Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A rechargeable Al-ion battery: Al/molten $AlCl_3$-Urea/graphite

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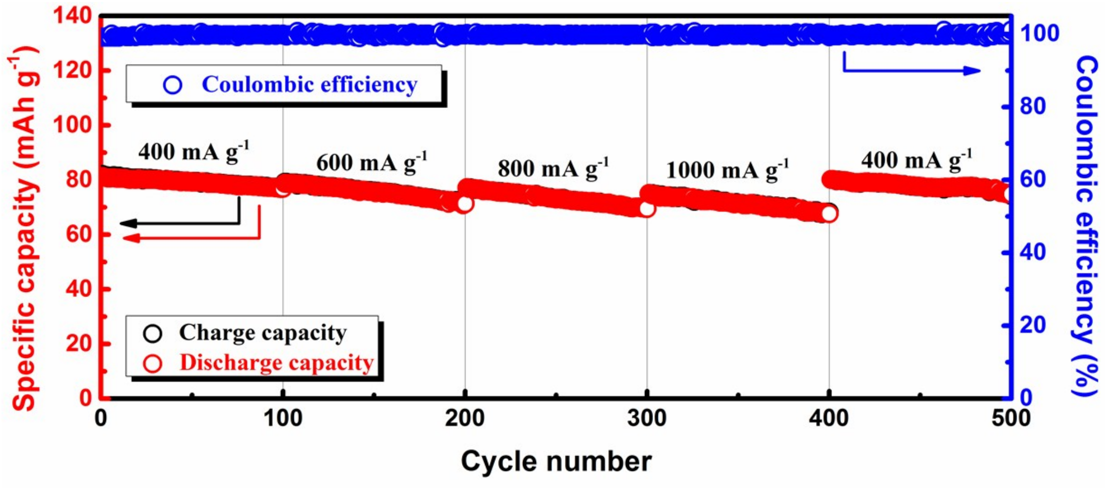
Experimental Section

Fabrication of Al-ion batteries: $AlCl_3$ (99.99 % purity) and urea (99.8 % purity) were purchased from Aladdin. Aluminum foil (0.2 mm thickness, 99.99 % purity), molybdenum foil (0.2 mm thickness, 99.0 % purity) and carbon paper (0.2 mm thickness, 99.999 % purity) were received from General Research Institute for Nonferrous Metals (Beijing, P.R. China). The liquid electrolyte was prepared by slowly mixing $AlCl_3$ and urea with a mole ratio of 1.5 in an Ar-filled glove box, and the solids reacted with each other immediately without external heating, resulting in transparent, yellow and viscous liquid at ambient temperature. Aluminium foil (20 mm × 20 mm) polished by fine sandpaper and cleaned in an ultrasonic bath was dried and used as anode. Carbon paper (15 mm × 15 mm) wrapped by a piece of glass fiber (GF/D) from Whatman was employed as cathode. Molybdenum foil (4 mm × 25 mm) attached to the cathode was used as current collector. The liquid electrolyte and those electrodes were placed in a glass electrolytic tank with a Teflon cap in an argon filled glove box. The assembled battery was operated in an oil-bath heater.

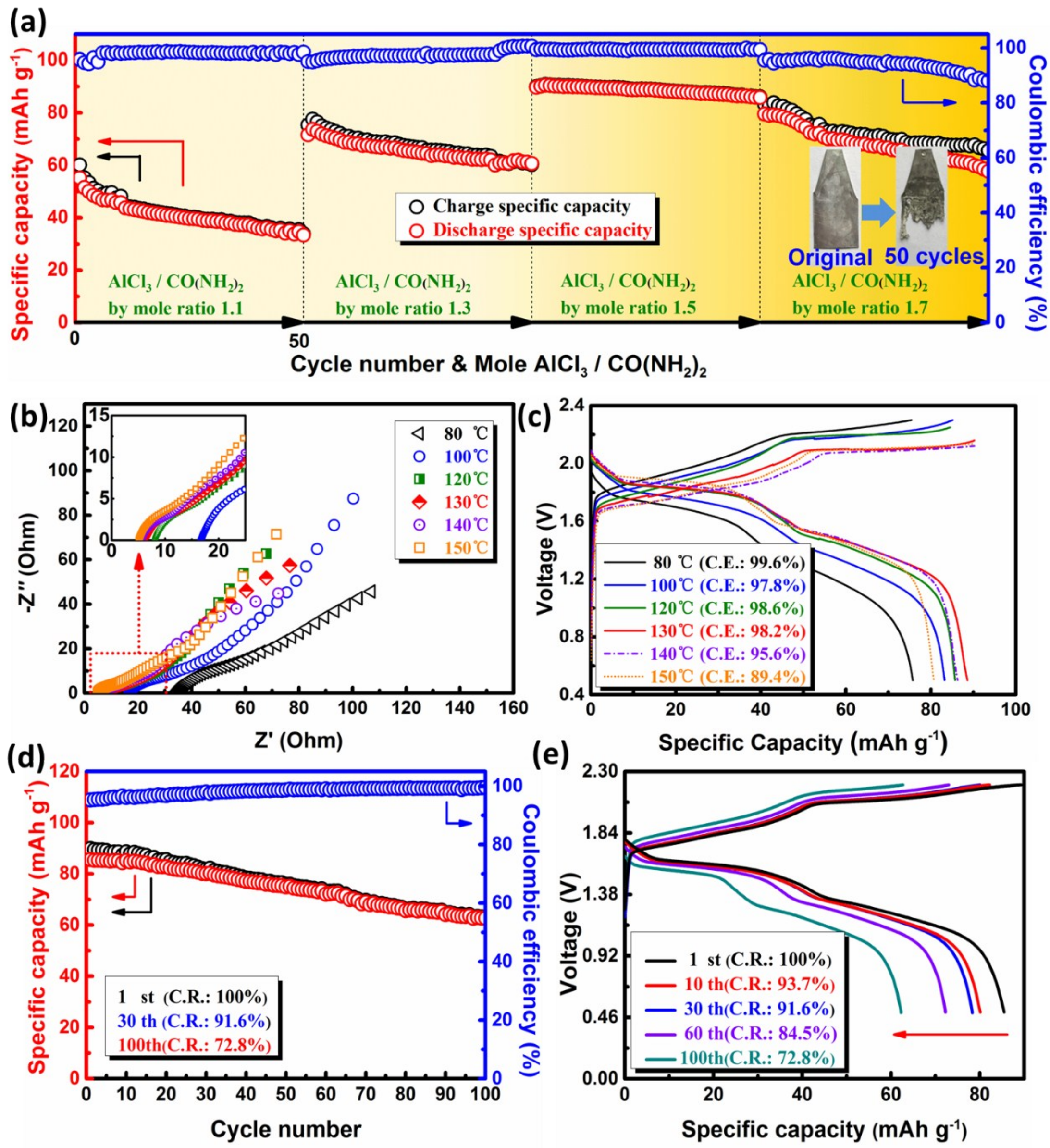
Electrochemical measurements: Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a two-electrode configuration with Solartron potentiostat (Solatron 1287/1255B). Carbon paper was used as working electrode, and the aluminum foil was used as the counter electrode. CV measurements were carried out in the voltage range 0.5 to 2.2 V (vs. Al^{3+}/Al) or 0.5 to 2.5 V at a scan rate of 1 mV s^{-1}. EIS was performed at a voltage bias of 0.0 V with a frequency range of 10^5 to 0.1 Hz various temperatures. Galvanostatic charge-discharge testing was performed at various current densities in the voltage range of 0.5 to 2.2 V using New BTS-53 tester.

Material and electrode Characterizations: XPS of the carbon paper electrodes was conducted using a XPS microprobe (XPS, Kratos AXIS Ultra DLD). AES was conducted for element analysis of the carbon electrodes using a PHI 700 Scanning Auger Nano probe operating at 10 kV and 10 nA. The fully charged graphite electrodes were washed with anhydrous ethanol and dried at a temperature of 60 °C to remove any residual electrolyte for XPS and AES analysis. *Ex-situ* X-ray diffraction (XRD, Model MAC, M21XVHF22) and Raman spectra were performed to study the crystal structure of the carbon paper during charging process. The morphologies of original and cycled carbon paper electrodes were characterized by transmission electron microscopy (TEM, JEOL, JEM-2010).

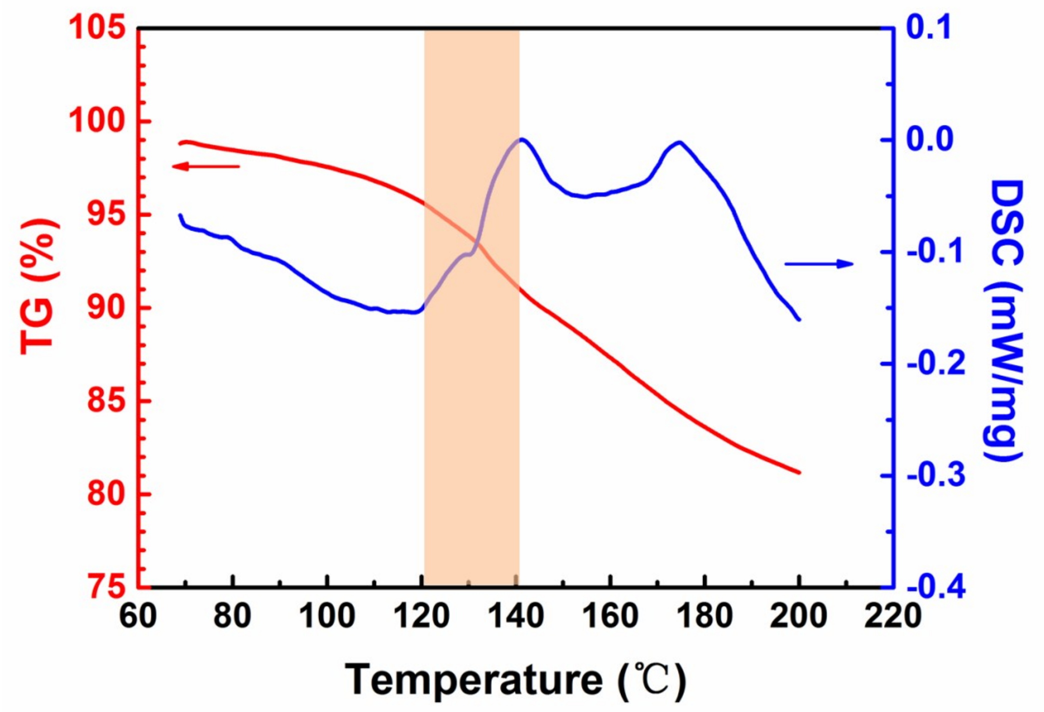
Simultaneous TG/DSC of the electrolyte: Simultaneous TG/DSC was performed using a Netzsch Model STA409C instrument with its SiC furnace. The electrolyte with mole ratio of 1.5 was contained in the manufacturer's alumina crucibles. Heating rate of 2 ºC min^{-1} was performed and the sample was typically heated to 200 °C to ensure complete decomposition.



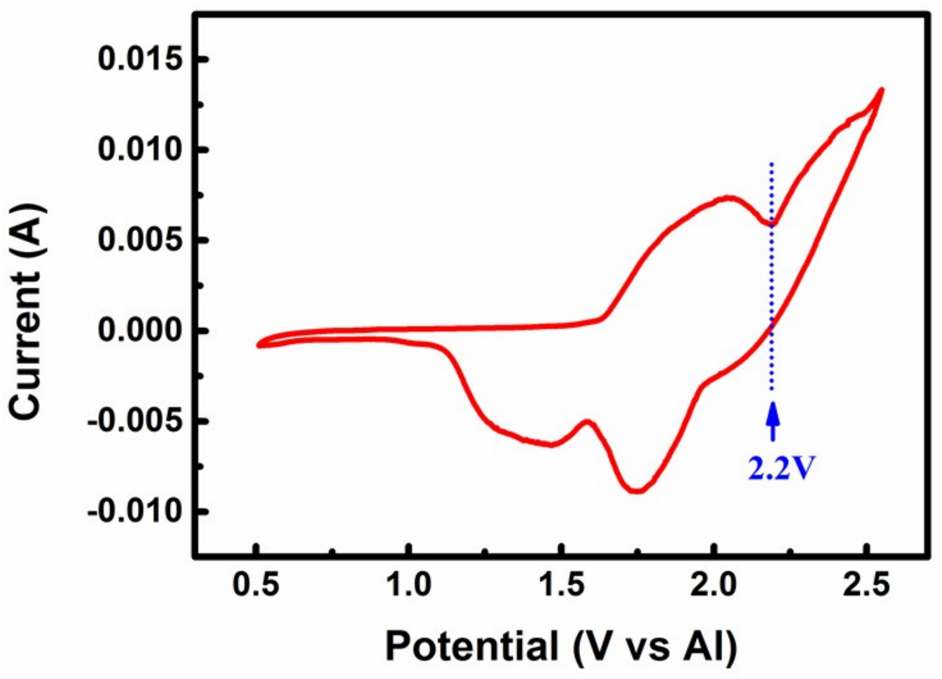
Supplementary Fig 1. High-rate capability performance and stability of the battery. The specific capacity and coulombic efficiency at large current densities ranging from 400 to 1000 mA g^{-1}.



Supplementary Fig 2. Optimization of the electrolyte molar ratio and temperature. (a). The specific capacity and coulombic efficiency at a current density of 200 mA g^{-1} in the $AlCl_3$/Urea electrolytes with various mole ratios (1.1, 1.3, 1.5 and 1.7), insert is photographs of the original and cycled Al electrodes in the $AlCl_3$/Urea with a mole ratio of 1.7. (b). Nyquist plots of the battery at different temperatures ranging from 80 to 150 °C. (c). The 1stgalvanostatic curves and coulombic efficiency (C.E.) of the battery at different temperatures ranging from 80 to 150 °C with a current density of 200 mA g^{-1}. (d). The cycling performance and (e). The 1st, 10th, 30th, 60th and 100th galvanostatic curves and corresponding capacity retention rates (C.R.) of the battery at 130 °C with a current density of 200mA g^{-1}, respectively.



Supplementary Fig 3. TG and DSC curves of the electrolyte with the mole ratio of 1.5.



Supplementary Fig 4. Electrochemical stability of liquid electrolyte. Cyclic voltammetry curve of the battery at 1 mV s^{-1}.