

Supplementary Information for

**Improved Reversibility of Lithium Deposition and Stripping with High Areal
Capacity under Practical Conditions through Enhanced Wettability of Polyolefin
Separator to Highly Concentrated Electrolyte**

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Supporting Experimental Section

Battery-grade 1 mol dm^{-3} LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3:7 in v/v), LiFSA:DMC = 1:1.1 (mol/mol), and purified fluoroethylene carbonate (FEC) were purchased from Kishida Chemical. FEC at 2 vol% was added to 1 M LiPF_6 in EC/DMC in an Ar-filled glovebox.

The aramid-coated polyolefin separator was prepared by slurry coating method. A meta-aramid/*N,N*-dimethylacetamide (DMAc) slurry containing dispersed BaSO_4 filler with an average particle size of 50 nm was prepared. The slurry was coated on both sides of the polyolefin microporous membrane (film thickness: 7 μm). Then, it was immersed in a mixture of DMAc/water (50/50 wt.) and subsequently rinsed with water and dried to form aramid-based porous layers containing BaSO_4 filler on both sides of the polyolefin microporous membrane. The thickness of the resulting aramid-coated polyolefin separator is approximately 11 μm .

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the separators were recorded using a FTIR spectrometer (FT/IR-6200, JASCO) with an ATR accessory (ATR PRO450-S, Pike JASCO) with a diamond prism at an incident angle of 45° at room temperature.

Chronopotentiometry was performed using two-electrode electrochemical cells (TJ-AC, Tomcell Japan) with the configuration of [Li/electrolyte/Cu], which were assembled in the Ar-filled glovebox. A disk-shaped Li-metal foil ($\varphi = 12 \text{ mm}$, Honjo Metal) was used as a counter electrode. Cu foil was used as a working electrode. A glass fiber filter (GB-100R, Advantec), polypropylene microporous membrane (Celgard2500, Celgard), and aramid-coated polypropylene membrane was used as separator between the working and counter electrodes. The cells were cycled at a current density of 0.35 mA cm^{-2} at room temperature.

The Li deposit on the Cu electrode was observed using a scanning electron microscope (SEM; SU8010, Hitachi High-Technologies). Li metal was deposited (2.1 mA h cm^{-2}) on the Cu electrode in Li/Cu cells with different electrolyte, and then the cells were disassembled in the Ar-filled glovebox. The Cu electrode was rinsed with DMC to remove the residual electrolyte components and dried under

vacuum. The sample was transferred to the SEM chamber using a transfer vessel without air exposure.

Supporting Tables and Figures

Table S1. Peak assignment of the ATR-FTIR spectrum for the polyolefin separator.

Wavenumber / cm ⁻¹	Vibrational mode
2952	CH ₃ asymmetric stretching
2920	CH ₂ asymmetric stretching
2871	CH ₃ symmetric stretching
2841	CH ₂ symmetric stretching
1456	CH ₃ asymmetric deformation or CH ₂ scissoring
1375	CH ₃ symmetric deformation

Table S2. Peak assignment of the ATR-FTIR spectrum for the aramid-coated polyolefin separator.

Wavenumber / cm ⁻¹	Vibrational mode
1656	amide C=O stretching
1608	aromatic C–C skeleton vibration
1538	N–H deformation and C–N stretching coupled mode
1481	aromatic C=C stretching

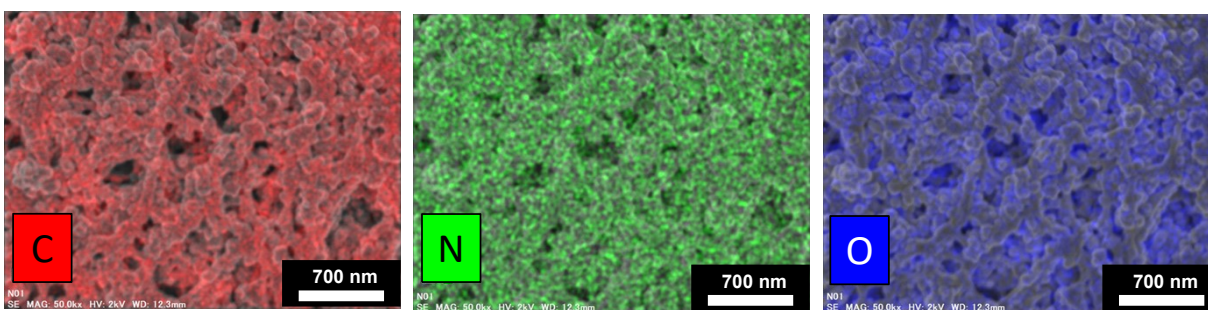
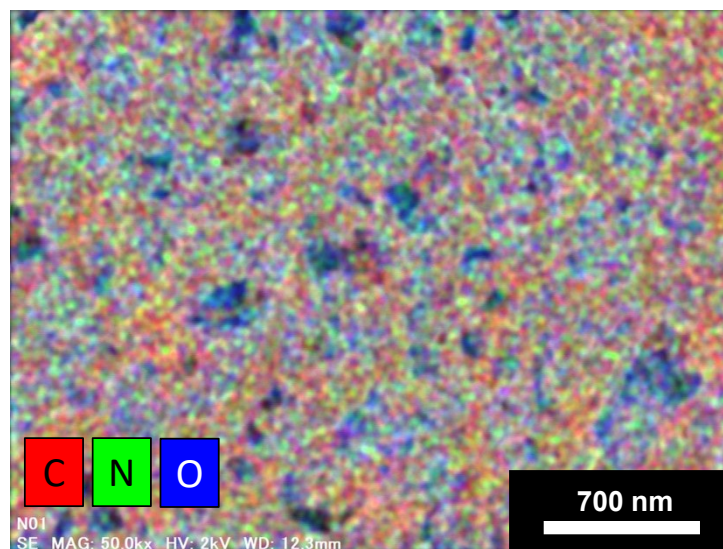


Fig. S1. SEM/EDX image of the aramid-coated polyolefin separator.

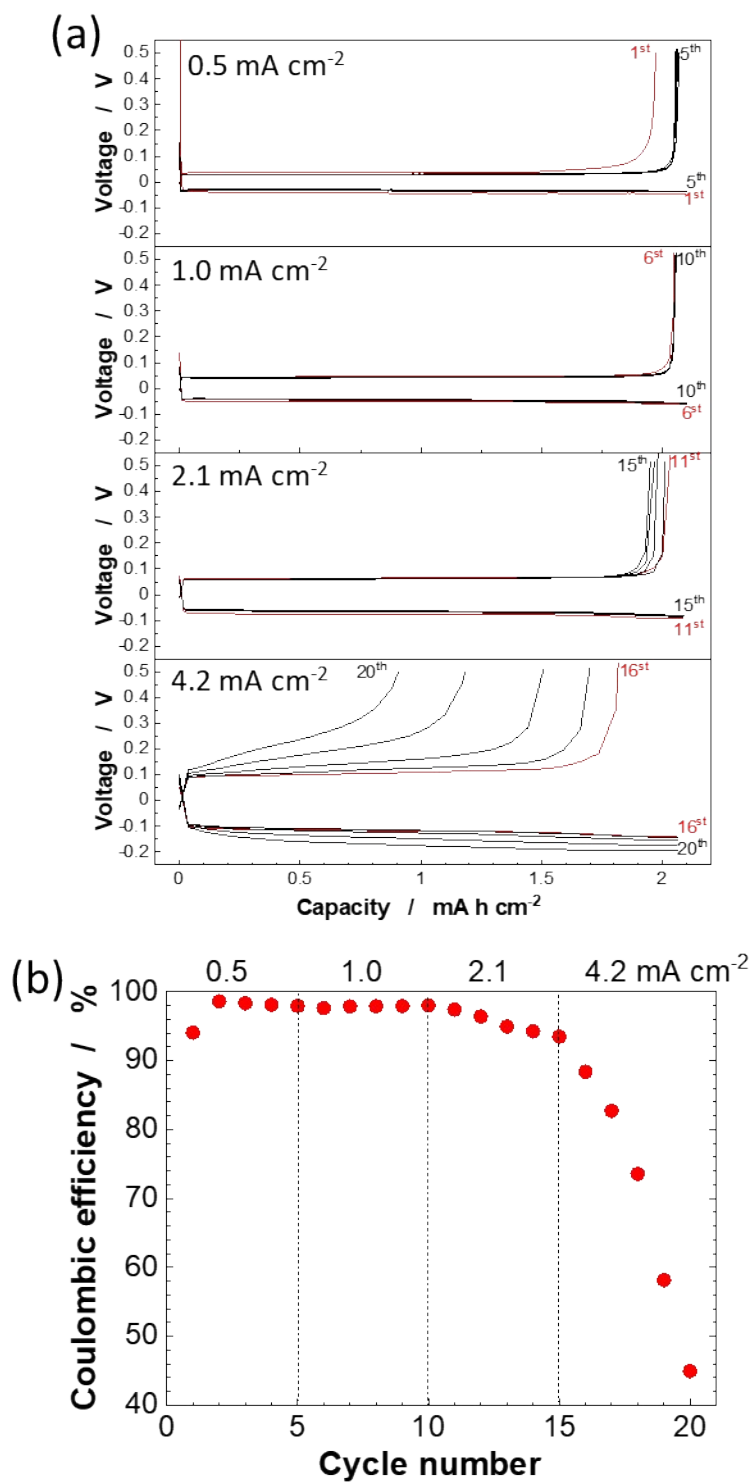


Fig. S2. (a) Chronopotentiometric curves of Li deposition/stripping in a Li/Cu cell with an aramid-coated separator and LiFSA:DMC = 1:1.1 electrolyte solution measured at various current densities. The Li deposition capacity was fixed at 2.1 mA h cm⁻². Coulombic efficiency of the cell is also shown in (b).

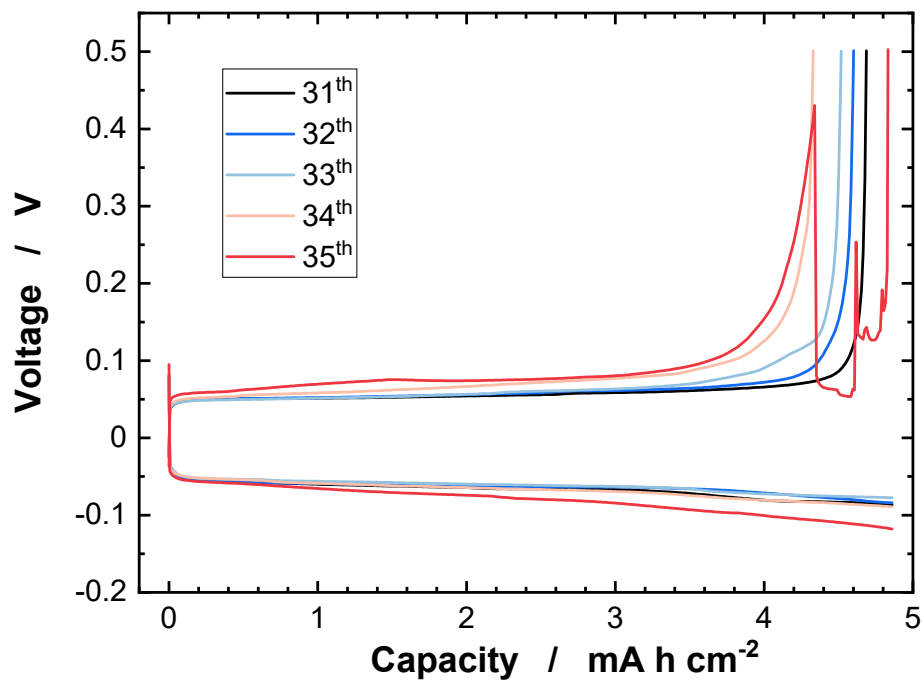


Fig. S3. Chronopotentiometric curves of Li deposition/stripping in Li/Cu cells with the aramid-coated separator at a current density of 0.35 mA cm^{-2} with Li deposition capacity of 4.9 mA h cm^{-2} .