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

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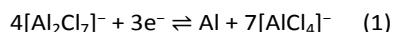
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Promising sulfurized polyethylene glycol (SPEG) composite cathodes with a high-rate capability over 3000 mA g⁻¹ at 393 K are fabricated for Al metal anode rechargeable batteries with a 61.0–26.0–13.0 mol% AlCl₃–NaCl–KCl inorganic ionic liquid electrolyte. The combination of the SPEG composite cathodes and chloroaluminate inorganic IL can readily enhance the performance of the Al-S batteries, e.g., discharge capacity and cycle stability.

Because effective utilization of renewable energy is globally required to achieve sustainable development, a wide variety of energy storage techniques are proposed for electric-load leveling, such as rechargeable batteries, electric double layer capacitors and pumped-storage power generation.¹ Considering future dissemination of smart grids, rechargeable batteries would be the best choice due to their ease of installation, high energy capacity, and high energy conversion efficiency. However, some disadvantages are also present. For example, current Li-ion batteries (LIBs) have insufficient power density, high installation costs, and safety issues. In addition, those are expected to have a higher charge-discharge capacity.

Recently, considerable efforts have been devoted to the research and development of metal anode rechargeable batteries using lightweight and multivalent metals such as Li, Mg, and Al.^{2,3} Of these, Al is attracting attention as a metal anode in future batteries for several reasons, including high theoretical volumetric and weight capacities (8046 mAh cm⁻³, 2980 mAh g⁻¹), moderate chemical stability, and rich natural abundance. Besides, Al electroplating/stripping processes with

a high coulombic efficiency are known to succeed in Lewis acidic chloroaluminate ionic liquids (ILs), which exist in a liquid state below 373 K. Classification as Lewis acidic means that the AlCl₃ molar fraction in the ILs is over 50 mol%. Under these conditions, two types of chloroaluminate complex anions, [AlCl₄]⁻ and [Al₂Cl₇]⁻, exist in the ILs. Only the latter anion causes Al metal electrodeposition/stripping via the following reaction.^{4–7}



Surprisingly, the assemblage of this Al anode reaction in the Lewis acidic AlCl₃–1-ethyl-3-methylimidazolium chloride ([C₂mim]Cl) IL, and a pyrolytic graphite foam cathode, enables the construction of an Al metal anode rechargeable battery with a high power density. This is due to the quick cathode reaction invoked by the insertion/deinsertion of chloroaluminate complex anions.⁸ After this milestone work by Dai and co-workers, various graphite materials that can reversibly store and release anions have been reported to date.^{9–15} However, the daunting issue of overcoming the hurdles of the insufficient cathode capacity in current Al metal anode rechargeable batteries exists, though they have a great potential to contribute to the dissemination of smart grids. For this reason, a number of research groups have applied high-capacity sulfur (S)-based composite materials, originally developed for Li-S batteries, to Al metal anode ones.^{16–23} As is the case with Li-S batteries, it is very difficult to attain both sufficient cyclability and capacity in the Al battery with the S-based composite cathode. In addition, a significant overpotential for the cathode reaction was recognized.

Herein, sulfurized polyethylene glycol (SPEG), which is synthesized from a mixture of polyethylene glycol and sulfur and is thermally stable below 573 K,^{24,25} is employed to prepare a sophisticated cathode for Al metal anode batteries. The resulting SPEG composite electrode is handled in an inorganic 61.0–26.0–13.0 mol% AlCl₃–NaCl–KCl inorganic IL (eutectic point: 366 K²⁶). The combination of the SPEG electrode and chloroaluminate inorganic IL greatly enhanced the performance of the Al metal anode battery. When a multiwalled carbon

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nanotube (MWCNT) is employed as a conduction-supporting agent, the SPEG cathode exhibits a reversible capacity of 266 mAh (g-SPEG)⁻¹, viz., 554 mAh (g-sulfur)⁻¹, at a current density of 5000 mA (g-SPEG)⁻¹ and is stable for up to 600 cycles. These findings will make it a possibility to fabricate Al metal anode batteries with great promise.

Understanding the electrochemical behavior of the current collector material (molybdenum (Mo)) and SPEG composite electrode in chloroaluminate IL is an essential first step in designing a high-performance cathode for an Al metal anode rechargeable battery. Cyclic voltammograms were recorded at a Mo electrode and an SPEG composite electrode consisting of 50 wt% SPEG, 45 wt% ketjen black (KB) and 5 wt% PTFE in two-electrode type sealed cells with a 61.0-26.0-13.0 mol% AlCl₃-NaCl-KCl inorganic IL electrolyte at 393 K (Fig. 1). The electrode composition was determined by referring to our previous papers.^{24,25} As described above, this IL has a eutectic point of 366 K, but is not a stable liquid at the temperature. This is because the Lewis acidity at the phase boundary between the electrodes and IL electrolyte varies during the electrochemical reaction, and variation in the acidity often causes AlCl₃ deposition or chloroaluminate complex adsorption on the electrode.^{27,28} Thus, in this study, all experiments were conducted at 393 K. At the Mo electrode, there is no redox wave in the voltammogram, implying that no impurities are present in the electrolyte, and the Mo electrode is available as a current collector for the SPEG composite electrode. Contrasting results were obtained with regard to the SPEG composite electrode. A pair of reduction and oxidation waves appear at ca. 1.05 V and 1.25 V, respectively. Given that the electrochemical reaction for elemental sulfur proceeds in an AlCl₃-[C₂mim]Cl organic IL electrolyte at similar potentials,²⁰ the redox waves shown in Fig. 1 can be regarded as the following electrochemical reaction:

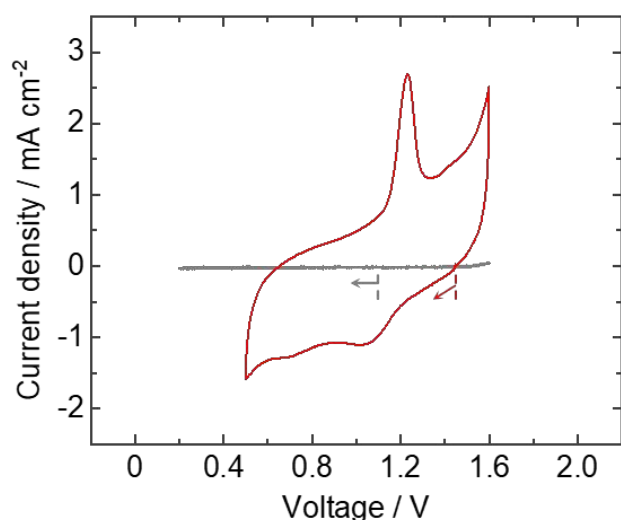
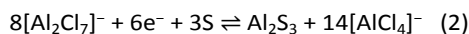


Fig. 1 Cyclic voltammograms recorded at (—) Mo and (—) SPEG composite electrode with KB (45 wt%) + PTFE (5 wt%) in a 61.0-26.0-13.0 mol% AlCl₃-NaCl-KCl inorganic IL electrolyte at 393 K. The scan rates were 1 mV s⁻¹.

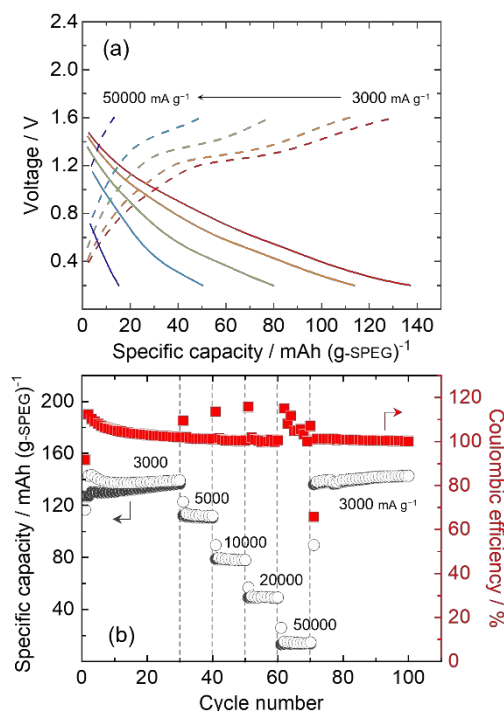


Fig. 2 (a) Galvanostatic charge-discharge curves recorded at the SPEG composite electrode consisting of SPEG (50 wt%), KB (45 wt%) and PTFE (5 wt%) in a 61.0-26.0-13.0 mol% AlCl₃-NaCl-KCl inorganic IL electrolyte at 393 K. The current densities were 3000, 5000, 10000, 20000 and 50000 mA (g-SPEG)⁻¹. (b) Specific capacity (●: charge; ○: discharge) and coulomb efficiency of the SPEG composite electrode at different current densities. The cut-off voltages were 1.60 and 0.20 V

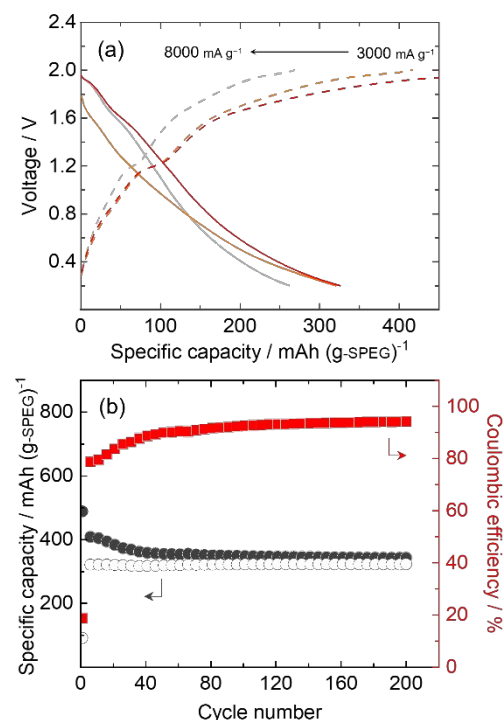


Fig. 3 (a) Galvanostatic charge-discharge curves recorded at the SPEG composite electrode consisting of SPEG (50 wt%), KB (45 wt%) and PTFE (5 wt%) in a 61.0-26.0-13.0 mol% AlCl₃-NaCl-KCl inorganic IL electrolyte at 393 K. The current densities were 3000, 5000, and 8000 mA (g-SPEG)⁻¹. (b) Specific capacity (●: charge; ○: discharge) and coulomb efficiency of the SPEG composite electrode at 5000 mA (g-SPEG)⁻¹ as a function of cycle number. The cut-off voltages were 2.00 and 0.20 V.

This result strongly suggests that the SPEG composite electrode can be used as a cathode for Al metal anode rechargeable batteries. However, sulfur in SPEG forms both S-S and C=S bonds.²⁵ The electrochemical reaction must be more complex than that for elemental sulfur. Further investigation is currently planned using several in situ or operando analytical techniques.

In order to assess the adequacy of the SPEG electrode as the cathode for Al metal anode rechargeable battery, galvanostatic charge-discharge test was carried out at five current densities between 3000 ~ 50000 mA (g-SPEG)⁻¹ under the cut-off voltage condition of 1.60 and 0.20 V (Fig. 2a). The discharge capacities of the SPEG electrode were ca. 140 and 80 mAh (g-SPEG)⁻¹ at 3000 and 10000 mA (g-SPEG)⁻¹, respectively. The capacities depend on the current density, as is the case with other battery systems, but charge-discharge behavior was recognized even at a very high current density of 50000 mA (g-SPEG)⁻¹. Fig. 2b shows the specific capacity and coulomb efficiency of the SPEG electrode, continuously obtained at various current densities. During the first 20 cycles, the electrode performance was not stable. In addition to an irreversible electrode reaction, insufficient electrolyte penetration into the SPEG composite should also be considered, as most ILs have higher viscosities than organic and aqueous electrolytes. Similar behavior is often seen in the articles on Al metal anode rechargeable batteries.^{8,11,29,30} After the first 20 cycles, a coulomb efficiency close to 100 % is attained, except at 50000 mA (g-SPEG)⁻¹. High-rate capability of the SPEG electrode is comparable to rapid chargeable-dischargeable Al anode-graphitic material cathode batteries.⁸⁻¹⁵ The impact of variation in cut-off voltage on the SPEG electrode performance was examined by changing the upper cut-off voltage from 1.60 V to 2.00 V. As shown in Fig. 3a, a discharge capacity of over 320 mAh (g-SPEG)⁻¹ was obtained when the current densities were 3000 and 5000 mA (g-SPEG)⁻¹. A higher current density, 8000 mA (g-SPEG)⁻¹, lowered the discharge capacity. Therefore, the cyclability test of the SPEG composite electrode was performed at 5000 mA (g-SPEG)⁻¹, which can achieve both rapid charge-discharge and high capacity. Fig. 3b shows the specific capacity and coulomb efficiency as a function of the cycle number. The discharge capacity of 323 mAh (g-SPEG)⁻¹, which corresponds to 673 mAh (g-sulfur)⁻¹, was maintained for up to 200 cycles. Unfortunately, the coulomb efficiency during the charge-discharge test was worse than in the case with the lower cut-off voltage condition. We think that this results from the oxidation state species related to sulfur yielded at the potential over ca. 1.60 V, because such oxidation state sulfur species are easily produced in the chloroaluminate molten salts.^{31,32}

Considering the areal capacity (mAh cm⁻²), it is desirable to contain more SPEG in the composite material. Composites consisting of SPEG (85 wt%), KB or MWCNT (10 wt%), and PTFE (5 wt%) were prepared. The cyclic voltammograms recorded for the SPEG electrodes are shown in Fig. S3 (ESI[†]). No clear redox waves appeared at the electrode with the KB. Meanwhile, a pair of distinct redox waves was recognized in the case of the one with MWCNTs. These results suggest that the latter electrode has a great potential as an SPEG composite cathode. Fig. S4

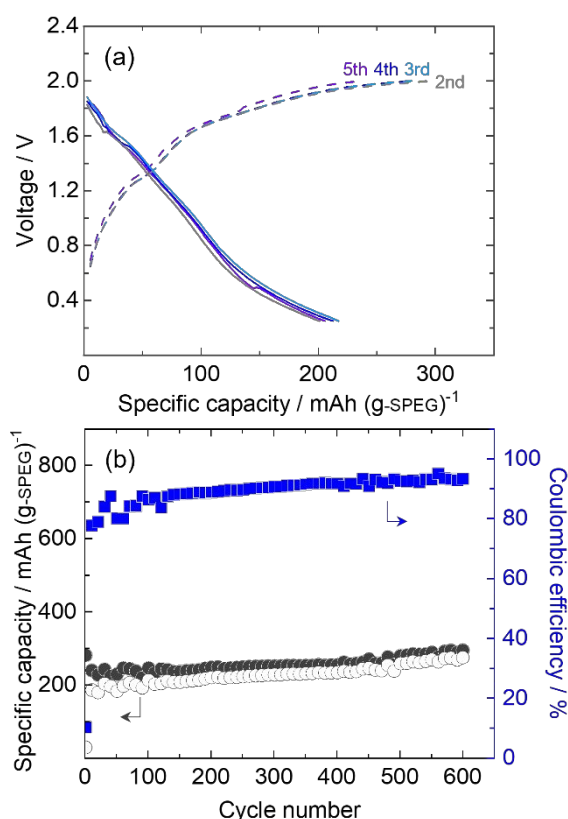


Fig. 4 (a) Galvanostatic charge-discharge curves recorded at the SPEG composite electrode consisting of SPEG (85 wt%), MWCNT (10 wt%), and PTFE (5 wt%) in a 61.0-26.0-13.0 mol% AlCl₃-NaCl-KCl inorganic IL electrolyte at 393 K. (b) Specific capacity (●: charge; ○: discharge) and coulomb efficiency of the SPEG composite electrode at 5000 mA (g-SPEG)⁻¹ as a function of cycle number. The cut-off voltages were 2.00 and 0.20 V.

(ESI[†]) indicates galvanostatic charge-discharge curves recorded at higher SPEG content cathodes. In this measurement, the cut-off voltages were 1.60 and 0.20 V. By applying 10 wt% KB, specific capacity greatly decreases, and the overpotential becomes quite large relative to the SPEG electrode with the 45 wt% KB (cf. Fig. 2a), because sufficient electron conduction pathways cannot be constructed in the composite. However, the use of MWCNTs enables a reduction in the amount of conduction supporting agent required and is very effective in improving the cathode performance. The discharge capacity exceeded 100 mAh (g-SPEG)⁻¹ at 3000 mA (g-SPEG)⁻¹. Fig. 4 exhibits charge-discharge curves over several cycles and results of the cyclability test for the SPEG composite electrode with MWCNT and PTFE at the cut-off voltages of 2.00 and 0.20 V. All the experimental conditions are the same as those employed for collecting the data shown in Fig. 3. Compared to the SPEG electrode with 45 wt% KB, the capacity decreased to 266 mAh (g-SPEG)⁻¹, that is, 554 mAh (g-sulfur)⁻¹, at 5000 mA (g-SPEG)⁻¹, but the cyclability was stable up to 600 cycles. Interestingly, the charge-discharge capacity gradually increased with the cycle number. As the SPEG-MWCNT composite cathode has smoother surface than the SPEG-KB one (Fig. S5 (ESI[†])), this capacity behavior would be caused by the difficulty of electrolyte penetration into the SPEG-MWCNT cathode. At the

same time, the smooth surface may bring out superior cyclability of the SPEG-MWCNT composite cathode. Given the above, we concluded that the SPEG composite electrodes prepared in the present study are promising cathodes for aluminum metal anode rechargeable batteries.

We have successfully designed novel high-capacity cathodes with high-rate capability and favorable cyclability for an Al metal anode rechargeable battery using SPEG as the active material. The SPEG cathode can work in the inorganic chloroaluminate IL at 393 K without any trouble, for example, no sublimation or melting of sulfur in the SPEG, while elemental sulfur is not stable under such heat conditions. The notable feature originates from the unique molecular structure of SPEG reported in our previous paper.²⁵ A combination of sophisticated sulfur-based cathodes and an inorganic IL electrolyte offers the opportunity to readily enhance the aluminum battery performance. This article provides useful information for the creation of next-generation rechargeable batteries utilizing aluminum metal anodes.

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T.T. and S.K. conceived the idea of this battery system. T.K. and H.S. prepared the SPEG. T.T., J.S., Y.U. and H.S. conducted the SPEG composite cathode preparation and electrochemical experiments. T.T. wrote the manuscript. All the authors participated in discussions of the results and in preparing the manuscript.

There are no conflicts to declare.

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