Electronic Supplementary Information for

Nanostructured liquid-crystalline Li-ion conductors with high oxidation resistance: molecular design strategy towards safe and high-voltage-operation Li-ion batteries

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Experimental Section

Materials and Syntheses.

2-(2-(2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethoxy)ethoxy)ethyl *p*-toluenesulfonate was synthesized according to the reported procedure.[1]

Synthesis of 2-((*trans*,*trans*)-4'-pentyl-[1,1'-bi(cyclohexan)]-4-yl)ethan-1-ol (S1)

To a solution of *trans*,*trans*-4-pentyl-4'-vinylbicyclohexyl (1.51 g, 5.75 mmol) in THF (10 mL) was added 0.5 M 9-borabicyclo[3.3.1]nonane (9-BBN) THF solution (23 mL, 11.5 mmol) at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was cooled to 0 °C again. Then, sodium hydroxide (0.281 g, 7.01 mmol) in water (5 mL) and 35% hydrogen peroxide (6 mL, 69.9 mmol) were successively added, and the mixture was stirred for additional 19 h at room temperature. After removing THF under reduced pressure, the resulting mixture was poured into 5% hydrochloric acid and extracted with ethyl acetate three times. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: dichloromethane/ethyl acetate = 97/3) to afford **S1** as a white solid (1.45 g, 5.16 mmol, 91%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.68 (q, J = 6.3 Hz, 2H), 1.78–1.67 (m, 8H), 1.46 (q, J = 6.8 Hz, 2H), 1.34–1.21 (m, 7H), 1.16–1.09 (m, 4H), 0.99–0.79 (m, 13H) ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 61.0, 43.4, 43.3, 40.4, 37.9, 37.5, 34.5, 33.6, 33.6, 32.2, 30.1, 29.9, 26.7, 22.7, 14.1 MS (MALDI-TOF): calcd for $[M + K]^+$, 319.24; found: 318.92.

Synthesis of 2-(2-(2-(2-((*trans*,*trans*)-4'-pentyl-[1,1'-bi(cyclohexan)]-4-yl)ethoxy)ethoxy)ethoxy)ethan-1-ol (S2)

To a stirred solution of sodium hydride (60% dispersion in paraffin liquid, 0.782 g, 19.6 mmol) in THF (10 mL) was added **S1** (0.607 g, 2.16 mmol) in THF (10 mL) dropwise at room temperature. After stirring for 30 min under reflux, 2-(2-(2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethoxy)ethoxy)ethyl *p*-toluenesulfonate (0.664 g, 1.71 mmol) in THF (10 mL) was added to the mixture dropwise and stirred for additional 9 h under reflux. The reaction was quenched by adding isopropyl alcohol and the solvent was evaporated under reduced pressure. The residue was poured into sat. NH_4Cl aq. and extracted with ethyl acetate three times. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: hexane/ethyl acetate = gradient from 90/10 to 67/33) to afford a crude intermediate compound as a transparent liquid. The crude intermediate compound was successively dissolved in ethanol (10 mL) and water (1 mL) and *p*-toluenesulfonic acid monohydrate (0.221 mg, 1.16 mmol) was added. After stirring for 3 h at room temperature, the solvent was evaporated under reduced pressure. The residue was poured into brine and extracted ethyl acetate three times. The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: hexane/ethyl acetate = gradient from 50/50 to 0/100) to afford **S2** as a white solid (0.422 g, 1.02 mmol, 60% in 2 steps). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.73–3.57 (m, 12H), 3.49 (t, J = 7.0 Hz, 2H), 2.49 (t, J = 6.1 Hz, 1H), 1.76–1.62 (m, 8H), 1.47 (q, J = 6.8 Hz, 2H), 1.33–1.19 (m, 7H), 1.18–1.08 (m, 3H), 1.03–0.79 (m, 13H) ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 72.5, 70.6, 70.4, 70.0, 69.6, 61.8, 43.4, 43.3, 37.9, 37.5, 37.0, 34.9, 33.6, 33.6, 32.2, 30.1, 29.9, 26.7, 22.7, 14.1 MS (MALDI-TOF): calcd for $[M + Na]^+$, 435.34; found: 435.01.

Synthesis of 4-(4-bromobutyl)-2,2-dimethyl-1,3-dioxolane (**S3**)

A solution of 4-(2,2-dimethyl-1,3-dioxolane-4-yl)butanol (5.44 g, 31.2 mmol) and carbon tetrabromide (11.4 g, 34.3 mmol) in CH_2Cl_2 were cooled at 0°C with an ice bass. Then, triphenyl phosphine (9.00 g, 34.3 mmol) was added in the reaction solution. After 3 h of stirring at room temperature, the solvent was evaporated, and the residue was quickly added into hexane. After filtration of the precipitates, the solvent was evaporated. The crude mixture was purified by column chromatography on silica gel using hexane–ethyl acetate (5:1 by volume) as the eluent afford the compound (5.16 g, 69.7% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 4.07$ (m, 2H, OCH_2), 3.52 (t, H, OCH), 3.42 (t, 2H, CH_2Br), 1.90 (m, 2H, CH_2), 1.67-1.50 (m, 4H), 1.41 (s, 3H, CH_3), 1.35 (s, 3H, CH_3).

Synthesis of 6-((*trans*,*trans*)-4'-penthyl-bicyclohexyl)hexyl-1,3-dioxolane-2,2-dimethyl (**S4**)

0.5M solution of 9-BBN (2.60 mmol) and *trans*,*trans*-4-pentyl-4'-vinylbicyclohexyl (0.683g, 2.60 mmol) were reacted. A solution of **S3** in THF (0.514 mg, 2.17 mmol), palladium acetate (0.02 g, 0.09 mmol), tricyclohexylphosphine (8mol% solution, 0.17 mmol) and tripotassium phosphate in H_2O (0.46 mg, 2.60 mmol) was added to the reaction solution. After stirred for 45 h at room temperature, the solvent was evaporated. The residue was purified by column chromatography on silica gel using dichloromethane–hexane (4:6 by volume) as the eluent (0.18 g, 19% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 4.1 – 4.0$ (m, 2H, OCH_2), 3.50 (m, H, OCH), 1.75-1.67 (m, 10H), 1.41 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.48-1.15 (m, 15H), 1.18-1.05 (m, 6H), 1.00-0.78 (m, 12H).

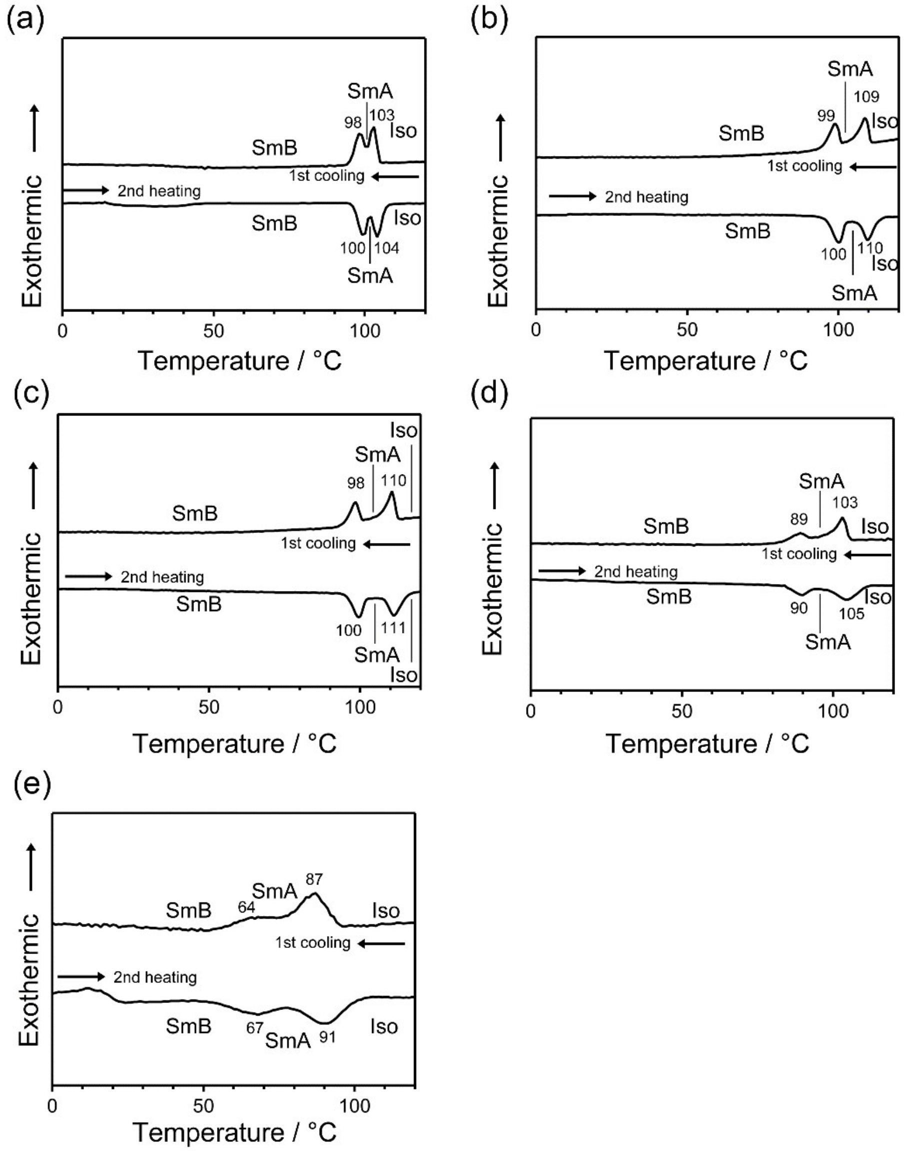

Figure S1. DSC curves of the LC mixture of compound **1** and LiTFSI with molar ratio of (a) 90:10, (b) 80:20, (c) 70:30, (d) 60:40, and (e) 50:50, respectively. SmA: smectic A phase, SmB: smectic B phase, Iso: isotropic phase.

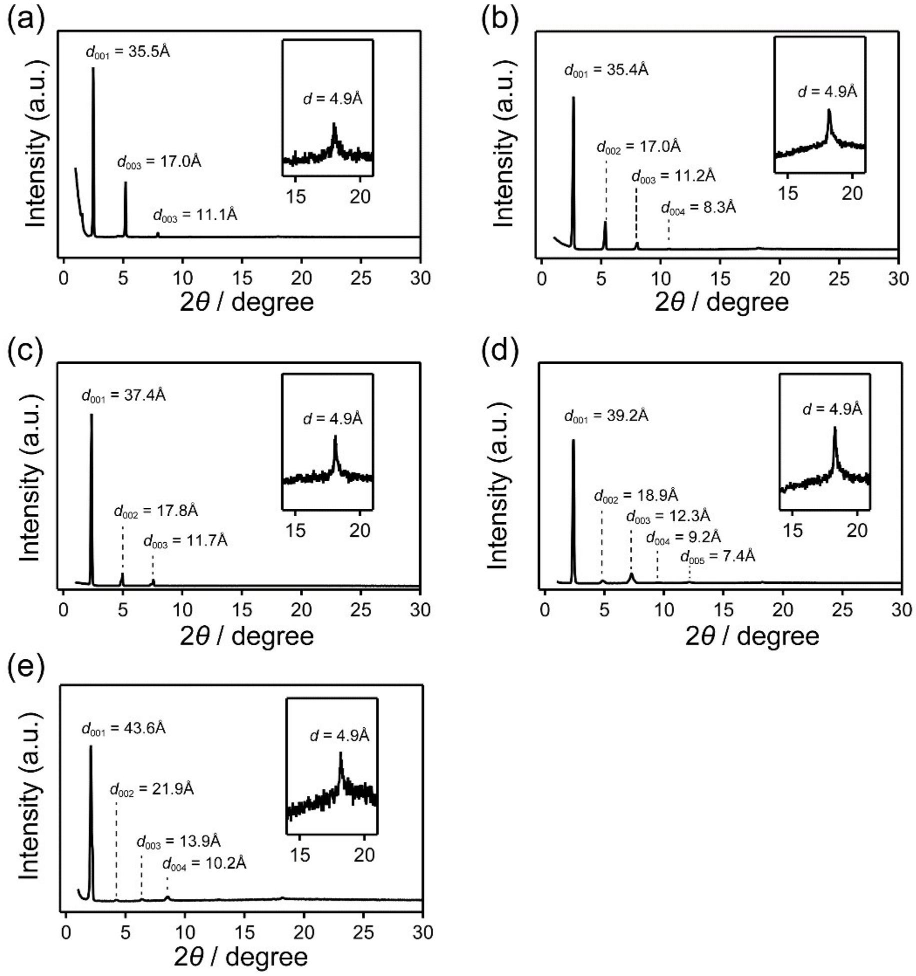

Figure S2. XRD patterns of the LC mixture of compound **1** and LiTFSI with molar ratio of (a) 90:10, (b) 80:20, (c) 70:30, (d) 60:40, and (e) 50:50, respectively, recorded at 30 °C.

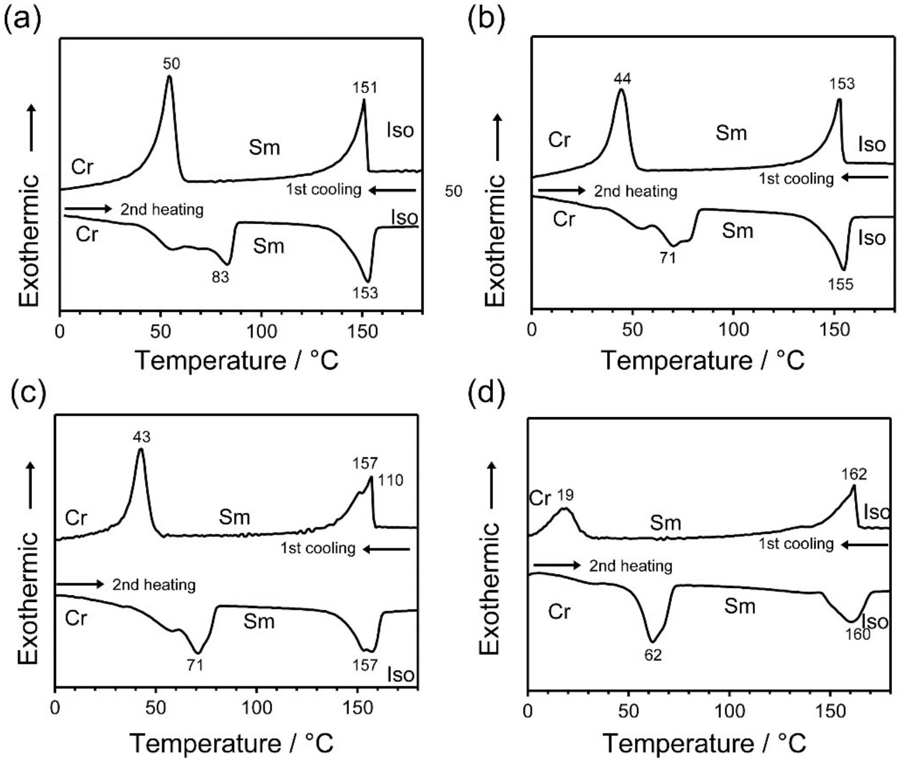

Figure S3. DSC curves of the LC mixture of compound **2** and LiTFSI with molar ratio of (a) 95:5, (b) 90:10, (c) 85:15, and (d) 80:20, respectively. Cr: crystal; Sm: unidentified smectic phase; Iso: isotropic phase.

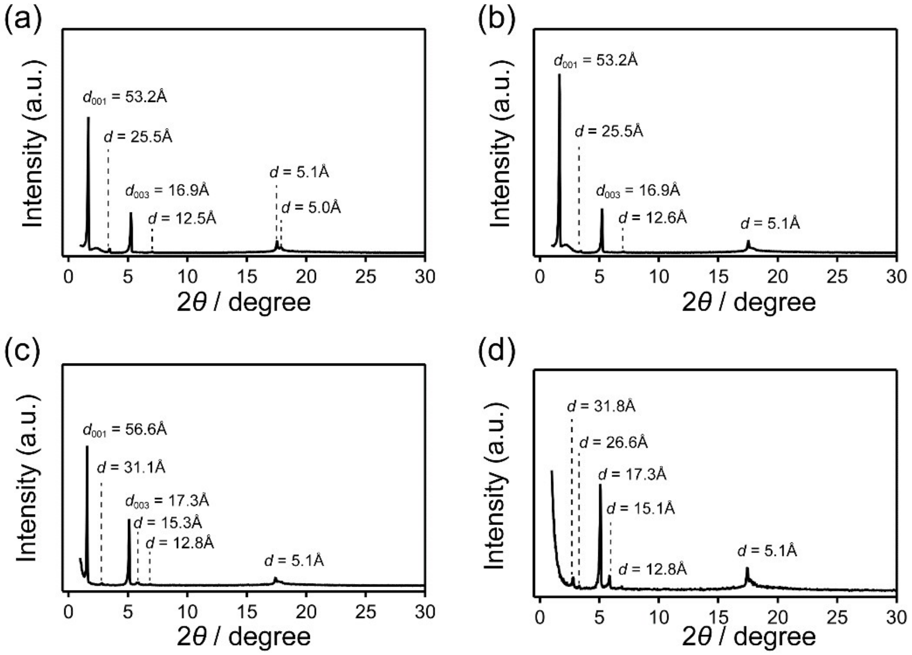

Figure S4. XRD patterns of the LC mixture of compound **2** and LiTFSI with molar ratio of (a) 95:5, (b) 90:10, (c) 85:15, and (d) 80:20, respectively, recorded at 100 °C.

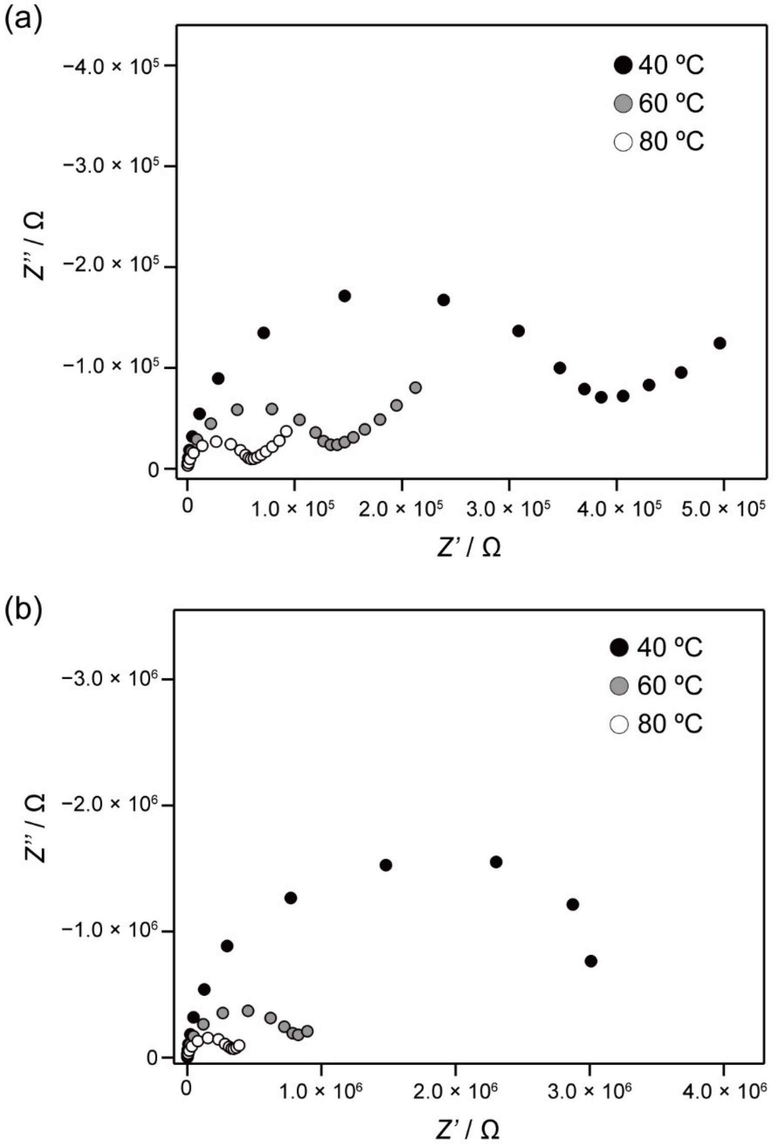

Figure S5. Nyquist plots of LC mixtures of (a) **1**/LiTFSI with molar fractions of 80:20, and (b) **2**/LiTFSI with molar fractions of 85:15.

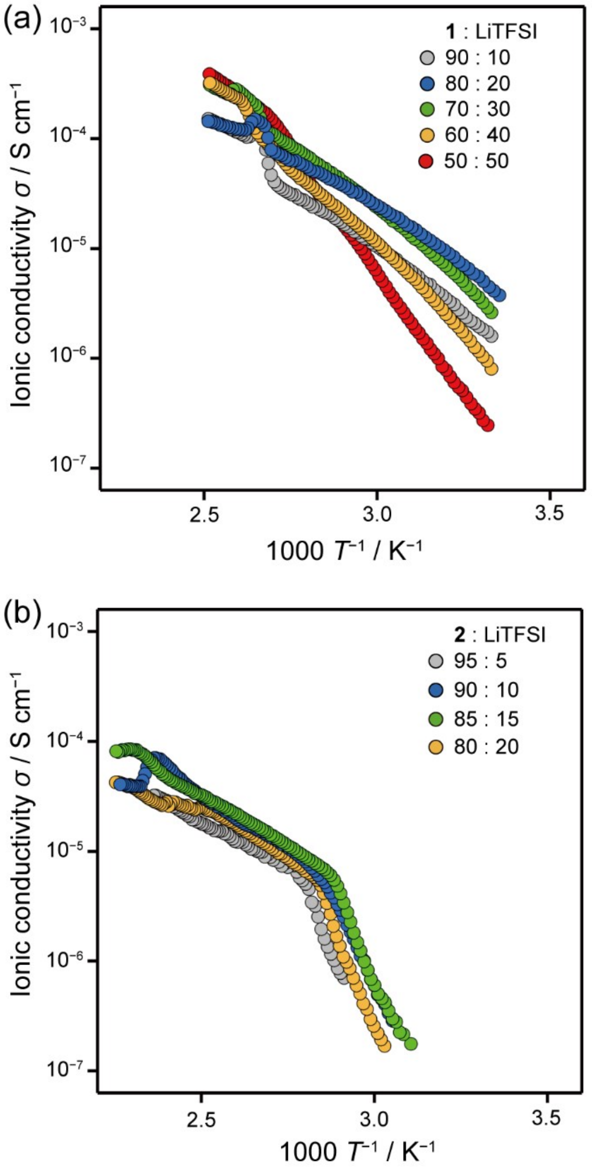

Figure S6. Ion conductivities of LC mixtures of (a) **1**/LiTFSI and (b) **2**/LiTFSI at different mixing ratios.

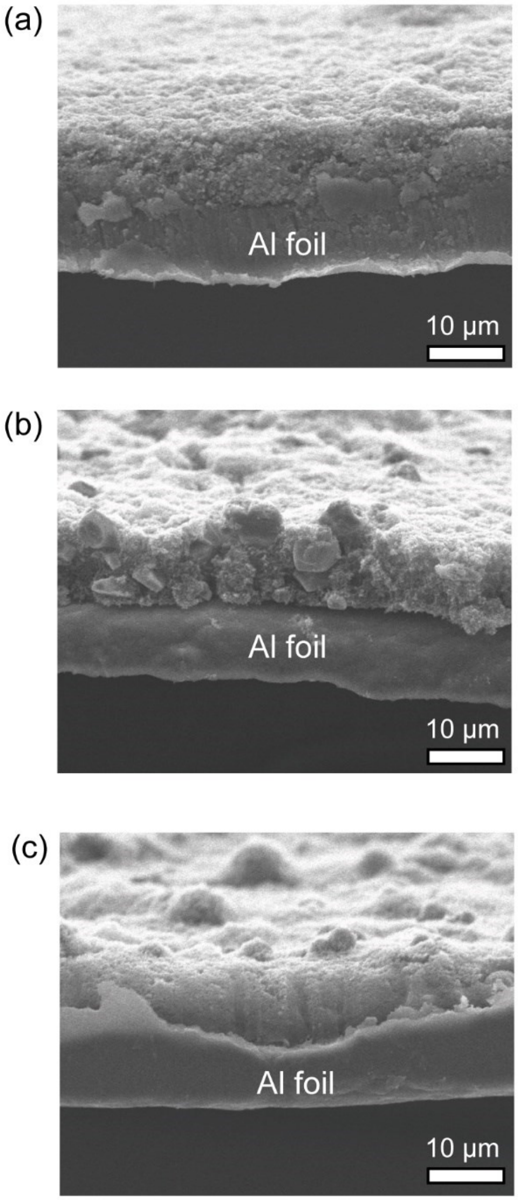

Figure S7. Cross-sectional surfaces of positive electrodes of (a) $LiFePO_4$, (b) $LiCoO_2$, and (c) $LiNi_{0.815}Co_{0.15}Al_{0.035}O_2$.

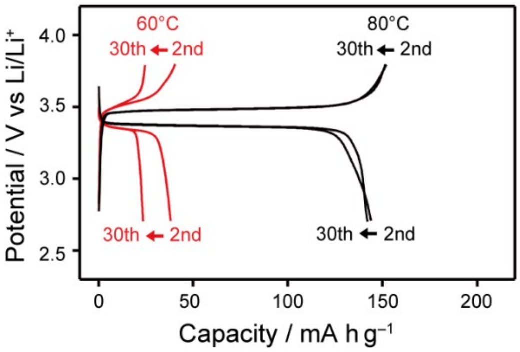

Figure S8. Charge-discharge curves of Li half-cells composed of LC electrolyte **1**/LiTFSI and $LiFePO_4$ positive electrode, recorded in the voltage range 2.7–3.8 V vs Li/Li^+ at 60 and 80 °C.

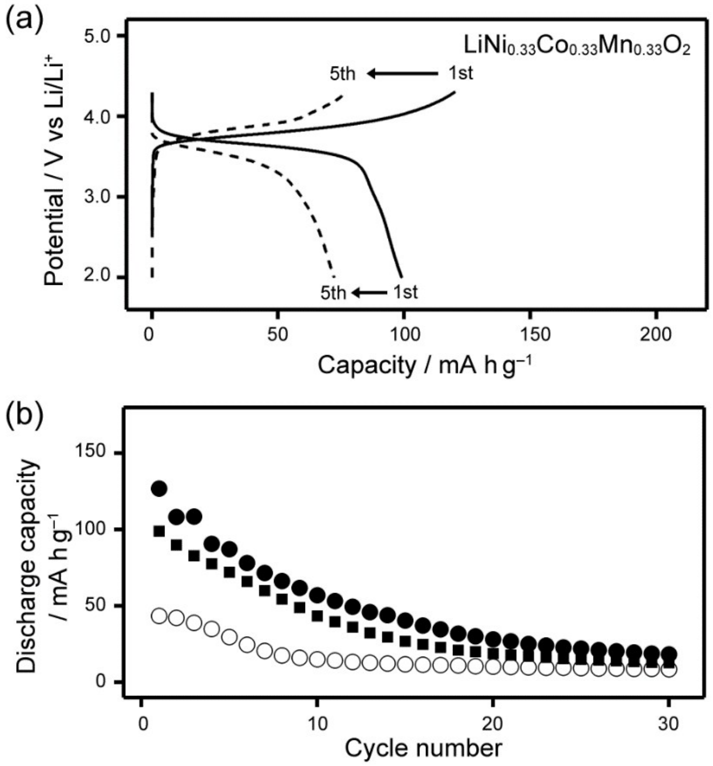

Figure S9. (a) Charge-discharge curves of Li half-cells composed of LC electrolyte **1**/LiTFSI and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ positive electrode, recorded in the voltage range 2.0–4.3 V vs Li/Li^+ at 80°C. (b) Cyclability of Li half-cells composed of LC electrolyte **1**/LiTFSI and various transition metal positive electrodes; (a) $LiCoO_2$ (white circle), $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (black square) and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (black circle).

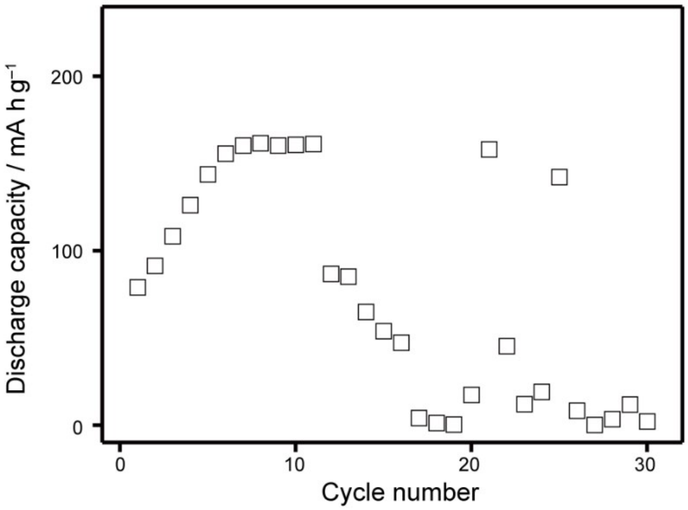

Figure S10. Cyclability of a Li half-cell composed of LC electrolyte **1**/LiTFSI and $LiNi_{0.815}Co_{0.15}Al_{0.035}O_2$ positive electrode.

Reference

1. W. Li, D. Wu, A. D. Schlüter and A. Zhang, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6630-6640.