Supplementary Information (SI) for ChemComm.

Supporting Information

Anhydrous Salts for Non-Corrosive Aluminium Battery Electrolytes

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Experimental

$Al(C_2H_5)_3$ (25 wt.% in toluene), trifluoromethanesulfonic acid (HOTf, ≥99%), and bis(trifluoromethane)sulfonimide acid (HTFSI, ≥95.0%) were purchased from Sigma-Aldrich. $Al(C_2H_5)_3$ and HOTf were used as received, while HTFSI was dried at 40 °C under vacuum for 72 h. Anhydrous $Al(OTf)_3$ and $Al(TFSI)_3$ were synthesized in a water-free atmosphere using anhydrous toluene dried using 3A molecular sieves (< 10 ppm water after being dried) as a solvent. The synthesis reactions are shown in Equation S1 and S2.

$$\mathrm{Al(C_2H_5)_3{+}3HOTf{\rightarrow}Al(OTf)_3{+}3C_2H_6} \quad \text{(S1)}$$

$$\mathrm{Al(C_2H_5)_3{+}3HTFSI{\rightarrow}Al(TFSI)_3{+}3C_2H_6} \quad \text{(S2)}$$

Although $Al(C_2H_5)_3$ is a strong Lewis acid, the formation of anionic complexes of $Al(C_2H_5)_n(X)_m$ (X = $[OTf]^-$ or $[TFSI]^-$, $n + m = 4$) activates the Lewis basicity of ethyl group[1] to proceed with the following reactions:

$$\mathrm{Al(C_2H_5)_3 + HX \rightarrow Al(C_2H_5)_3X^- + H^+ \rightarrow Al(C_2H_5)_2X + C_2H_6} \uparrow \quad \text{(S3-1)}$$

$$\mathrm{Al(C_2H_5)_2X + HX \rightarrow Al(C_2H_5)_2X_2^- + H^+ \rightarrow Al(C_2H_5)X_2{+}C_2H_6} \uparrow \quad \text{(S3-2)}$$

$$\mathrm{Al(C_2H_5)X_2{+}HX{\rightarrow}Al(C_2H_5)_2X_2^-{+}H^+ \rightarrow AlX_3 + C_2H_6} \uparrow \quad \text{(S3-3)}$$

For the synthesis, 0.5 m $Al(C_2H_5)_3$ in 20 g toluene and 0.5 m HOTf/HTFSI in 60 g toluene solutions were prepared separately. Then, the $Al(C_2H_5)_3$ solution was added to the acid solution slowly (~1 drop per 1 s). Rapid gas (C_2H_6) and heat generation were observed during mixing. Then, the mixtures were stirred at room temperature for 3 h. The mixture was sealed in a glass bottle under Ar and kept at 3 ± 2 °C for 7 days in the case of $Al(TFSI)_3$ because of the slow crystallization. The precipitates were filtrated and washed with anhydrous toluene and anhydrous hexane thoroughly and dried at 60°C under vacuum for 72 h. The obtained salts were used for the characterization without further purifications. All procedures, except for the cooling in a refrigerator for $Al(TFSI)_3$, were conducted in an Ar-filled glove box of well-controlled moisture (< 3.0 ppm). Note that atmosphere control is essential for the safety and purity of the products because $Al(C_2H_5)_3$ reacts violently with water and oxygen. For comparison, two different commercial $Al(OTf)_3$ samples were obtained from Sigma-Aldrich (99.9% trace metals basis) and Thermo Fisher Scientific, and $Al(TFSI)_3$ (>97%) was purchased from Boron Molecular.

The Al salts were characterized using various analytical techniques. Fourier-transform infrared spectra were obtained using a Bruker Alpha attenuated total reflection (ATR-FTIR) spectrometer with a diamond window. Karl

Fischer titration was used to quantify the water content in the salts using a Coulometer (831 KF Coulometer, Metrohm). The FTIR and Karl Fischer measurements were conducted in the glove box without air exposure. The atomic ratios of Al and S in the sample were determined by ICP-AES (SPS3520UV, Hitachi High-Tech Science) after dissolving the samples in deionized water. The thermal behavior was tested using a thermogravimetric analyzer (TG 209 F1, Netzsch) at a scan rate of 5 °C $\mathrm{min^{-1}}$ in a N_2 atmosphere.

0.3 mol $\mathrm{kg^{-1}}$ (m) Al salts in acetonitrile (Sigma-Aldrich, 99.8%, anhydrous) or 1-butylimidazole (Sigma-Aldrich, 98%) electrolytes were prepared by mixing the Al salts with dried solvents. These solvents were dried by 3A molecular sieves for more than 3 days before electrolyte preparation to ensure the water content was < 10 ppm. It should be noted that tetrahydrofuran and glymes exhibit limited stability with these salts, likely due to their strong Lewis acidity.

Electrochemical measurements were conducted using cyclic voltammetry (CV) with a beaker-type three-electrode cell in the glove box. The reference electrode was Ag^+/Ag with an inner solution of 0.05 m silver triflate (Sigma-Aldrich, ≥99%) in N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid (Solvionic, 99.9%). The potential of the reference electrode was calibrated by a redox pair of 5 mM ferrocene on a Pt electrode (+0.344 V *vs.* ferrocenium/ferrocene). CV measurements were performed on Al and glassy carbon (GC) working electrodes.

To analyze the deposit, constant potential deposition was performed at −2.5 V vs. Ag^+/Ag in a hydrate $Al(TFSI)_3$ on Pt substrate in BIm electrolyte. The resulting deposit was analyzed using scanning transmission electron microscopy (JEM-ARM200F, JEOL) and electron energy loss spectroscopy without air exposure to preserve the sample integrity.

Table S1. Compositional analysis results of $Al(OTf)_3$ and $Al(TFSI)_3$ salts.

Sample	**Water content by Karl Fischer titration**	**S/Al ratio by ICP-AES**
$Al(OTf)_3$ (Sigma-Aldrich)	$Al(OTf)_3 \cdot 3H_2O$	3.06
$Al(OTf)_3$ (synthesized)	$Al(OTf)_3 \cdot 0.02H_2O$	3.15
$Al(TFSI)_3$ (Boron Molecular)	$Al(TFSI)_3 \cdot 5H_2O$	5.70
$Al(TFSI)_3$ (synthesized)	$Al(TFSI)_3 \cdot 0.03H_2O$	6.40

Table S2. Water contents of AN electrolytes measured by Karl Fischer titration

Sample	Water content / ppm	Standard deviation
AN	7.0	1.2
0.3 m Al(OTf)$_3$ in AN (synthesized)	120	10
0.3 m Al(TFSI)$_3$ in AN (synthesized)	138	4
0.3 m Al(OTf)$_3$ in AN (synthesized) + 0.01 m Al**(C$_2$H$_5$)$_3$**[a]	65.0	1.3
0.3 m Al(OTf)$_3$ in AN (synthesized) treated by molecular sieves [b]	21.5	0.4

a. Al(C$_2$H$_5$)$_3$ (25 wt.% in toluene) was added to the electrolyte and stirred for three days in the glove-box.

b. Approximately 30 wt.% 3A molecular sieves were added to the electrolyte for 3 days.

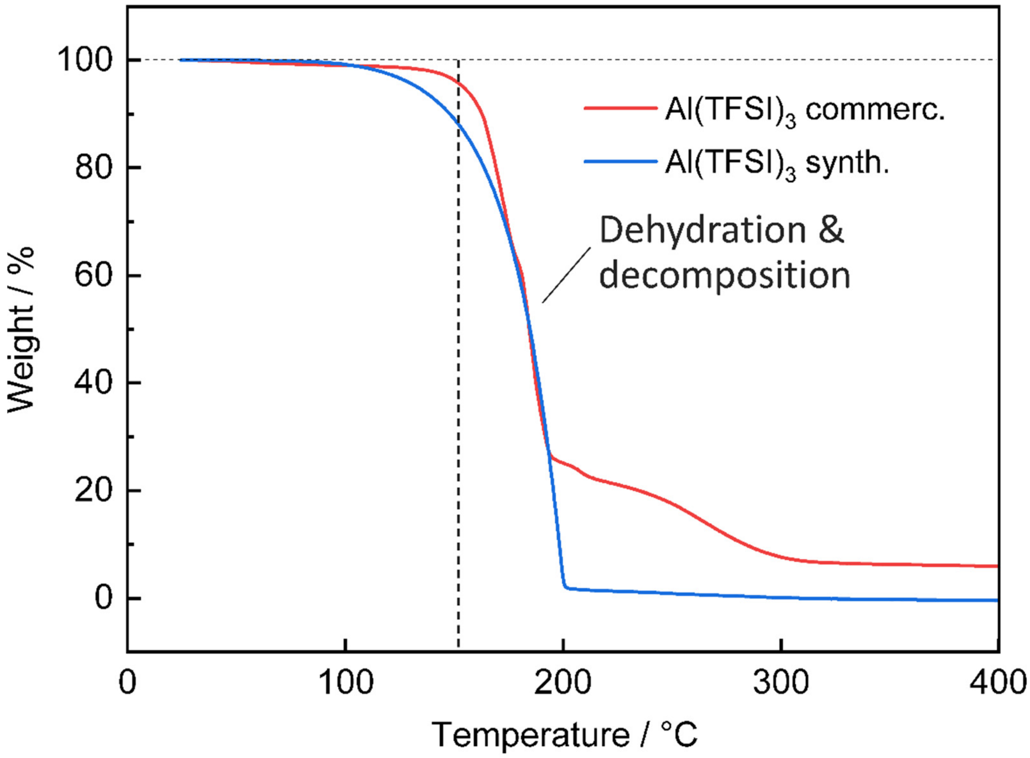

Figure S1. TGA curve of commercial and synthesized Al(TFSI)$_3$ at the heat rate of 5 °C min^{-1}.

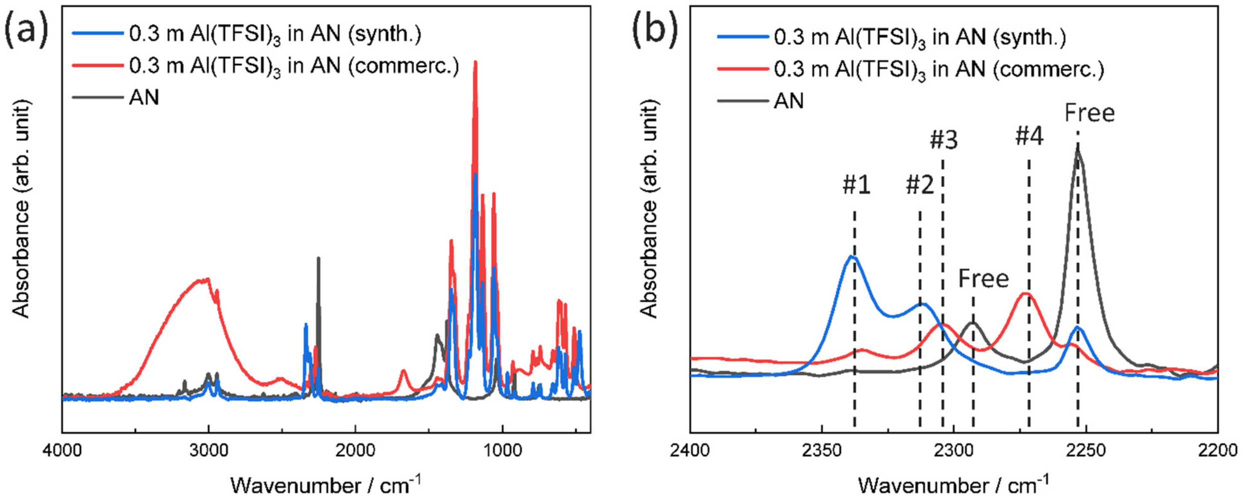

Figure S2. ATR-FTIR spectra of anhydrous and hydrous (a) $Al(TFSI)_3$ in AN and (b) enlarged figures in the range of 2400–2200 cm^{-1}.

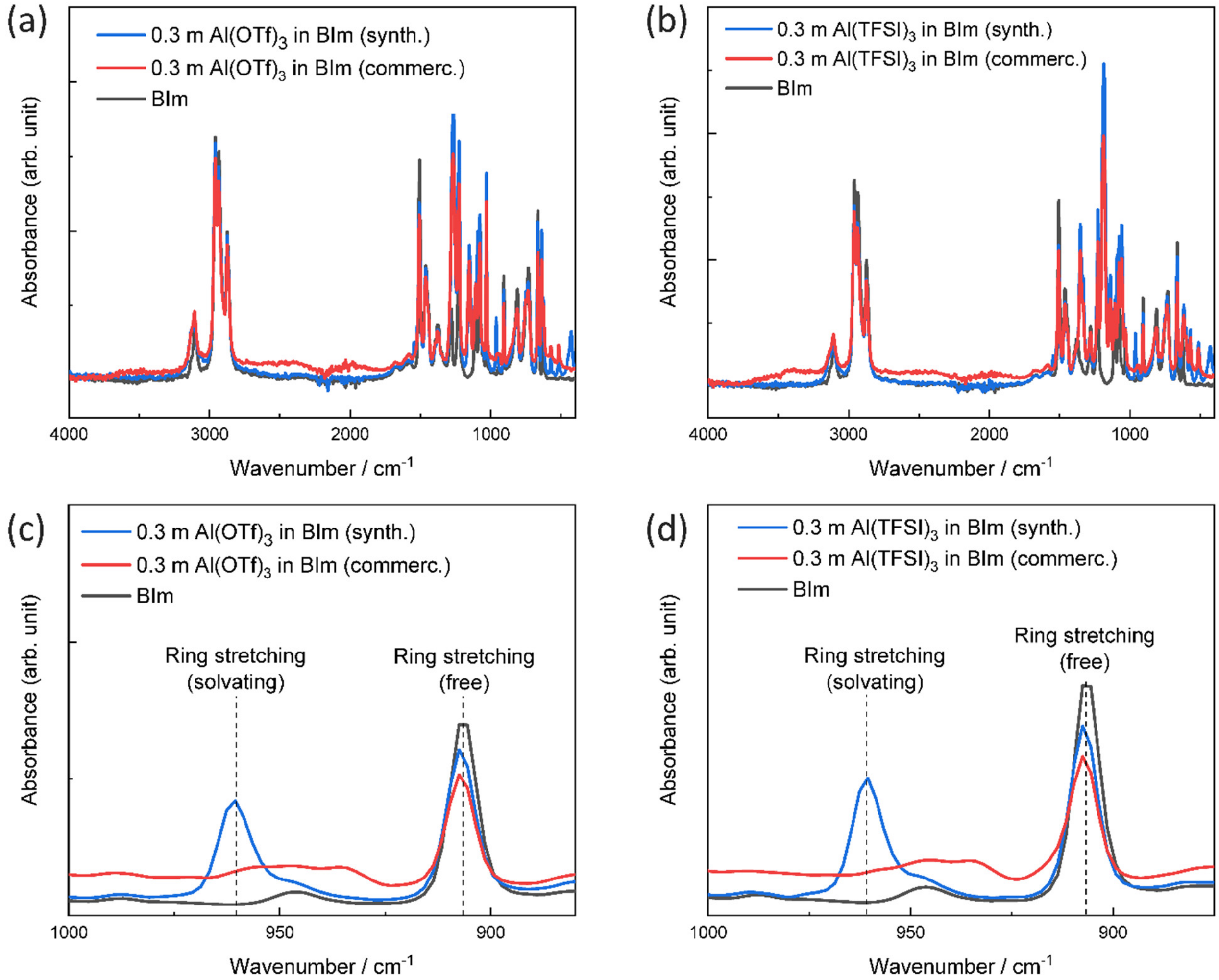

Figure S3. ATR-FTIR spectra of anhydrous and hydrous (a) $Al(OTf)_3$ and (b) $Al(TFSI)_3$ in BIm and enlarged figures of $Al(OTf)_3$ electrolytes in the range of (c) 1600–1420 cm^{-1} (d) 1000–875 cm^{-1}.

Table S3. Open-circuit potential (OCP) of an Al electrode in various electrolytes.

	OCP / V vs. Ag^+/Ag	OCP / V vs. SHE
$Al(OTf)_3$ in AN	-1.106	-0.122
$Al(OTf)_3 \cdot 3H_2O$ in AN	-1.099	-0.115
$Al(TFSI)_3$ in AN	-1.020	-0.036
$Al(TFSI)_3 \cdot 3H_2O$ in AN	-1.080	-0.096
$Al(OTf)_3$ in BIm	-1.804	-0.82
$Al(OTf)_3 \cdot 3H_2O$ in BIm	-1.814	-0.83
$Al(TFSI)_3$ in BIm	-2.204	-1.22
$Al(TFSI)_3 \cdot 3H_2O$ in BIm	-1.781	-0.797
$AlCl_3$-[EMIm]Cl (2:1)	-	-0.7

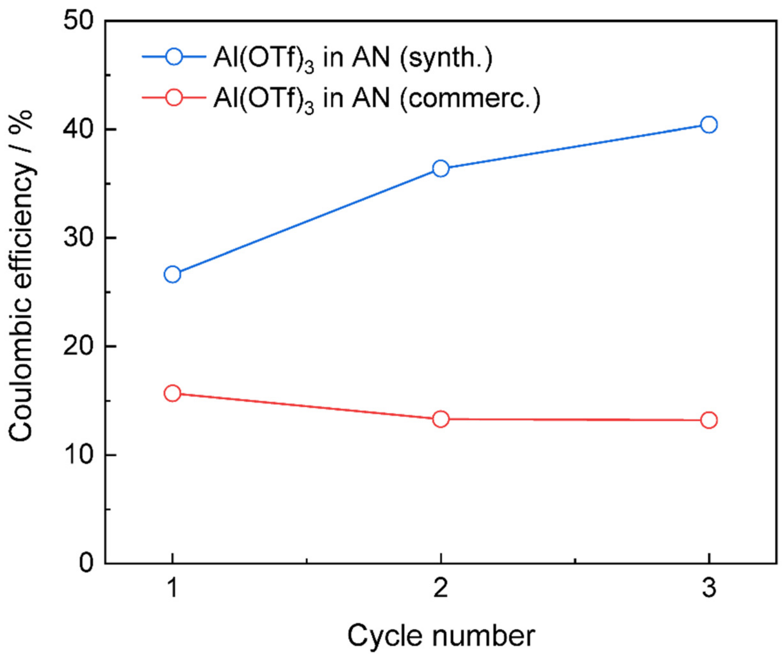

Figure S4. Coulombic efficiency for the CV cycles on GC electrode (Figure 3b).

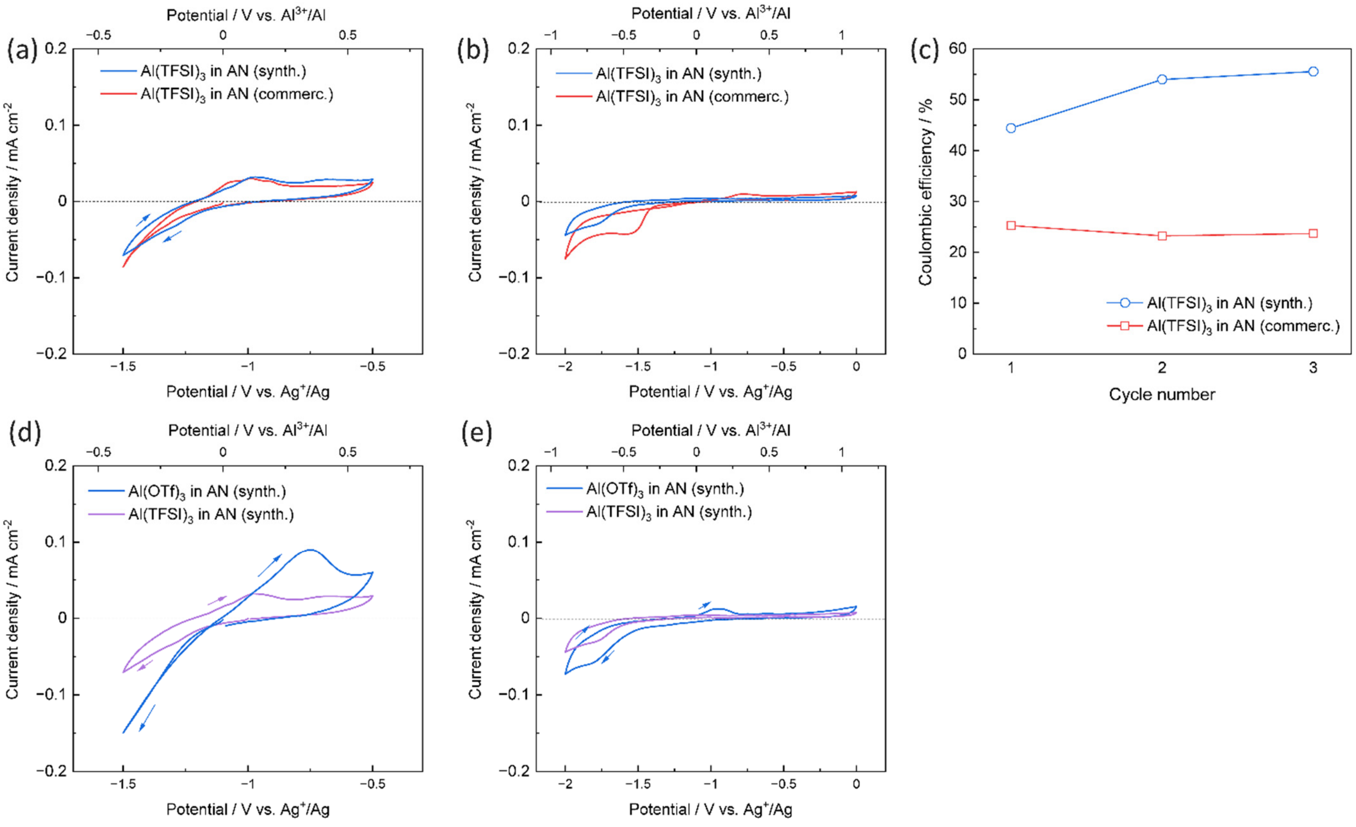

Figure S5. CV curves of (a) Al and (b) GC electrodes in Al(TFSI)$_3$ in AN electrolytes and (c) Coulombic efficiency for GC electrodes, (d) Al and (e) GC electrode in synthesized Al(TFSI)$_3$ and Al(OTf)$_3$ electrolytes.

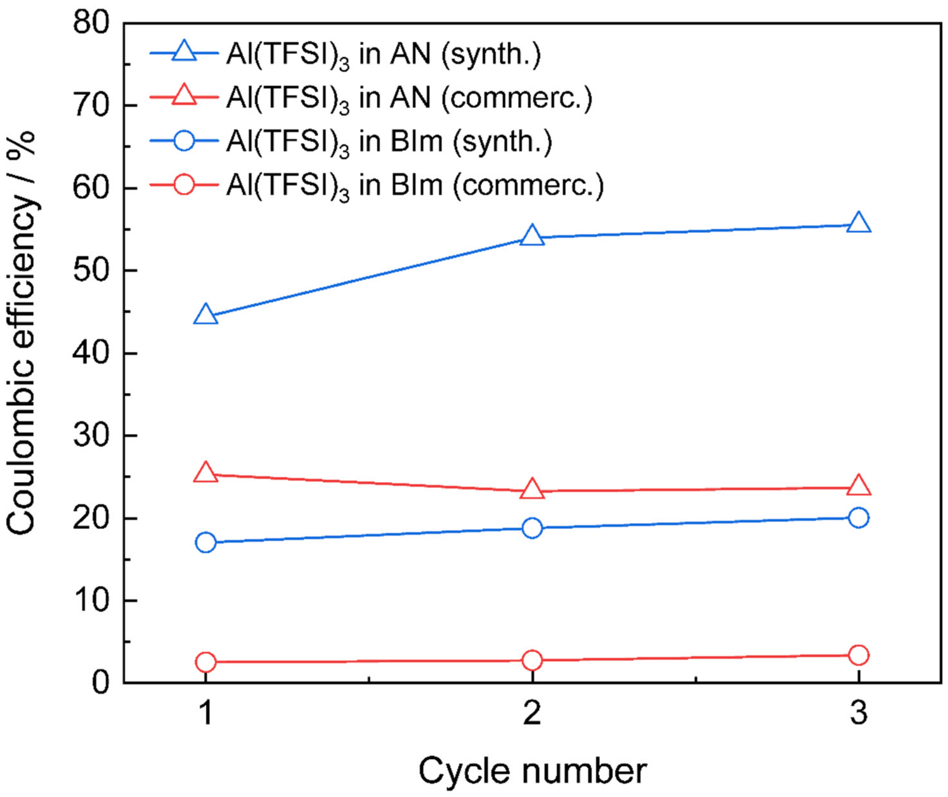

Figure S6. Coulombic efficiency for the CV cycles on GC electrode in Al(TFSI)$_3$ electrolytes.

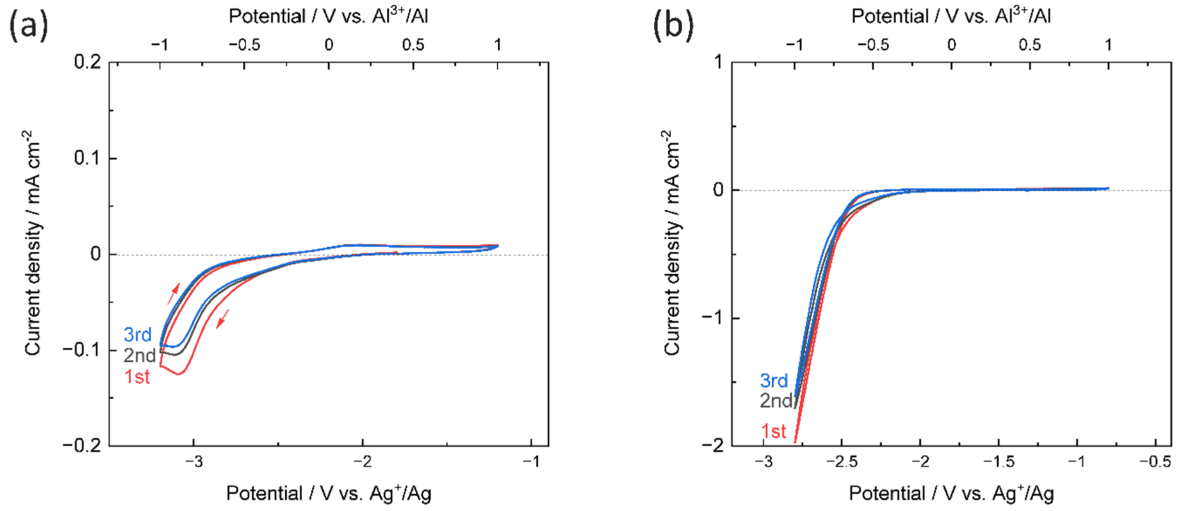

Figure S7. CV of GC electrode in (c) synthesized Al(TFSI)₃ and (d) commercial Al(TFSI)₃ in Bim electrolytes.

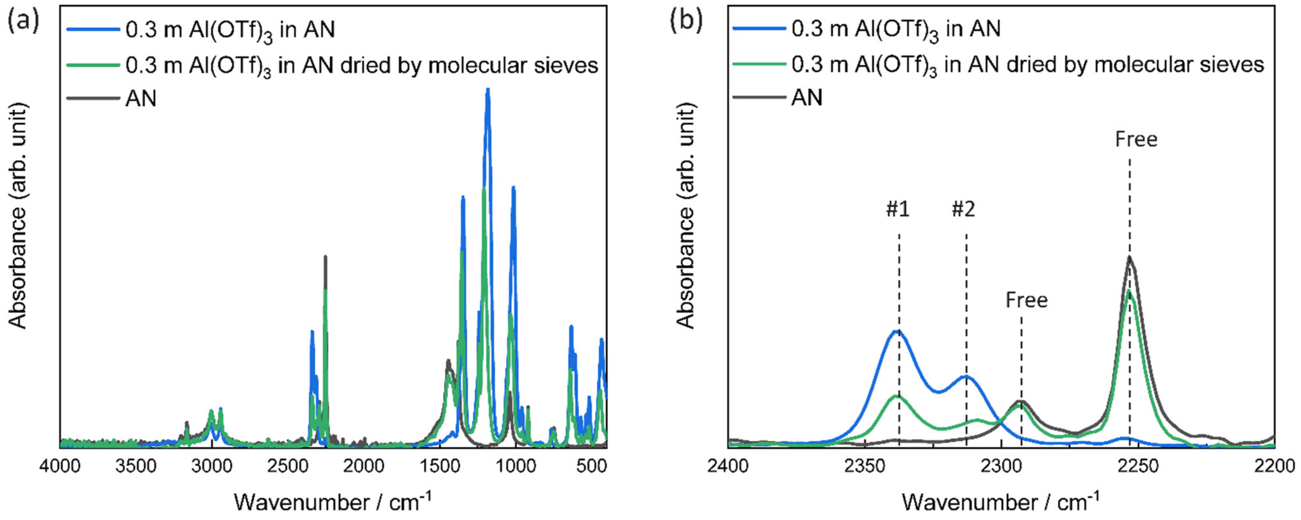

Figure S8. ATR-FTIR spectra of 0.3 m anhydrous and hydrous (a) $Al(OTf)_3$ in AN and (b) enlarged figures in the range of 2400‒2200 cm^{-1}.

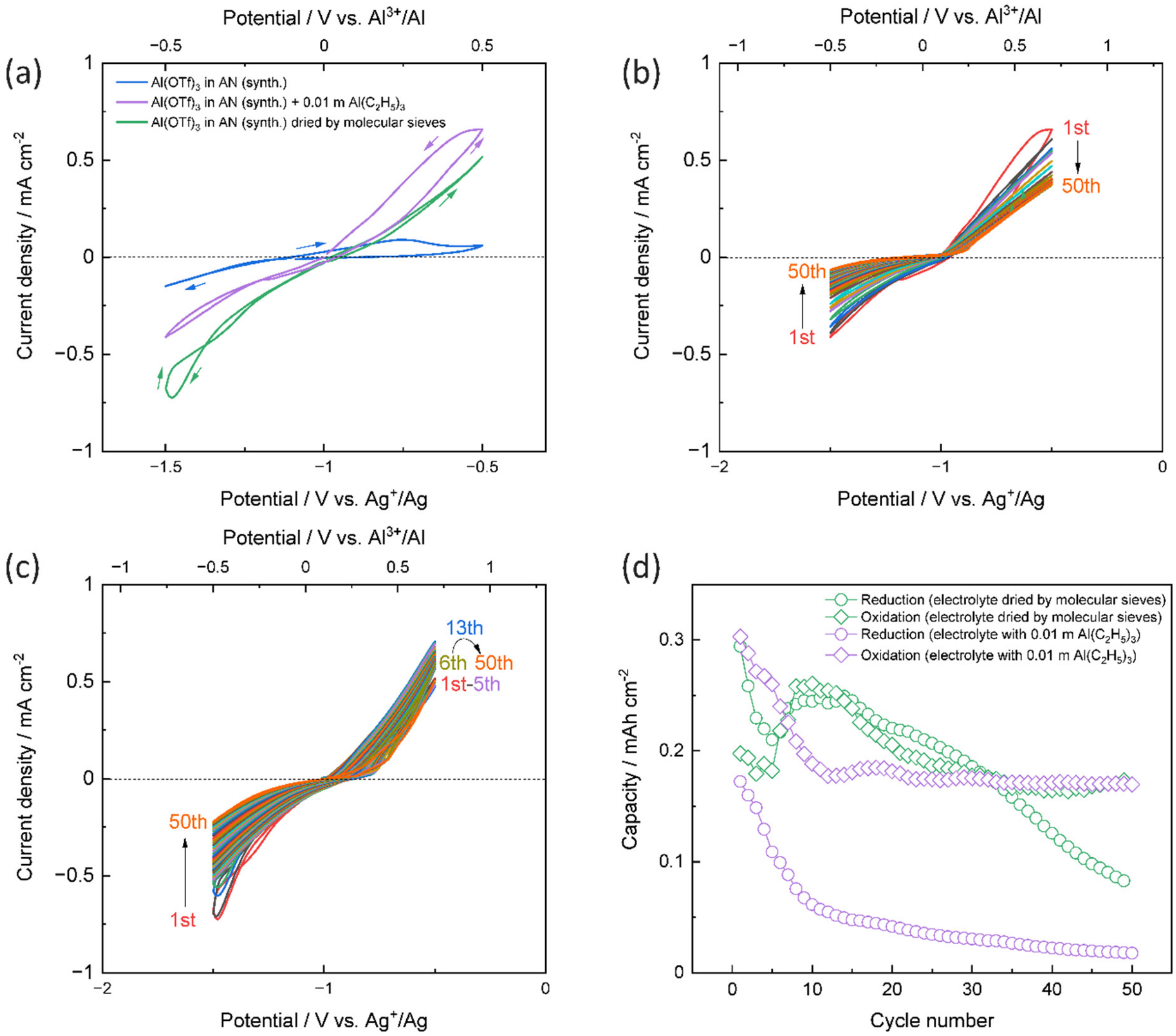

Figure S9. The initial CV curves of Al electrode in 0.3 m Al(OTf)$_3$ in AN (synthesized) electrolytes (a), CV curves in 0.3 m Al(OTf)$_3$ in AN with 0.01 m Al(C$_2$H$_5$)$_3$ (b) and dried by molecular sieves (c), and their capacity retention (d).

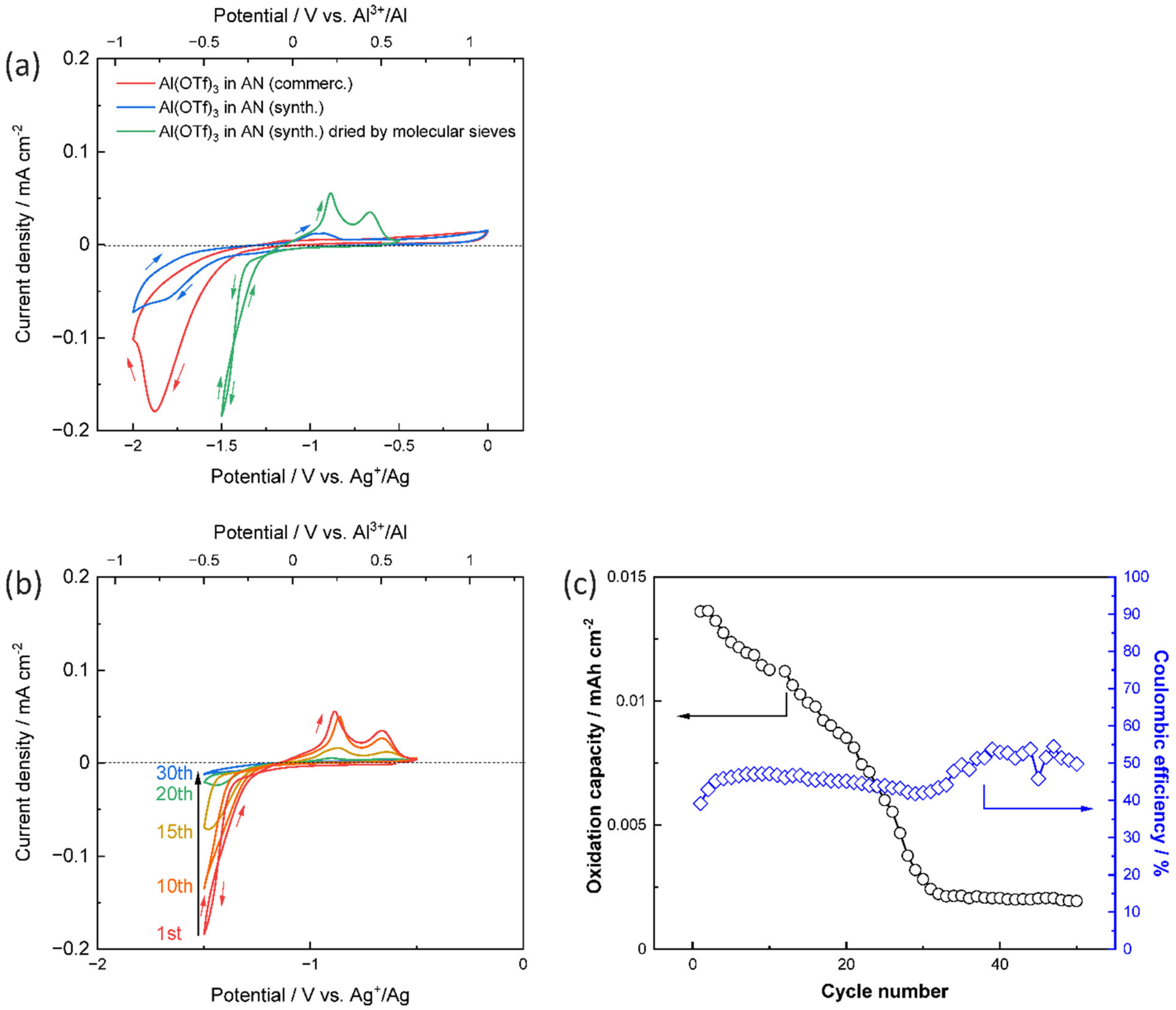

Figure S10. (a) CV of GC working electrodes *vs.* 0.3 m Al(OTf)$_3$ in AN electrolytes, (b) extended cycles, and (c) the capacity retention and Coulombic efficiency of 0.3 m Al(OTf)$_3$ in AN dried by molecular sieves.

Reference:

1 B. B. Snider, D. J. Rodini, M. Karras, T. C. Kirk, E. A. Deutsch, R. Cordova and R. T. Price, *Tetrahedron*, 1981, **37**, 3927–3934.