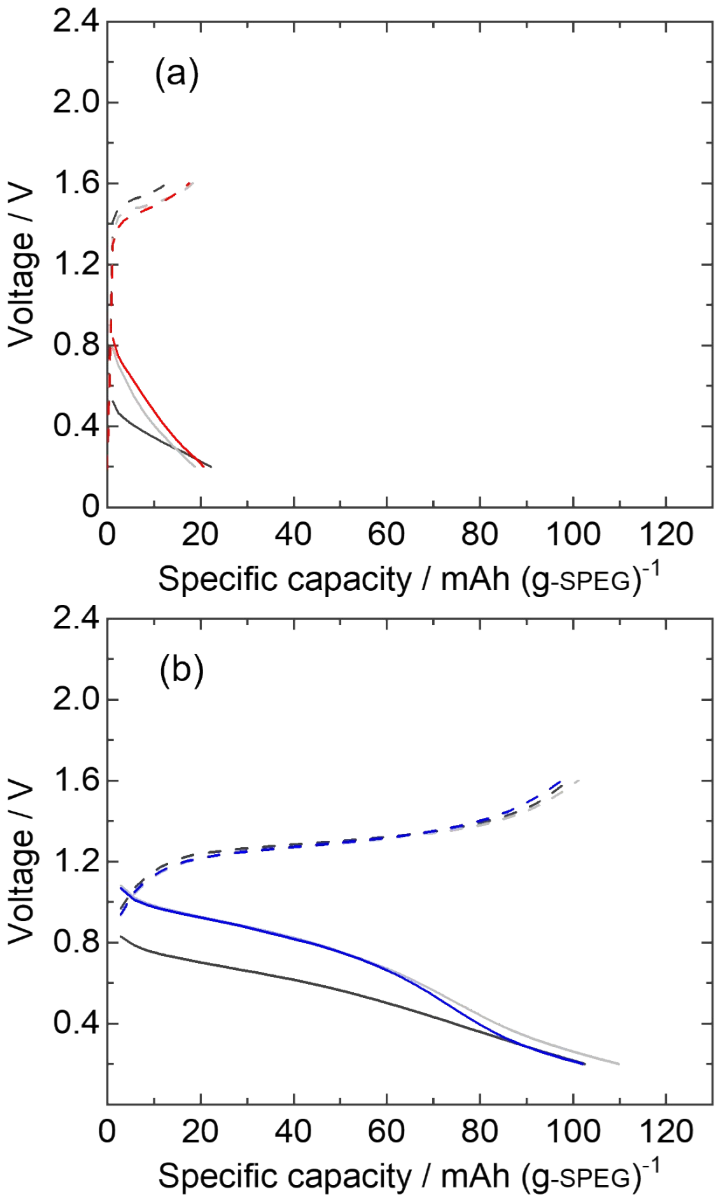

Fig. S4 Galvanostatic charge-discharge curves recorded at (—) first, (—) second and (—, —) third cycles using the SPEG composite electrodes consisting of (a) SPEG (85 wt%), KB (10 wt%) and PTFE (5 wt%) and (b) SPEG (85 wt%), MWCNT (10 wt%) and PTFE (5 wt%) in a 61.0-26.0-13.0 mol% $AlCl_3$–NaCl–KCl inorganic IL electrolyte at 393 K. The current densities were 3000 mA $(g\text{-SPEG})^{-1}$. The cut-off voltages were 1.60 and 0.20 V.

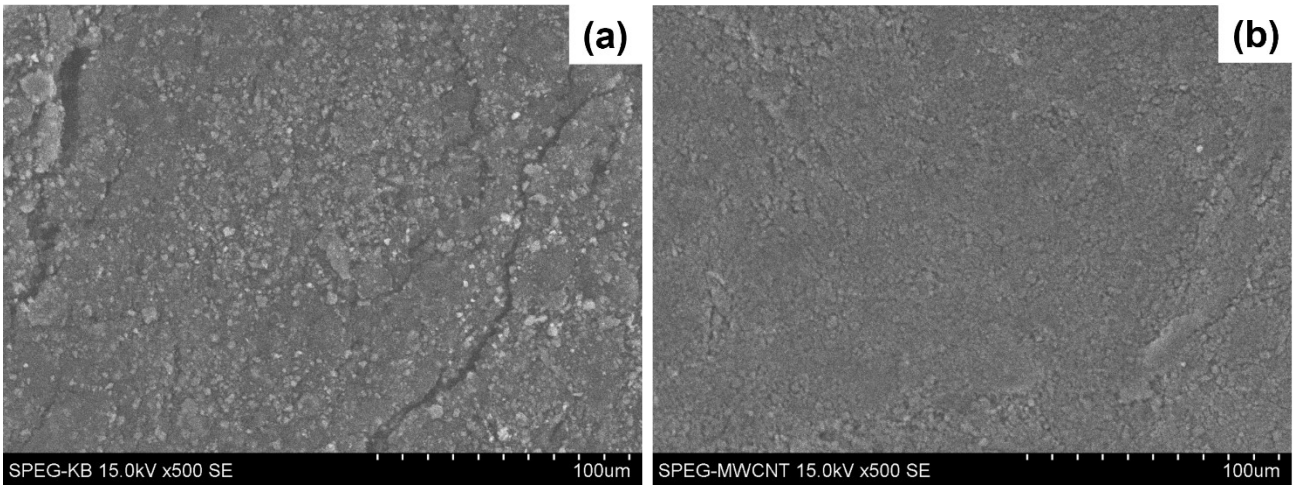

Fig. S5 SEM images of SPEG composite electrodes consisting of (a) SPEG (50 wt%), KB (45 wt%), PTFE (5 wt%) and (b) SPEG (85 wt%), MWCNT (10 wt%), PTFE (5 wt%).