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Electronic Supplementary Information

Rechargeable aluminum batteries utilizing a chloroaluminate inorganic ionic liquid electrolyte

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Experimental details

Electrolyte preparation

The procedures used to prepare the electrolytes, $AlCl_3$–NaCl–KCl (61-26-13 mol%) and $AlCl_3$–[C_2mim]Cl (60-40 mol%), were the same as those reported by Hussey et al.[1,2] Anhydrous $AlCl_3$ (either Nippon Light Metal Company, specially-manufactured ultra-high purity grade, or Fluka, Fe free) was used as received. Anhydrous NaCl (Wako Pure Chemical Industries, Ltd.) and anhydrous KCl (Wako Pure Chemical Industries, Ltd.) were used after vacuum drying at 473 K. 1-Ethyl-3-methylimidazolium chloride [C_2mim]Cl (Merck) was purified according to a previous report.[2] For $AlCl_3$–NaCl–KCl, the salts were mixed and then fused at 423 K. The melt was further purified by leaving small pieces of pure Al wire in the reagent bottle for one week at 423 K. For $AlCl_3$–[C_2mim]Cl, $AlCl_3$ was slowly added to [C_2mim]Cl to prevent thermal decomposition of the [C_2mim]$^+$ cations. The resulting Lewis acidic IL was purified by a constant current electrolysis between the two Al electrodes for three days under agitation at room temperature. All preparation processes were conducted in an Ar-filled glovebox (Vacuum Atmospheres Co., NEXUS II system) with O_2 and H_2O < 1 ppm.

Electrochemical measurements

All electrochemical experiments were conducted in a two-electrode cell assembled in an Ar-filled glovebox. Measurements were carried out with a potentiostat/galvanostat (Princeton Applied Research, VersaSTAT 4), as described previously. Prior to cell assembly, all components were vacuum dried at 373 K for 24 h to remove residual water. Grafoil® (GrafTech Co.) electrodes were prepared without the use of any binder, solvent, or conductive additive in order to ensure that the measured electrochemical characteristics were fully attributed only to the cathode itself. The loading per electrode area is approximately 15 mg cm^{-2}. Aluminum foil (99.999% purity) served as both the reference and counter electrodes. Two sheets of glass fiber (Whatman, GF/A) soaked in the electrolyte were used as the separator. To prevent any unexpected chemical reactions derived from the Lewis acidic electrolyte, a glass container and a molybdenum plate (99.95% purity) current collector were used in the cathode assembly. The set-up is schematically illustrated in Fig. S2. Electrochemical

impedance spectroscopy (EIS) measurements were carried out over a frequency range from 200 kHz to 5 mHz with an AC perturbation amplitude of 10 mV.

Characterization

The ionic conductivity of the two electrolytes was measured with a conductivity meter (S230 SevenCompact, Mettler Toledo) paired with an InLab 751 probe. The electrolytes were thermally equilibrated at each temperature for at least 30 min prior to measurement. X-ray diffraction (XRD) data were collected on a Rigaku Ultima IV diffractometer with Cu Kα radiation at room temperature. The measurements were performed at 40 kV and 40 mA with a step size of 0.01°. For the ex situ XRD study, Grafoil® electrodes were prepared in the cells by applying a constant current of 100 mA g^{-1} for a fixed period, followed by a constant potential charging to complete the anion intercalation. The electrodes recovered from the cells were instantly placed in an air-tight sample holder. Afterwards, the electrodes were immediately removed from the glovebox for XRD measurements. Charged electrodes prepared in $AlCl_3$–[C_2mim]Cl were not rinsed with a solvent before XRD measurements, while those prepared in $AlCl_3$–NaCl–KCl were rinsed with $AlCl_3$–[C_2mim]Cl at 393 K, with an awareness that the electrolyte removal process might alter the electrode chemistry,[3,4] otherwise no XRD signals from Grafoil® could be obtained. The molar concentration of chloroaluminate ILs are calculated based on the method as reported.[5,6] Because the equilibrium constant for the autosolvolysis reaction ($2[AlCl_4]^- \rightleftarrows [Al_2Cl_7]^- + Cl^-$) is quite small,[7] the concentration of Cl^- is vanishing small in Lewis acidic ILs. The total concentration of $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ in the ILs is therefore equal to the total concentration of the cationic species and can be readily evaluated. The weight of the binary RTIL containing one mole of cation is given by[5]

$$M = M_C + 133.34 N_{AlCl_3} / (1 - N_{AlCl_3})$$

where M_C is the molecular weight of the 1-ethyl-3-methylimidazolium chloride, N_{AlCl_3} represents the apparent mole fraction of $AlCl_3$. The bulk concentration of anionic species is then

$$C^*_{Anion} = C^*_{Cation} = 10^3 \rho / M$$

where ρ is the density of the ILs. The concentration of the ternary inorganic IL electrolyte can be derived using the same approach, except that M_C must be apportioned between the two alkali metal chloride salts. The density information for the calculation can be found in the previous reports by Fannin et al.[5] and Midorikawa.[8] The molar concentration obtained for 60-40 mol% $AlCl_3$–[C_2mim]Cl is 3.89 M at 298 K, whereas for 60-30-10 mol% $AlCl_3$–NaCl–KCl, it is 6.56 M at 423 K.

References

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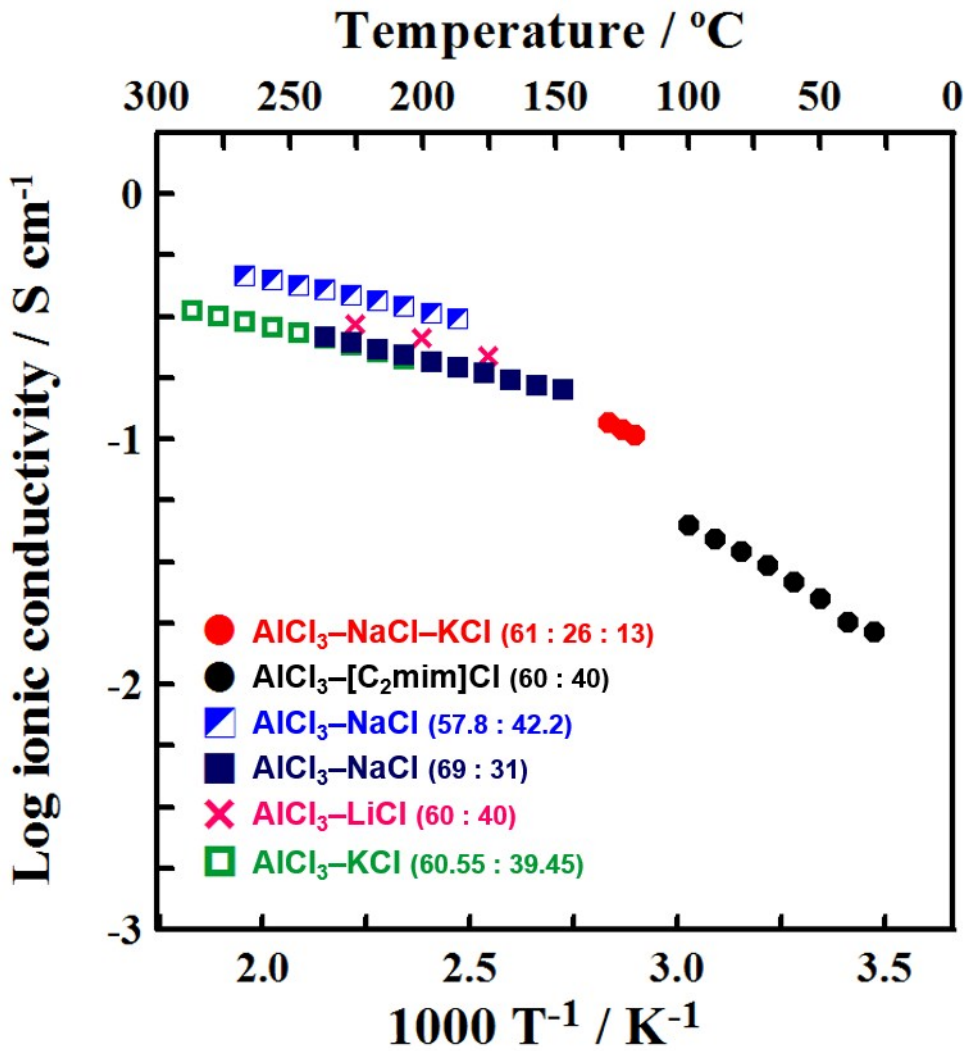

Fig. S1 Arrhenius plots for ionic conductivities of the 61-26-13 mol% $AlCl_3$–NaCl–KCl (red) and the 60-40 mol% $AlCl_3$–[C_2mim]Cl (black) ILs. Some binary $AlCl_3$–alkali metal chloride molten salt systems are included for comparison (G. J. Janz et al. *J. Phys. Chem. Ref. Data*, 1975, **4**, 871.).

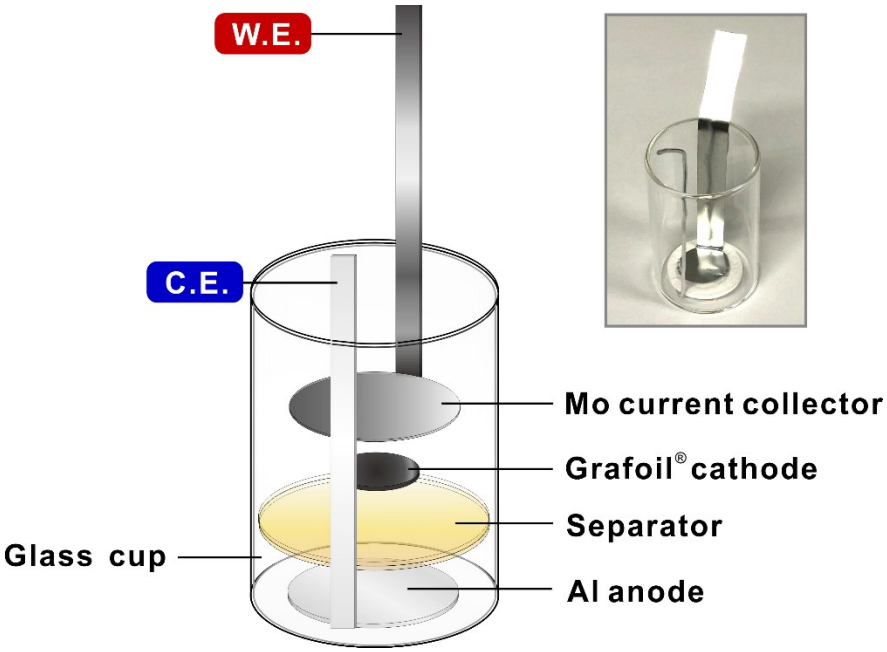

Fig. S2 Schematic illustration and photograph of the assembled Al/Grafoil® cell. A glass container and a molybdenum plate (99.95% purity) current collector were used to prevent any side reactions with the Lewis acidic electrolyte.

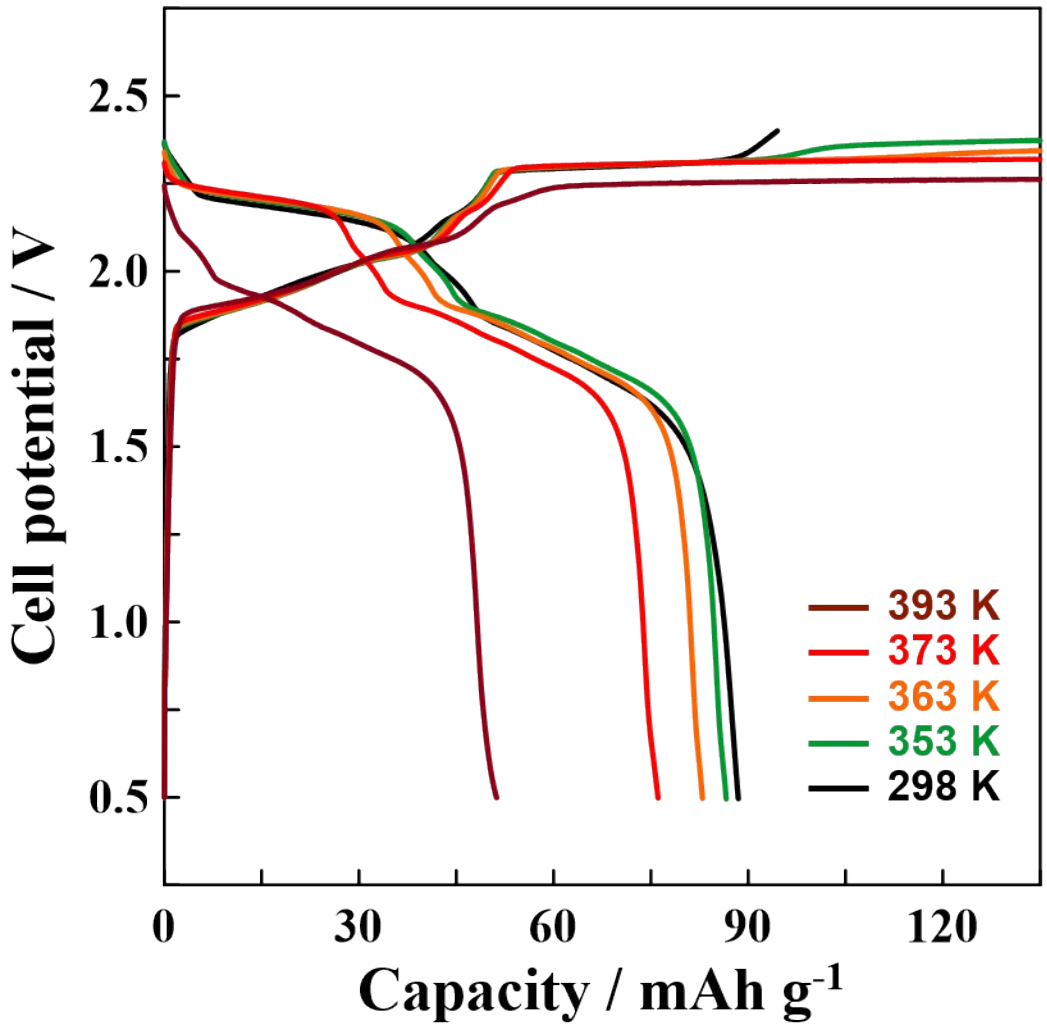

Fig. S3 Galvanostatic charge-discharge curves for a Grafoil® electrode measured at 100 mA g^{-1} in 60-40 mol% $AlCl_3$–[C_2mim]Cl IL over 298–393 K.

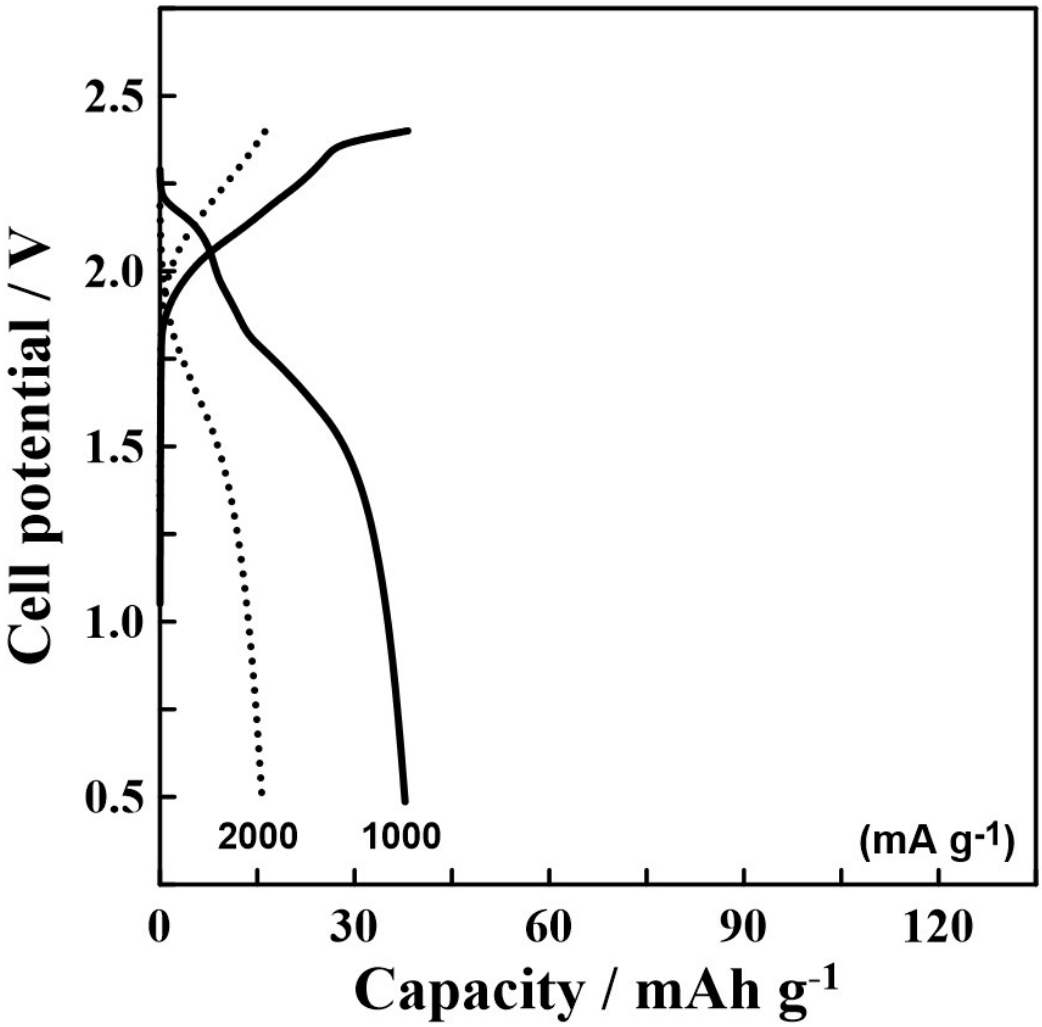

Fig. S4 Galvanostatic charge-discharge curves for a Grafoil® electrode measured at 1000 and 2000 mA g^{-1} in 60-40 mol% $AlCl_3$–[C_2mim]Cl RTIL at 298 K.

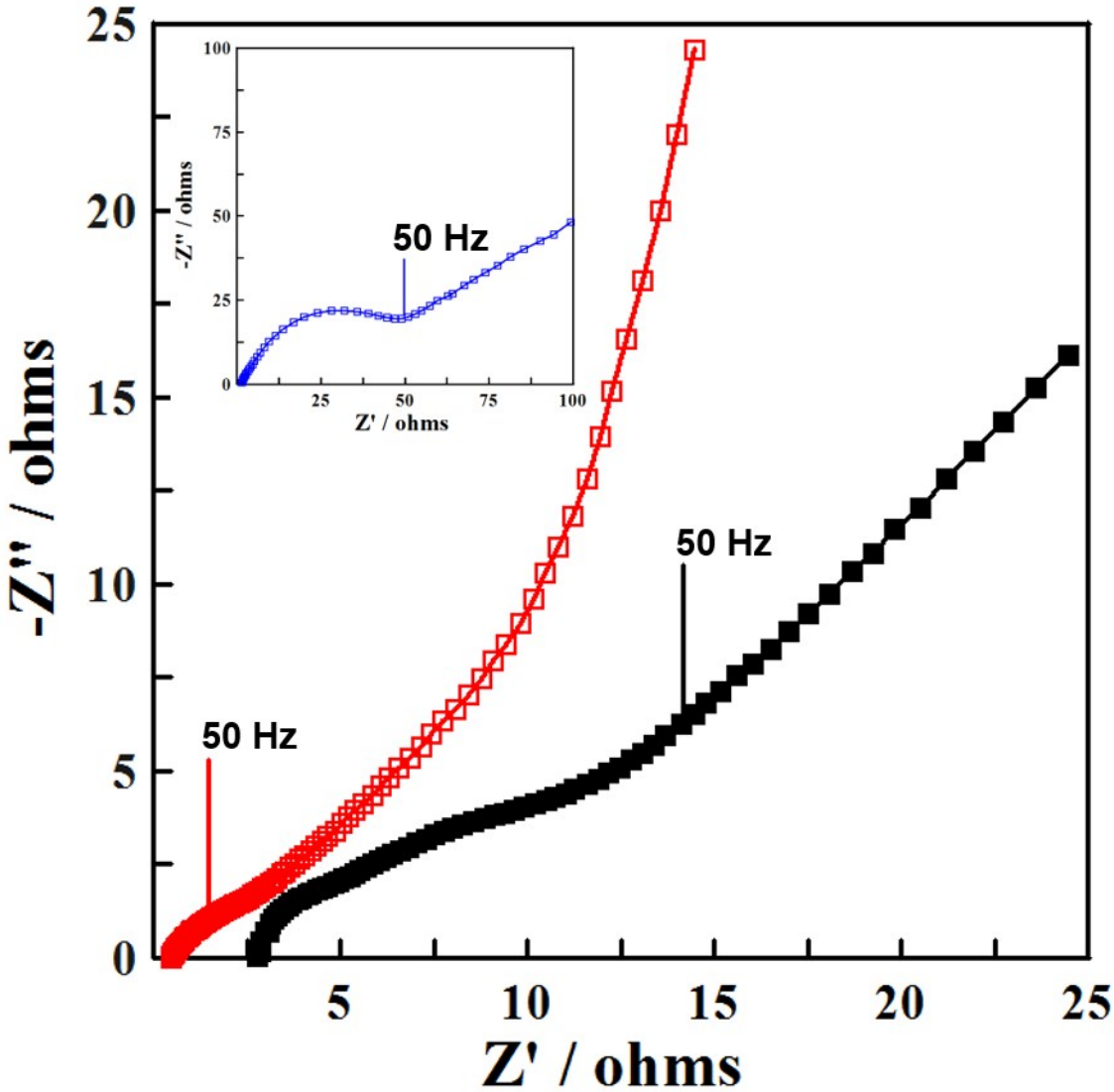

Fig. S5 Nyquist plots of the Al/Grafoil® cell with 61-26-13 mol% $AlCl_3$–NaCl–KCl IL at 393 K (red) and 60-40 mol% $AlCl_3$–[C_2mim]Cl RTIL at 298 K (black). These data were obtained at open circuit potential with an AC perturbation amplitude of 10 mV. An Al/Al symmetrical cell with the RTIL was assembled and measured to identify the characterizing frequency for Al deposition/striping (inset, blue).

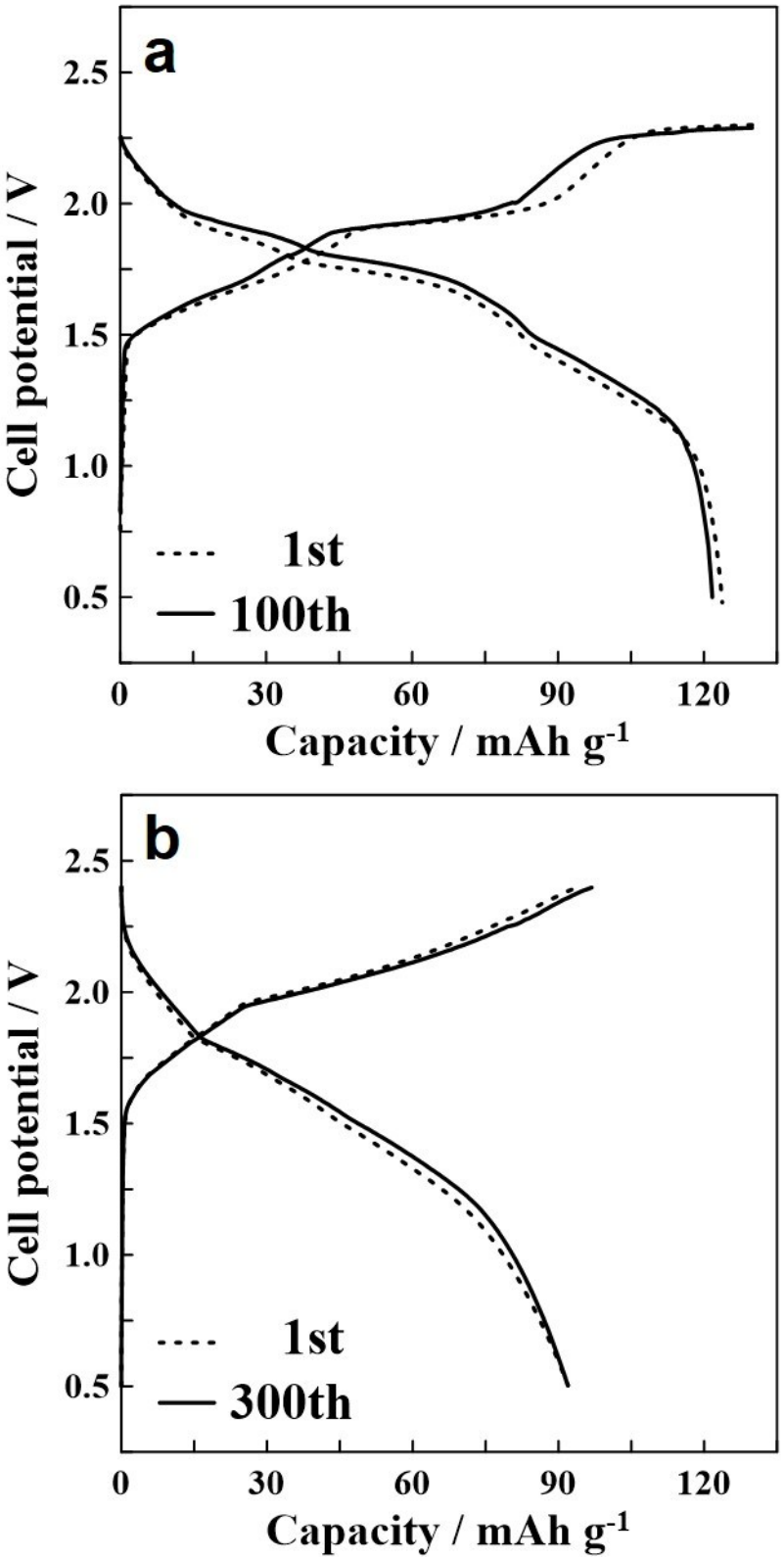

Fig. S6 Corresponding charge-discharge curves of the Al/Grafoil® cell measured in the inorganic IL at 393 K at current densities of (a) 1000 and (b) 4000 mA g^{-1}.