

## Electronic Supplementary Information

### **A low-cost and dendrite-free rechargeable aluminium-ion battery with superior performance**

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### **Methods**

#### **Preparation of the “water-in-salt” aqueous electrolytes**

An aqueous  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  electrolyte with various concentrations was made by mixing aluminium chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , AR 97%, Aladdin) with deionized water (18.2 M $\Omega$  cm, Barnstead Smart2Pure, Thermo Scientific, USA). The  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  electrolyte was first baked at 60°C in air to remove the absorbed water. After mixing, the electrolytes were stirred to form a uniform state (Fig. S1 (b)). The mass ratio of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  to  $\text{H}_2\text{O}$  varied from 4–16. At the high mass ratio, the electrolyte looked like salt and the predominant anions are  $\text{Al}_2\text{Cl}_7^-$ ; the electrolyte became transparent and more  $\text{AlCl}_4^-$  and  $\text{Al}^{3+}$  were formed<sup>26</sup> at a lower mass ratio. The PMMA cell was mainly filled with electrolyte at a mass ratio of 12. Raman spectra (120-600  $\text{cm}^{-1}$ ) were obtained using a 514-nm laser with a resolution of 2  $\text{cm}^{-1}$ .

#### **Preparation of the electrodes**

Commercial graphite powder (99.95%, Aladdin, China) was used as a positive electrode material. The positive electrode ink comprised graphite, acetylene black (STREM Chemicals, USA) and polyvinylidene fluoride (PVDF, HSV900, Arkema, France) (8:1:1) dissolved in absolute ethanol (VWR International, USA), which was then treated in a supersonic bath for 1 h. The ink was dropped onto a carbon paper substrate (060, Toray, Japan) and then dried at 80°C for 12 h in air. Carbon paper was selected as the collector because it does not react with the  $\text{AlCl}_3$  solution, thereby avoiding the possibility of side reactions. Because the non-rechargeable Al-air battery reaction occurred at roughly 0.8V with a carbon substrate as the air-breathing positive electrode the discharge-cutoff voltage was set at 0.8V. High-purity aluminium foil (99.9%, Aladdin, China) was used as the negative electrode material. The microstructure and chemistry of the graphite positive electrode and the aluminium negative electrode were probed using atomic force microscope (AFM) (Biker Multimode 8), high-resolution transmission electron microscopy (HR-TEM) (FEI Tecnai G2) and field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4800) and an EDX detector (X-Max 80 EDS Detector, Oxford Instruments, UK).

### Electrochemical measurements

All of the electrochemical tests were conducted in air at room temperature ( $\approx 25^\circ\text{C}$ ) rather than in a glove box environment. The PMMA cell was constructed using a graphite positive electrode and an Al electrode with filter paper (Whatman No.1) as separator. The “water-in-salt” electrolyte (prepared with mass ratios of 16, 12, 8 and 4) was dropped into the batteries. The batteries were then cycled at various current densities using a battery testing system (CT2001A, Wuhan Land, China). For the long-term cycling stability tests, an Al/graphite cell using the “water-in-salt” electrolyte ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O} : \text{H}_2\text{O} \approx 12$ , by mass) was charged/discharged at a current density of  $500 \text{ mA g}^{-1}$  (Fig. 1b). To test the rate capability and the fast-charge/slow-discharge behaviors of the Al/graphite battery, the current densities varied from  $250\text{--}1000 \text{ mA g}^{-1}$  (Figs. 1c, d).

Cyclic voltammetry measurements were performed using an electrochemical workstation (CHI 760D, Shanghai Chenhua, China) in either three-electrode or two-electrode mode. The working electrode was an Al foil/a graphite attached to a platinum disk electrode instead of carbon paper (to avoid oxidation reduction reaction (ORR)), and an Ag/AgCl (in saturated KCL) electrode was used as the reference electrode in the three-electrode mode. The scanning voltage range was set from  $-4$  to  $0.6\text{V}$  (versus Ag/AgCl) and  $-1.8$  to  $1.8\text{V}$  (versus Ag/AgCl) for the Al electrode and the graphite positive electrode, respectively, with a scan rate of  $10\text{mV s}^{-1}$  (Fig. 3a). To investigate the working voltage range of the full battery, measurements under the two-electrode mode were obtained using a graphite positive electrode against an Al electrode in a PMMA cell with the “water-in-salt” aqueous  $\text{AlCl}_3$  electrolyte (mass ratio: 12). The scanning voltage range was set from  $-0.2\text{V}$  to  $4.2\text{V}$  at a scan rate of  $5\text{mV s}^{-1}$  (Fig. 3b).

### XRD and XPS studies of graphite positive electrodes

For the *ex situ* XRD study, an Al/graphite battery with a “water-in-salt” electrolyte was charged at a constant current density of  $50 \text{ mA g}^{-1}$ . The reactions were stopped at half-way of the fully charged state (reaching  $80\text{mAh g}^{-1}$ ) and the fully charged state (reaching  $165\text{mAh g}^{-1}$ ) to observe shifts in the peaks of the X-ray diffraction patterns (e.g., Fig. 2d).

The GICs exhibited well-defined patterns, which related to the stages ( $n$ ), periodic repeat distance ( $I_C$ ), the intercalant gallery height ( $d_i$ ) and the gallery expansion ( $\Delta d$ ). The intercalant gallery height can be calculated using equation (3)<sup>29</sup>:

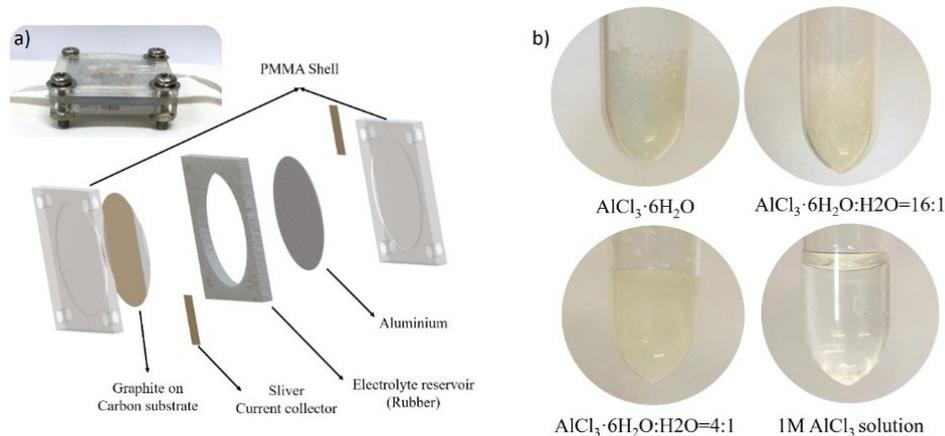
$$I_C = d_i + 3.35\text{\AA} \cdot (n - 1) = \Delta d + 3.35\text{\AA} \cdot n = l \cdot d_{obs} \quad (3)$$

where  $l$  is the index of the  $(00l)$  planes oriented in the stacking direction and  $d_{\text{obs}}$  is the observed value of the spacing between two adjacent planes (Fig. 2d). The  $d$  spacing of pristine graphite is 3.35 Å. During the charging process, many new peaks arose, representing a stage  $n$  GIC. The dominant peak was  $(00n+1)$ , and the second most dominant peak was  $(00n+2)$ . Based on our experimental data, by increasing the charging state from half-way of the fully charged state ( $80\text{mA h g}^{-1}$ ) to the fully charged state ( $165\text{mA h g}^{-1}$ ) the distance between the  $(00n+1)$  and  $(00n+2)$  peaks varied as more ions intercalated/de-intercalated. The  $d$  spacing values of the  $(00n+1)$  and  $(00n+2)$  peaks were calculated from the XRD data. By determining the ratio of the  $d_{(n+2)}/d_{(n+1)}$  peak position and correlating these measurements with the ratios of stage pure GICs<sup>29</sup>, the most dominant stage phase of the observed GIC can be determined. After assigning the  $(00l)$  indices, the intercalant gallery height ( $d_i$ ) can be calculated using equation (3).

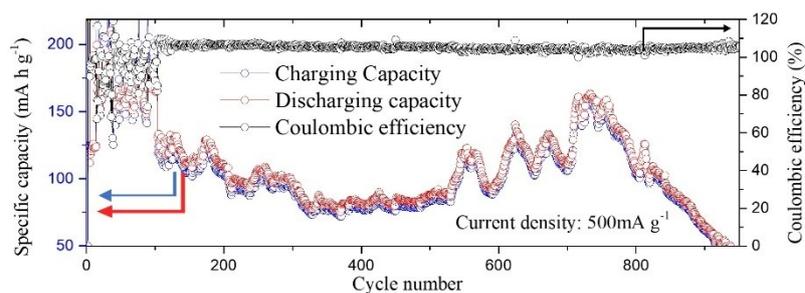
Al/graphite batteries were fully charged/discharged at a current density of  $500\text{ mA g}^{-1}$  for XPS analysis. The graphite positive electrodes were washed with methanol and D.I water to remove the residual  $\text{AlCl}_3$  electrolyte and then baked at  $80^\circ\text{C}$  to remove the residual methanol. The XPS spectra were collected on a PHI Model 5820 XPS Microprobe (PHI, USA).

**Supplementary Note 1:** Corrosion is easily occurred in coin cells, resulting in decreased performance (Fig. S2&S3). Thus, PMMA was utilized as battery shells (Fig. S1a), and no corrosion was observed under this configuration.

**Supplementary Note 2:** Al ion batteries using pure powder of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and “water-in-salt”  $\text{Al}(\text{NO}_3)_3$  ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : \text{H}_2\text{O} \approx 12$ , by mass;  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , ACS 98%, Aladdin, China) as electrolyte (Figure S10) were demonstrated, but both shown no capacity. It revealed the significance of water and  $\text{AlCl}_4^-$  anions to the battery system.



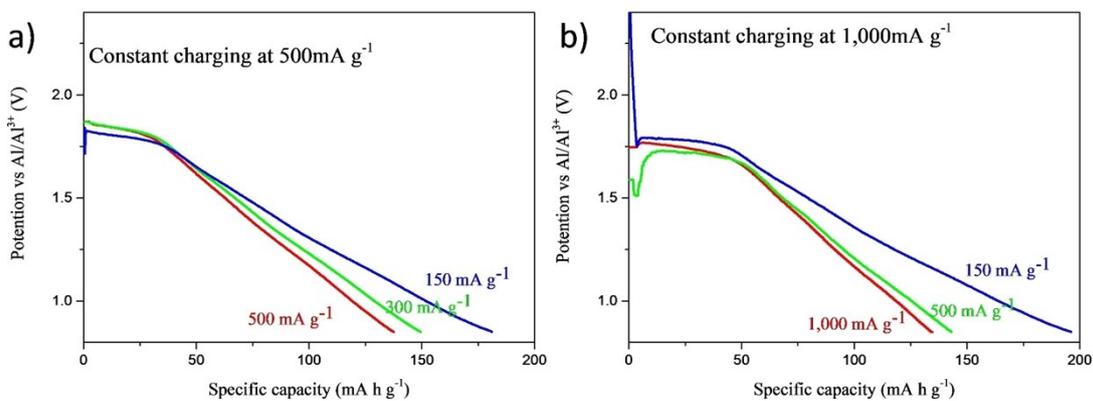
**Figure S1.** a) Assembly of Al/graphite PMMA cell. b) “Water-in-salt” aqueous  $\text{AlCl}_3$  electrolyte in different concentrations.



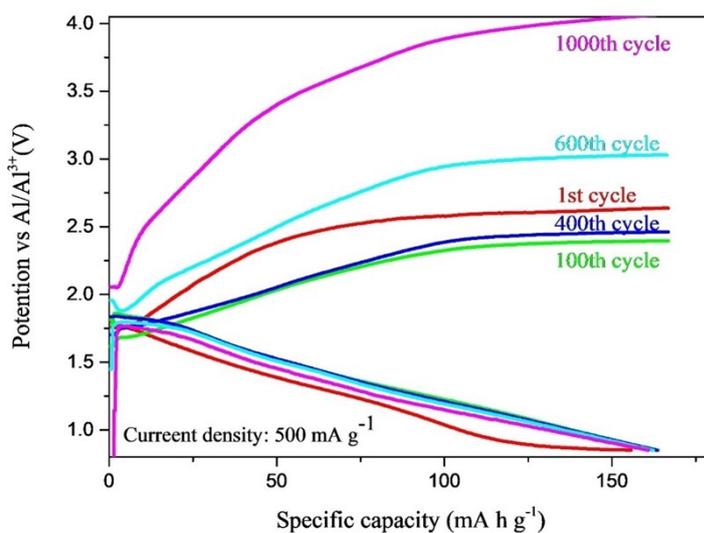
**Figure S2.** Charge-discharge performance of a coin battery with “water-in-slat” aqueous  $\text{AlCl}_3$  electrolyte (failed after 900 cycles due to corrosion).



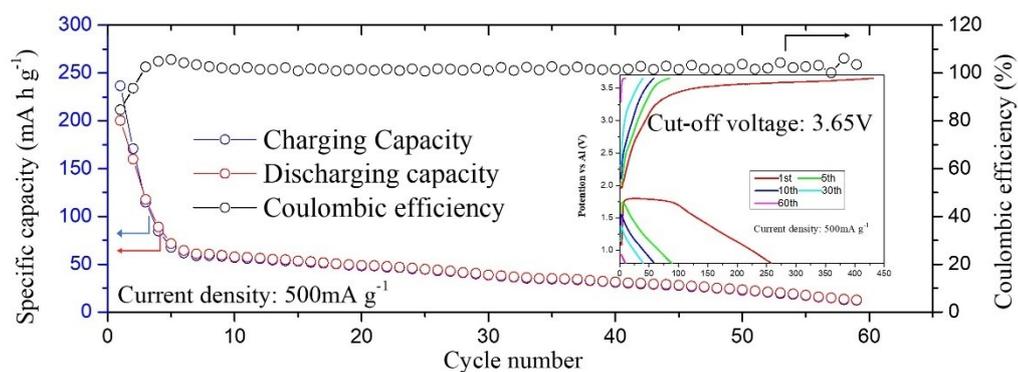
**Figure S3.** Photographs of coin shells after 1000 cycles, showing heavy corrosion in the positive electrode shell.



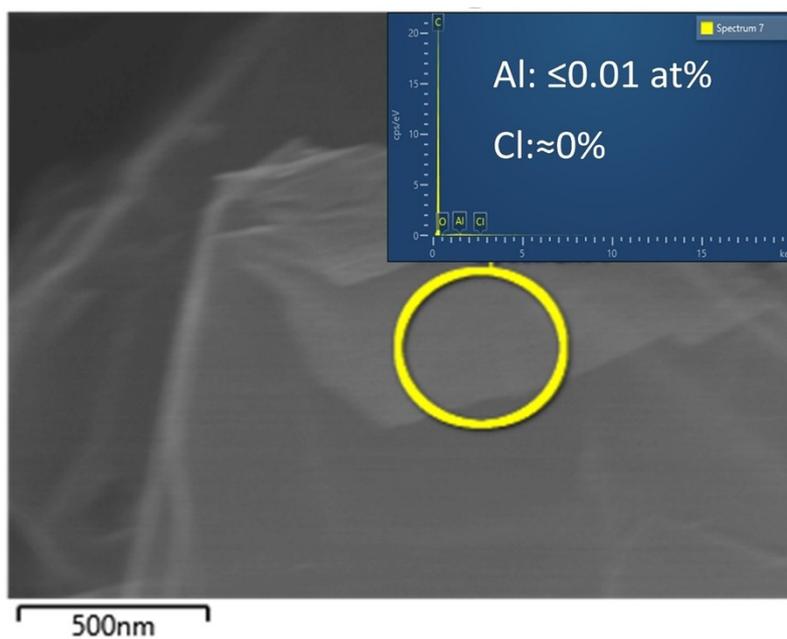
**Figure S4.** Discharge curves at different current densities under constant charging at a)  $500 \text{ mA g}^{-1}$ ; and b)  $1000 \text{ mA g}^{-1}$ .



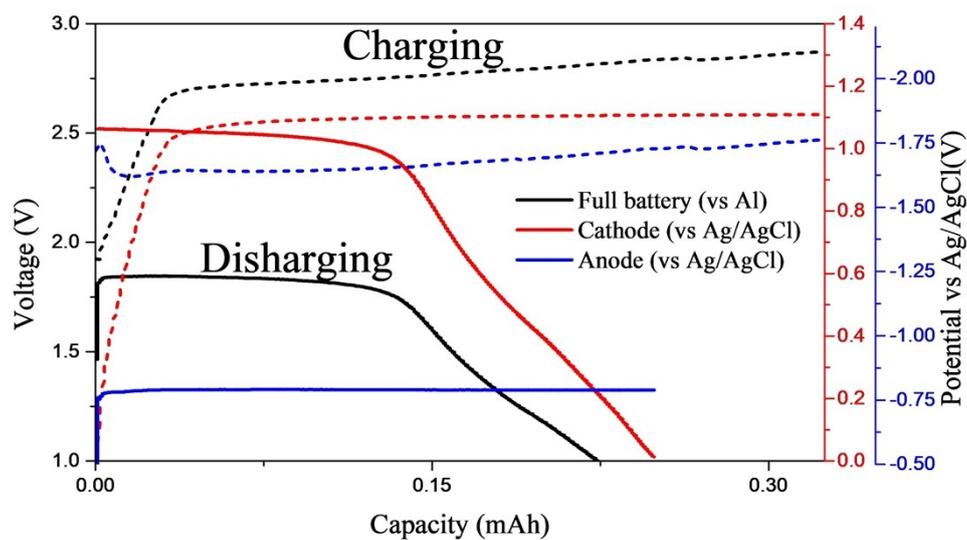
**Figure S5.** Charge–discharge curves at  $500 \text{ mA g}^{-1}$  under different cycles a) of 1<sup>st</sup>, 100<sup>th</sup>, 400<sup>th</sup>, 600<sup>th</sup> and 1000<sup>th</sup> cycles.



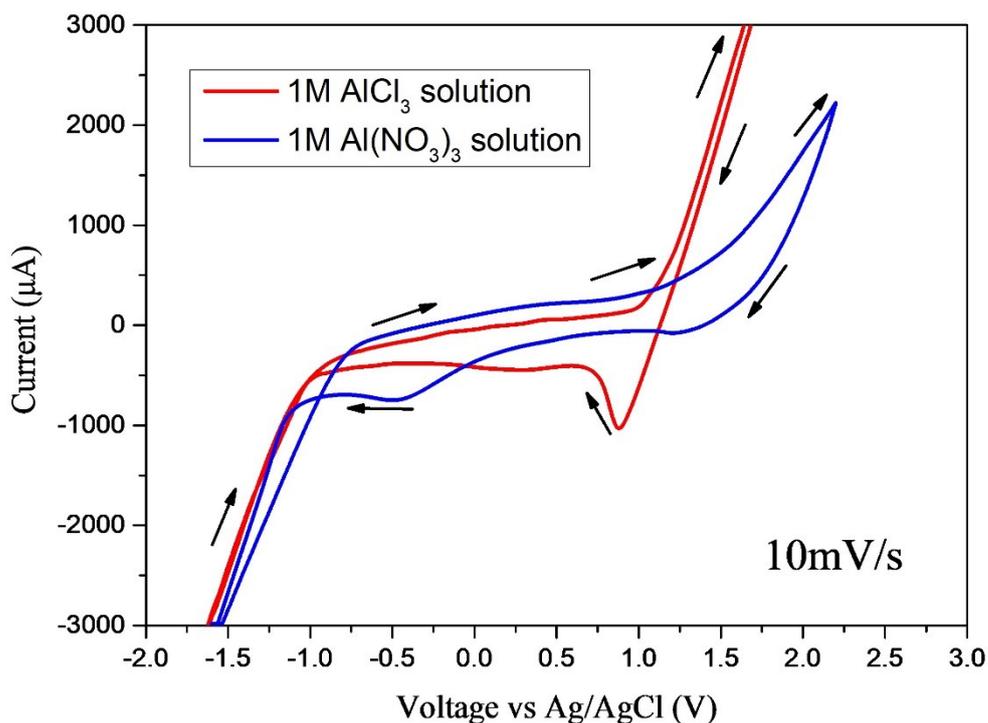
**Figure S6.** Charge-discharge performance showing capacity declines quickly by the charging cut-off voltage.



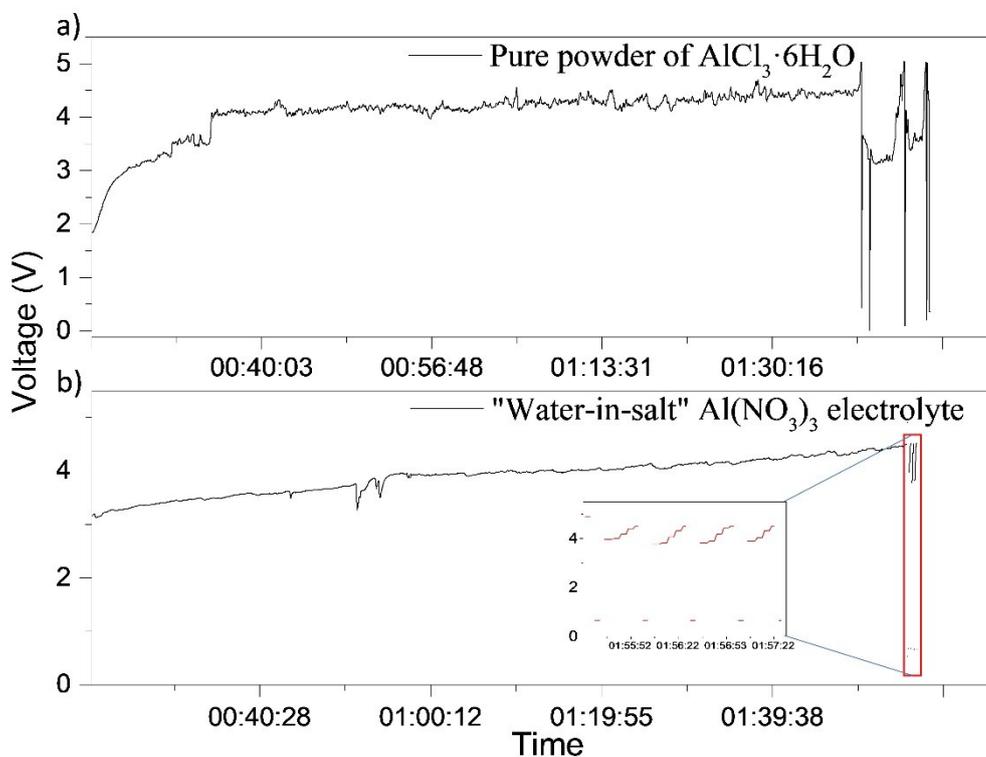
**Figure S7.** EDX element analyse images for Al and Cl for pristine graphite positive electrode.



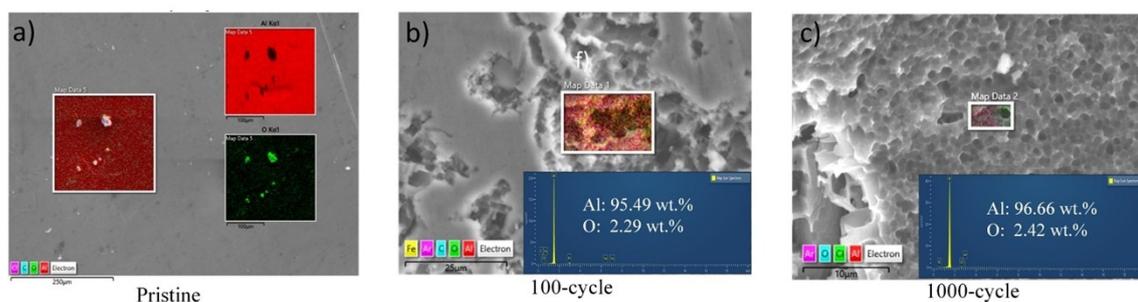
**Figure S8.** Charge-discharge curves in 2-electrode and 3-electrode (vs Ag/AgCl) mode.



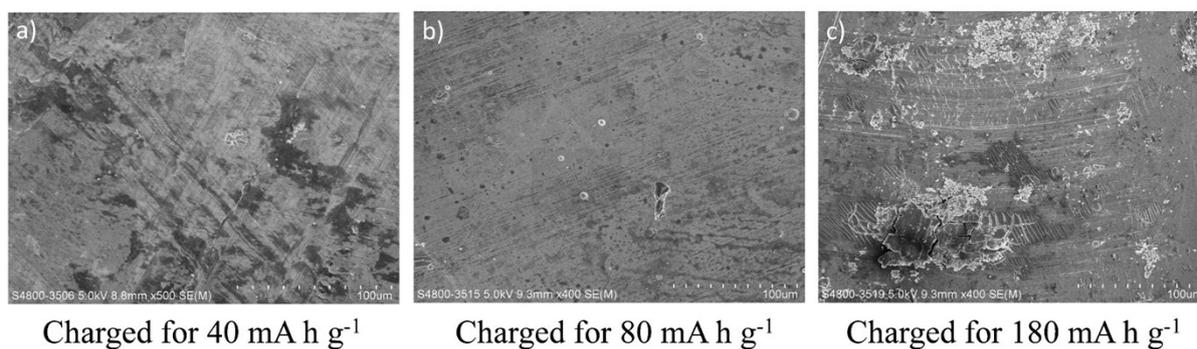
**Figure S9.** CV curves of positive electrode in AlCl<sub>3</sub> and Al(NO<sub>3</sub>)<sub>3</sub> at a scan rate of 10 mV s<sup>-1</sup> against an Ag/AgCl reference electrode.



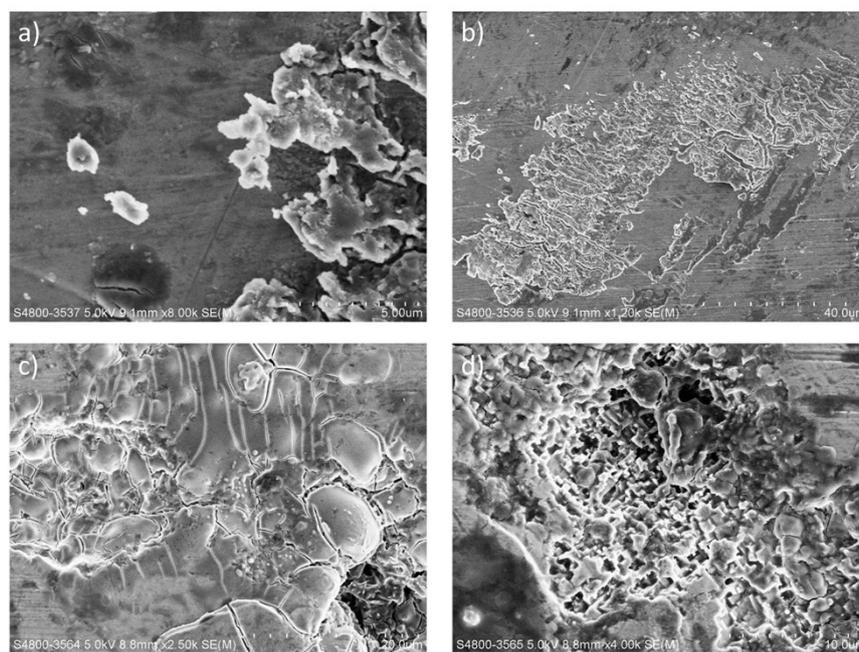
**Figure S10.** Charge-discharge of the Al-ion battery using (a) pure powder of AlCl<sub>3</sub>·6H<sub>2</sub>O and (b) "water-in-salt" Al(NO<sub>3</sub>)<sub>3</sub> electrolyte. Base curves showed no discharging capacity.



**Figure S11.** EDX element analyse images for Al and O of the Al electrode at pristine (a), 100-cycle (b) and 1000-cycle (c). Scale bars are shown on the images.



**Figure S12.** A large-scale image of deposited Al on the Al metal electrode at a current of 500 mA g<sup>-1</sup> charging for various capacities. Scar bar: 100 μm.



**Figure S13.** Deposited Al on Al metal (a, b) charged for 160 mA h g<sup>-1</sup> at a current density of 100 mA g<sup>-1</sup>; (c, d) fully discharged after charged for 330 mA h g<sup>-1</sup> at a current density of 500 mA g<sup>-1</sup>. Scar bar: 5 μm (a), 40 μm (b), 20 μm (c) and 10 μm (d).