

Supporting Information

**Electrochemical properties of aluminum anode
in an ionic liquid electrolyte
for rechargeable aluminum-ion batteries**

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Experimental Section

Preparation of aluminum anode

Two types of aluminum anodes were used. High-purity aluminum foil (99.99%, Samyoung Electronics) was cleaned with distilled water and sonicated in ethanol and acetone for 30 min each. Afterward, the aluminum was electropolished in perchloric acid + ethanol solution (1:3 volume ratio) at 20 V, 1 A cm⁻² for 1 min, using a Pt plate as the counter electrode. After electropolishing, sequentially, thin oxide film can be reformed in solution with water. However, the advantage of using perchloric acid is to achieve the proper pH to ensure that Al ionizes into Al³⁺ and does not form oxides in the anodic reaction. Water and ethanol can be adsorbed on Al surface and they can reduce the transport of ions to the Al electrode/electrolyte interface. Therefore, it suggests that the electropolished Al surface has a very thin oxide film and uniform surface, compared to as-is aluminum surface.¹ Finally, the electro-polished aluminum surface became shiny like a mirror. Scanning electron microscopy (FE-SEM, Hitach S-4300) was used to observe the difference between electro-polished aluminum and native aluminum.

Preparation of β -MnO₂/C cathode

Potassium permanganate (KMnO₄, ≥99.0%, Sigma Aldrich) and manganese sulfate monohydrate (MnSO₄·H₂O, ≥99.0%, Sigma Aldrich) were dissolved in distilled water, followed by stirring for 30 min. Afterward, Ketjen black solution was added drop-wise to the mixture solution for 1 h. Then, the solution was placed into an autoclave and reacted at 170°C for 12 h. After the reaction, the mixture was cleaned with distilled water and ethanol several times, following by drying at 80 °C to remove the solvent. Finally, the MnOOH/C obtained was ground and sintered at 250 °C for 1 h, resulting in the formation of fine β -MnO₂/C.

Preparation of liquid electrolyte

A room temperature ionic liquid (RTIL) was prepared by mixing 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl, ≥97%, TCI) and anhydrous aluminum chloride (AlCl₃, 99.99%, Sigma-Aldrich) via a eutectic system. The ionic liquid electrolyte was prepared in an argon-filled glove box (O₂ ppm < 1.0), resulting in the light-yellow colored transparent liquid. The mole ratio of [EMIm]Cl to AlCl₃ used in electrochemical test was 1:1.3. Chloroaluminate anions (AlCl₄⁻ and Al₂Cl₇⁻) in the electrolyte were confirmed by FT-Raman analysis because, as in previous studies,² the electrolyte composition was varied to achieve the best performance by choosing different chloroaluminate anions (Fig. S4).

Electrochemical measurements

All electrochemical measurements were performed at room temperature. A custom-built Swagelok-type cell (diameter 14 mm) was used for the cell test, which composed of loaders in both side made by SUS316, and upper cap, bottom cap and body were made by PTFE. As is well known, SUS 316 (loader) and PTFE (teflon) have good corrosion resistance in acid solution. Therefore, this cell is greatly stable in the acidic electrolyte for Al-ion battery (Fig. S5). 5 mg weight of β -MnO₂/C cathode and electro-polished or native aluminum anode were used as electrode materials. A glass fiber filter paper (Whatman GF/B) was placed between the two electrodes as a separator. The electrolyte was 400 μ l of [EMIm]Cl + AlCl₃ ionic liquid (mole ratio of 1:1.3). All cells were assembled in an argon filled glove box (O₂ ppm < 1.0). Cyclic voltammetry (CV) was carried out using a potentiostat with a platinum wire as the counter electrode and aluminum metal as reference electrode.²⁻⁵ The galvanostatic charge/discharge cycle was operated at different current densities in the potential range of 2.45 – 0.01 V, with a battery cycler system (WBCS3000, WonATech). In this study, all specific capacity data were calculated based on cathode weight. The surface morphologies of the aluminum anodes were investigated by scanning electron microscopy (FE-SEM, Hitach S-4300) and atomic force microscopy (AFM).

Figure S1. Full-cell cyclic voltammetry of aluminum for (a) electro-polished Al and (b) native Al with β -MnO₂/C as cathode in 1.3:1 mole ratio AlCl₃/[EMIm]Cl at a scan rate 10 mV s⁻¹.

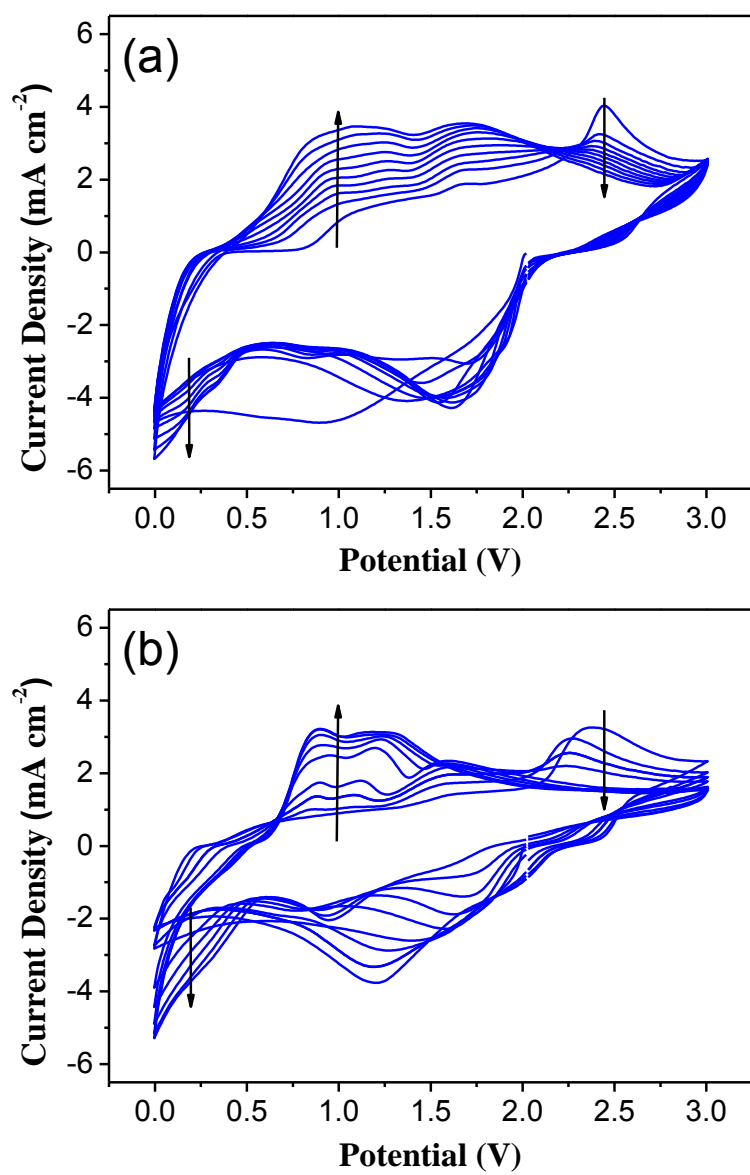


Figure S2. Charge and discharge curves of a rechargeable Al cells in the potential range of 2.45 – 0.01 V at current density of 15 mA g^{-1} (0.1 mA cm^{-2}) for (a) electro-polished Al and (b) native Al, 75 mA g^{-1} (0.5 mA cm^{-2}) for (c) electro-polished Al and (d) native Al, and 150 mA g^{-1} (1.0 mA cm^{-2}) for (e) electro-polished Al and (f) native Al with an electrolyte solution with 1.3:1 ratio of AlCl_3 : $[\text{EMIm}]\text{Cl}$.

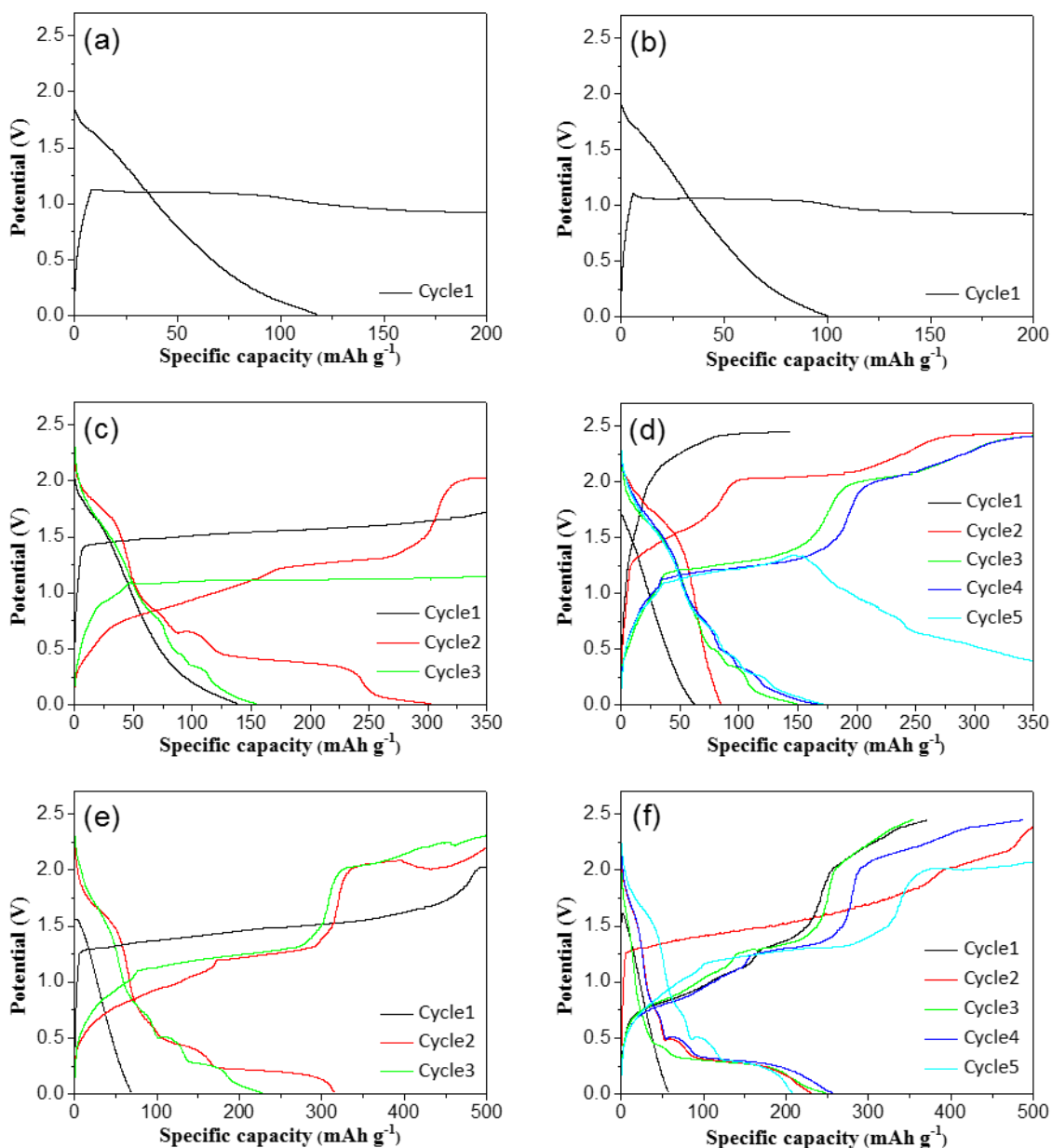


Figure S3. Galvanostatic charge/discharge curves of electro-polished Al cell in the potential range of 2.45 – 0.01 V at a current rate of 6.0 A g⁻¹ after 100cycle.

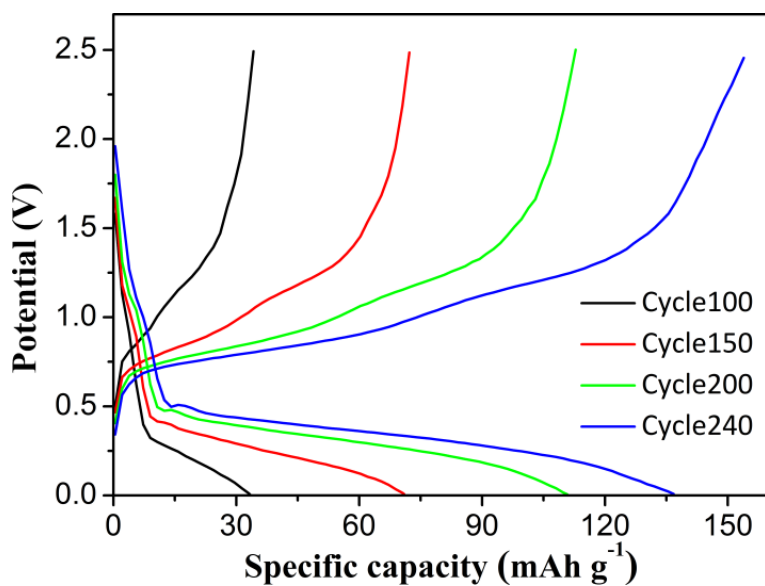


Figure S4. Raman spectra of the ionic liquid electrolyte with a mole ratio of AlCl₃/[EMIm]Cl = 1.3.

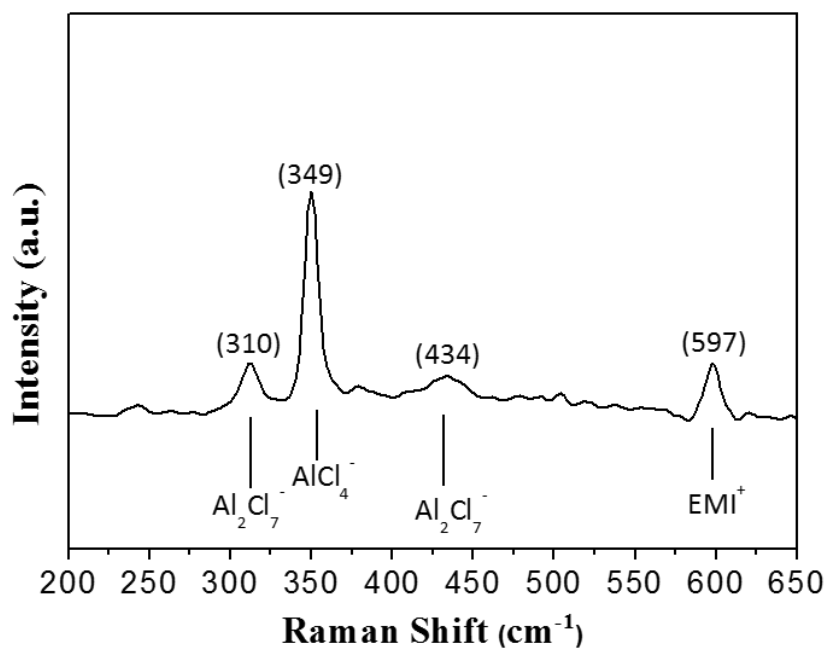
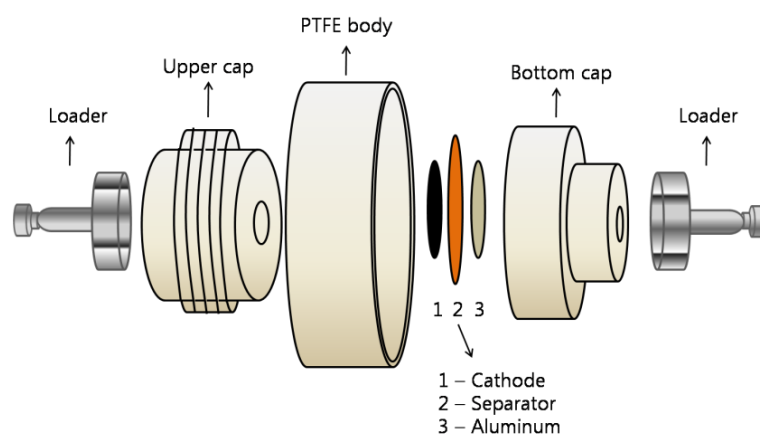


Figure S5. Scheme of custom-built Swagelok-type cell made by stainless steel (SUS316), PTFE(Teflon) to resist from a chloride-containing acidic electrolyte.



References

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