Supporting Information

Highly Concentrated NaN(SO₂F)₂/3-Methylsulfolane Electrolyte Solution Showing High Na-Ion Transference Number under Anion-Blocking Conditions

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Table S1. Temperature dependences of viscosity (η), density (ρ), Na^+ concentration (c), and ionic conductivity (σ) of NaFSA/MSL electrolytes.

[NaFSA]/[MSL]=1/10

Temp. / °C	η /mPa s	ρ /g cm^{-3}	c /mol dm^{-3}	σ /mS cm^{-1}
25	39.0	1.27	0.821	1.54
30	31.2	1.26	0.818	1.87
35	25.4	1.26	0.816	2.24
40	20.9	1.26	0.813	2.64
45	17.5	1.25	0.810	3.08
50	14.8	1.25	0.807	3.57
55	12.6	1.24	0.804	4.07
60	10.9	1.24	0.802	4.60

[NaFSA]/[MSL]=1/2

Temp. / °C	η /mPa s	ρ /g cm^{-3}	c /mol dm^{-3}	σ /mS cm^{-1}
25	1888.2	1.49	3.15	0.19
30	1126.7	1.48	3.14	0.30
35	710.4	1.48	3.13	0.45
40	468.3	1.47	3.12	0.64
45	321.0	1.47	3.11	0.89
50	227.6	1.46	3.10	1.20
55	166.2	1.46	3.09	1.58
60	124.6	1.45	3.08	2.03

Table S2 Temperature dependences of viscosity (η), density (ρ), and ionic conductivity (σ) of 1 M NaPF$_6$/PC + 0.5 vol% FEC.

Temp. / °C	η /mPa s	ρ /g cm^{-3}	σ /mS cm^{-1}
25	7.09	1.29	7.64
30	6.18	1.29	8.51
35	5.42	1.28	9.43
40	4.80	1.28	10.4
45	4.27	1.27	11.3
50	3.83	1.27	12.2
55	3.46	1.26	–
60	3.14	1.26	13.2
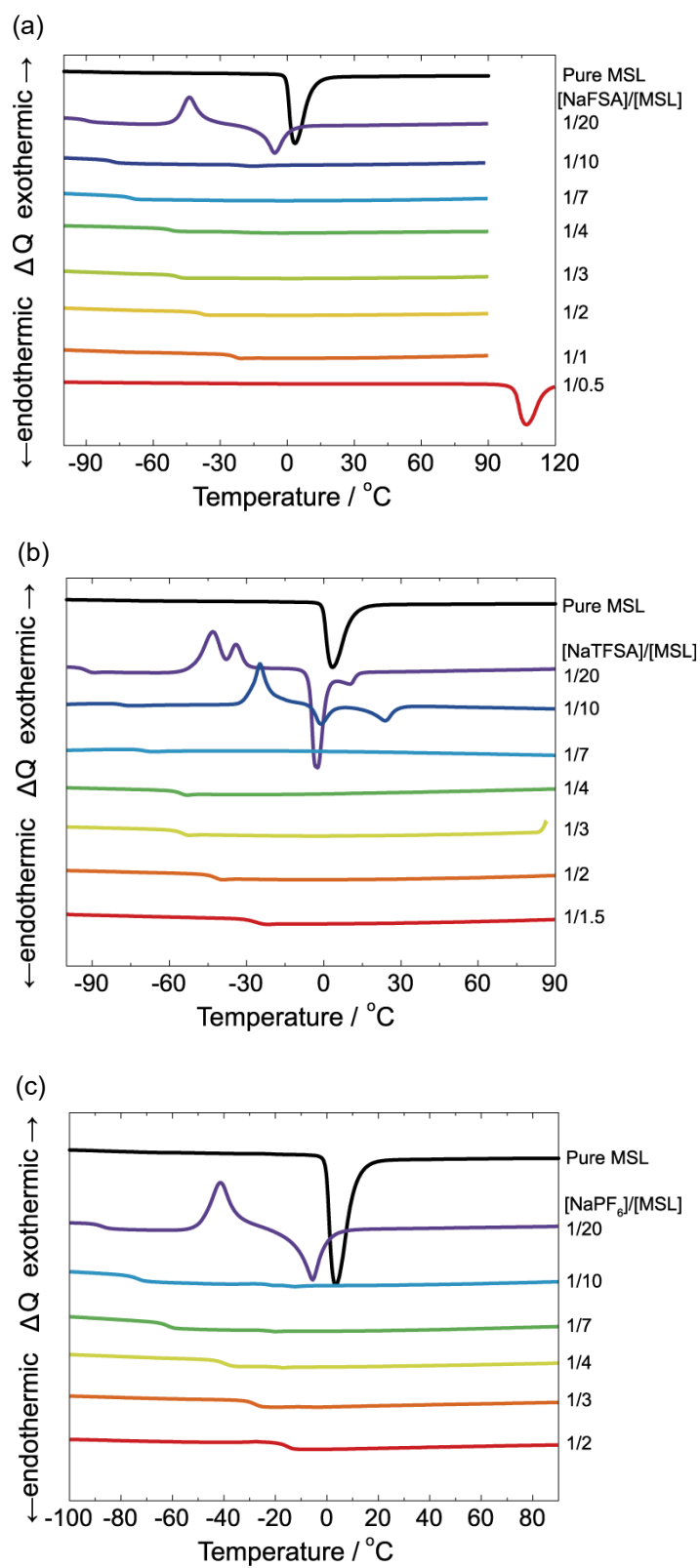
Figure S1. DSC thermograms of (a) NaFSA/MSL, (b) NaTFSA/MSL, and (c) NaPF$_6$/MSL binary mixtures.
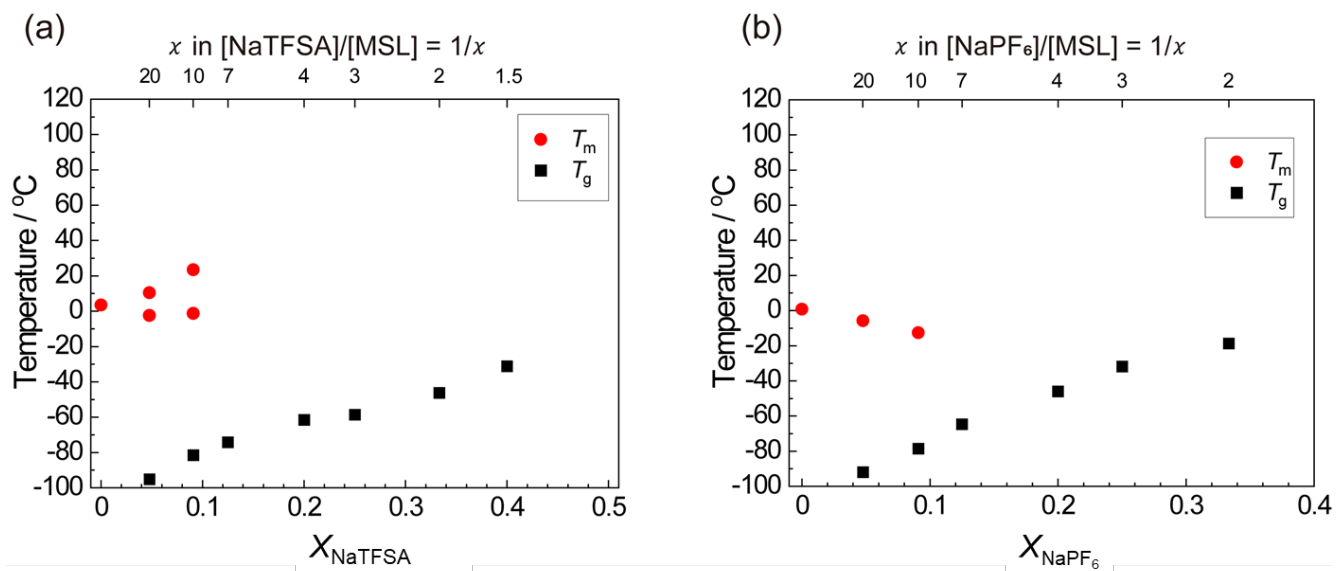
Figure S2. Melting points (T_m) and glass transition temperatures (T_g) of the binary mixtures of (a) NaTFSA/MSL and (b) NaPF$_6$/MSL. $X_{\text{Na salt}}$ is the Na salt mole fraction; $X_{\text{Na salt}} = 1/(1+x)$, where x in the molar ratio of [Na salt]/[MSL] = $1/x$.

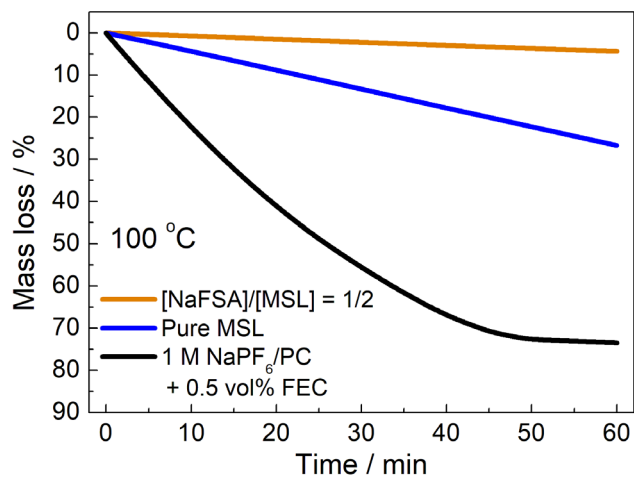**Figure S3.** Isothermal TG results of the electrolytes measured at 100 °C.

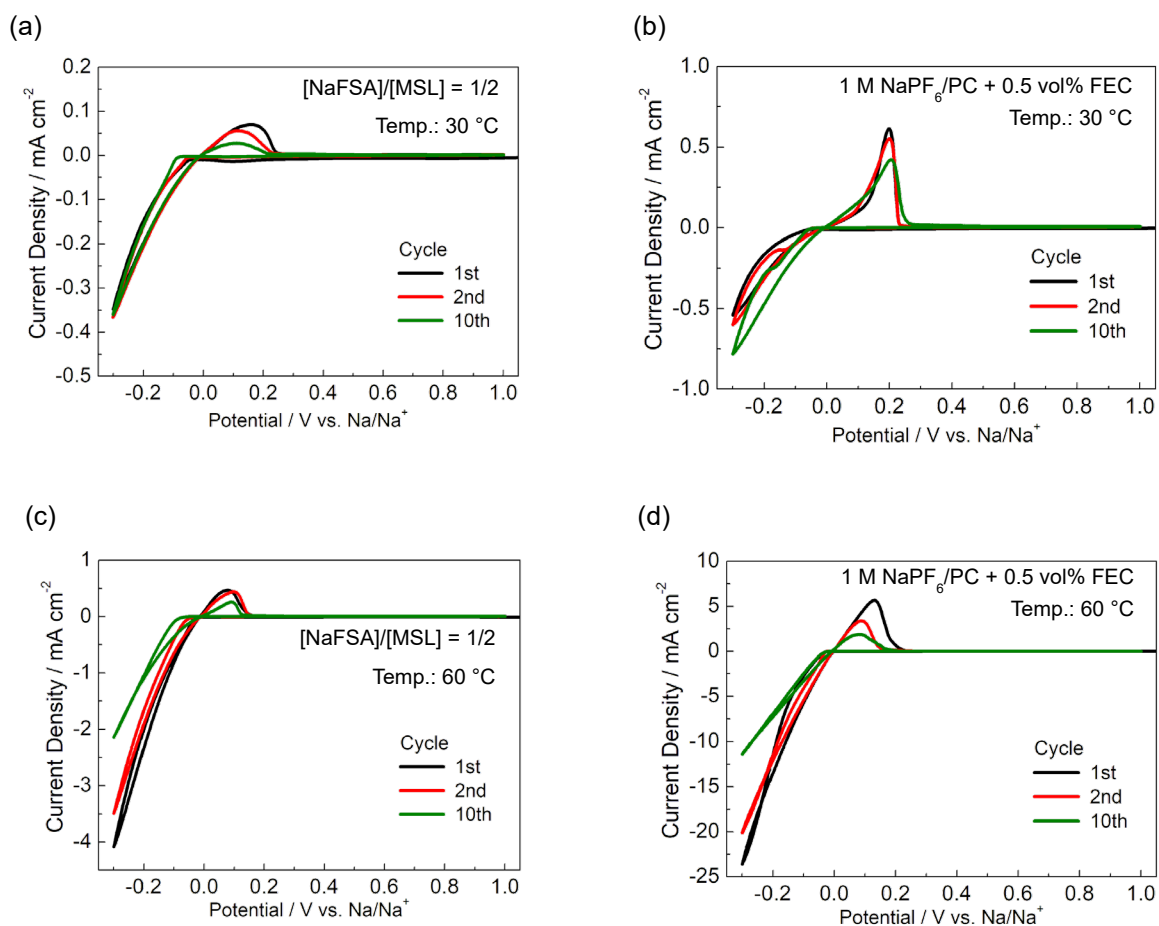**Figure S4.** Cyclic voltammograms of the electrolytes. Cyclic voltammetry (CV) was performed using a 2032-type coin cell with the configuration [Na | electrolyte/separator (GA-55) | Cu] at a scan rate of 1 mV s^{-1}.
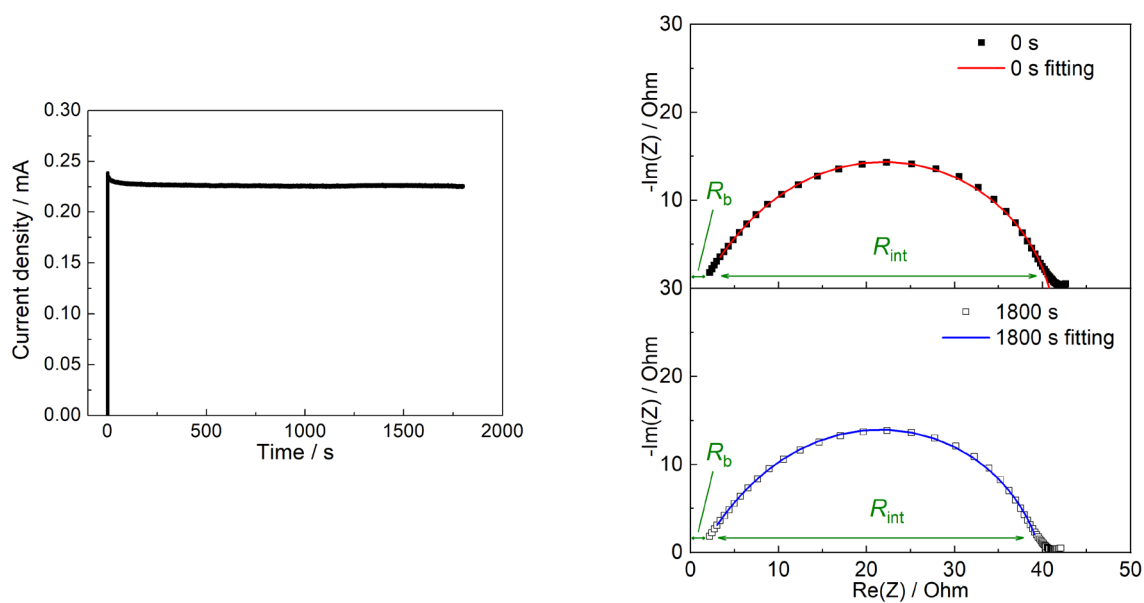
Figure S5. Chronoamperogram of the [Na | 1 M NaPF$_6$/PC + 0.5 vol% FEC | Na] cell at a constant voltage ΔV of 10 mV (left). Nyquist plots of the cell before and after potentiostatic polarization measurements (right). The measurements were conducted at 60 °C.
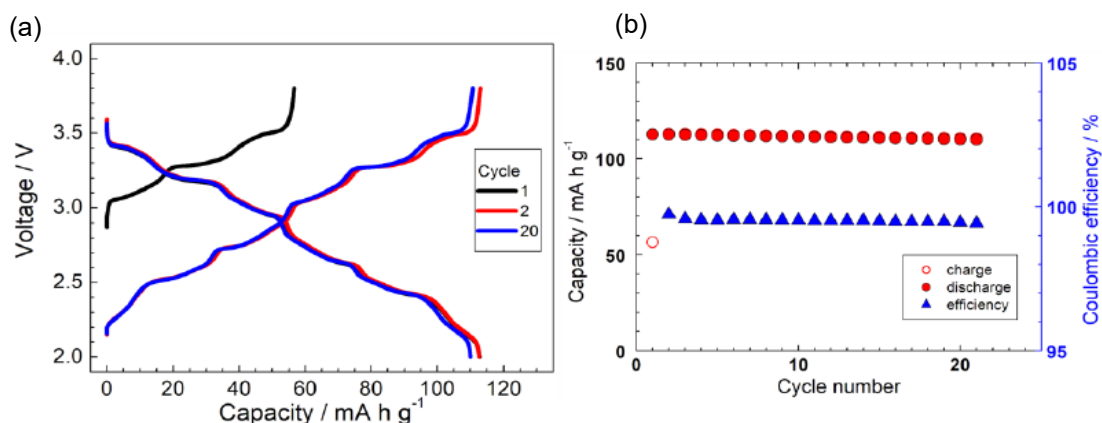
Figure S6. (a) Charge-discharge curves and (b) capacity retention and Coulombic efficiency of the [Na|[NaFSA]/[MSL] = 1/2|Na$_{0.44}$MnO$_2$] cell at a current density of 12.7 mA g^{-1} (0.1C, ~44 µA cm^{-2}) at 30 °C.
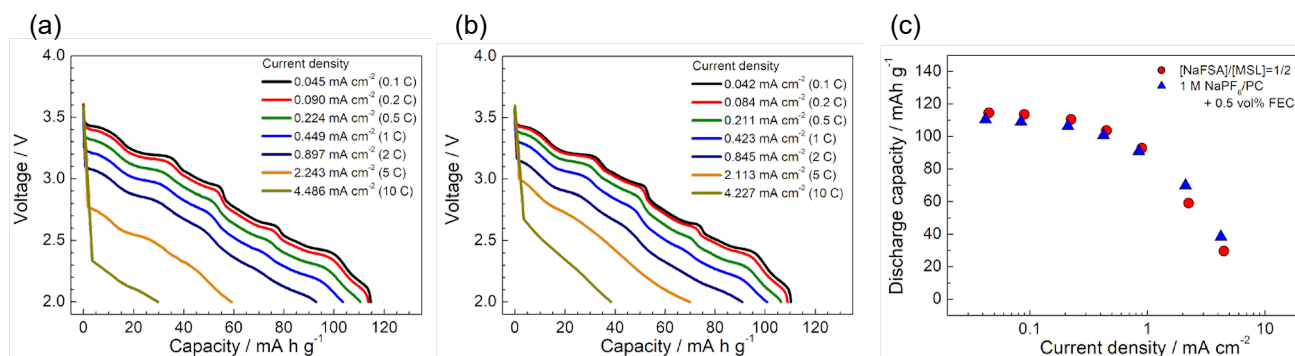
Figure S7. Discharge curves of Na/Na$_{0.44}$MnO$_2$ cells with   (a) [NaFSA]/[MSL] = 1/2 and (b) 1 mol dm^{-3} NaPF$_6$/PC + 0.5 vol% FEC electrolytes at 30 °C. (c) Discharge capacities of the cells as a function of current density. The Na$_{0.44}$MnO$_2$ electrodes were charged to 3.8 V at a constant current density of 0.1C (12.7 mA g^{-1}) prior to each discharge.