Supplementary Information (SI)

Cyclic ether-based electrolyte solutions for potassium metal batteries

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Table S1. Ionic conductivity (κ), dynamic viscosity (η), density (ρ), and K^+ concentration (c_{K+}) of THF-KFSI electrolyte solutions, measured at 25 °C.

Solvent-to-salt mole ratio	κ at 25 °C (mS cm^{-1})	η at 25 °C (mPa×s)	ρ at 25 °C (g cm^{-3})	c_{K+} (mol L^{-1})
50:1	2.4	0.6	0.92	0.24
40:1	2.7	0.6	0.93	0.30
30:1	4.2	0.7	0.94	0.39
20:1	5.8	0.8	0.97	0.58
15:1	7.3	0.9	0.99	0.76
12:1	8.2	1.2	1.02	0.94
10:1	9.4	1.3	1.04	1.11
9:1	9.7	1.5	1.06	1.22
8:1	10.4	1.8	1.07	1.35
7:1	11.7	2.1	1.10	1.51
6:1	12.7	2.5	1.12	1.72
5:1	12.6	3.5	1.16	2.00
4:1	11.5	5.1	1.21	2.38
3:1	11.1	9.3	1.28	2.94

Table S2. Ionic conductivity (κ), dynamic viscosity (η), density (ρ), and K^+ concentration (c_{K+}) of MeTHF-KFSI electrolyte solutions, measured at 25 °C.

Solvent-to-salt mole ratio	κ at 25 °C (mS cm^{-1})	η at 25 °C (mPa×s)	ρ at 25 °C (g cm^{-3})	c_{K+} (mol L^{-1})
50:1	0.3	0.5	0.88	0.19
40:1	0.4	0.6	0.88	0.24
30:1	0.7	0.7	0.90	0.32
20:1	1.3	0.8	0.92	0.47
15:1	1.9	0.8	0.94	0.62
12:1	2.6	1.0	0.96	0.77
10:1	3.5	1.2	0.98	0.91
9:1	3.5	1.4	1.00	1.00
8:1	3.9	1.5	1.01	1.11
7:1	4.7	1.9	1.03	1.26
6:1	5.4	2.2	1.06	1.44
5:1	5.7	3.1	1.09	1.68
4:1	6.4	4.8	1.14	2.02

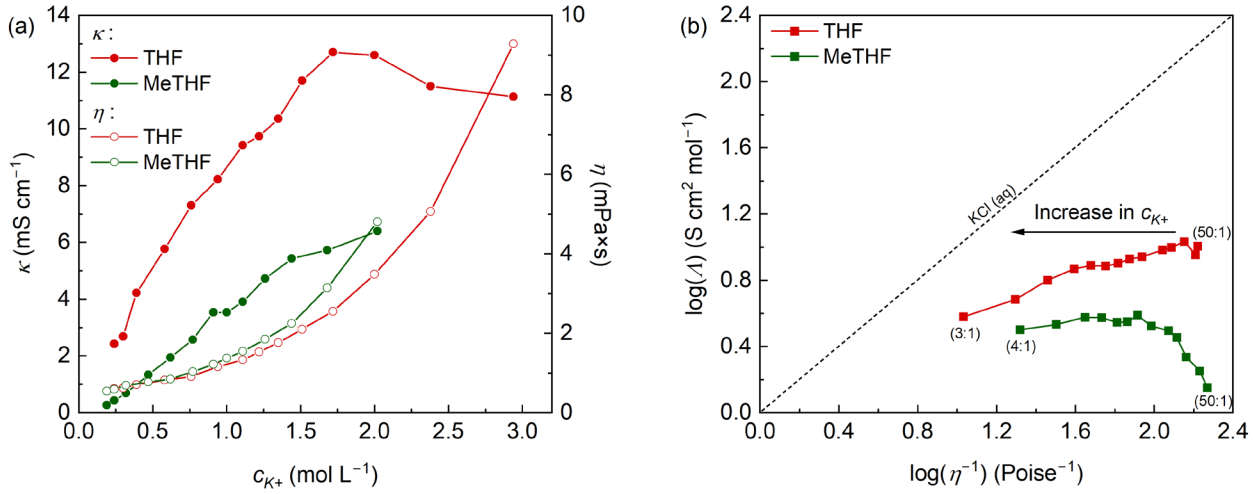

Figure S1. (a) Ionic conductivity and dynamic viscosity of the THF/MeTHF-KFSI binary mixtures *vs.* the K^+ concentration in molarity, measured at 25 °C. (b) Walden plot of the THF/MeTHF-KFSI binary mixtures.

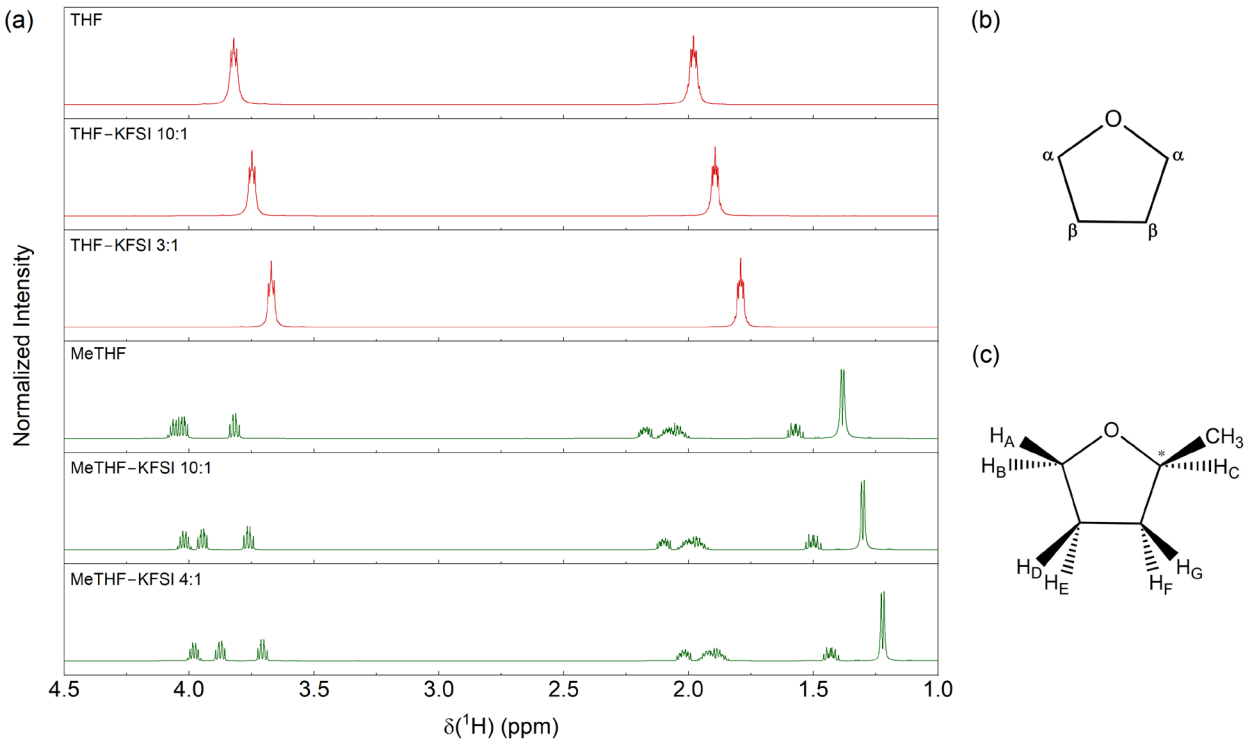

Figure S2. (a) Concentration dependence of the ^{1}H NMR (600.35 MHz) chemical shifts for THF/MeTHF-KFSI binary mixtures. The spectra were individually, vertically scaled to equal intensity of the largest signal. Structural formula of (b) tetrahydrofuran and (c) (*S*)-2-methyltetrahydrofuran, with the different proton environments assigned.

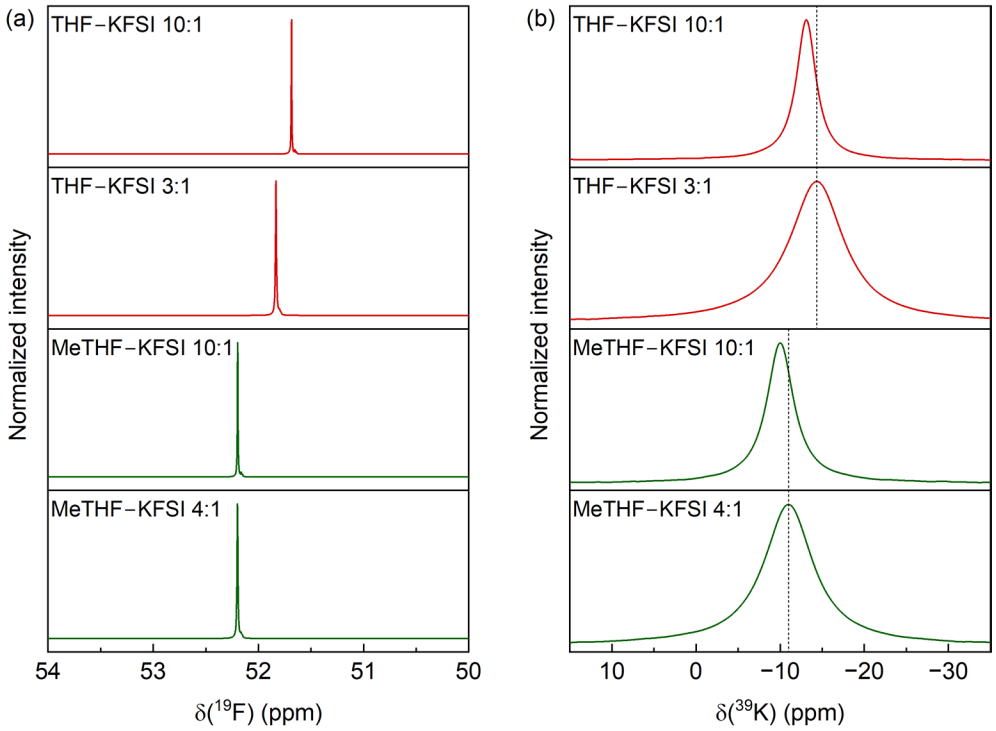

Figure S3. Concentration dependence of the ^{19}F NMR (564.89 MHz, (a)) and ^{39}K NMR (28.01 MHz, (b)) chemical shifts for THF/MeTHF-KFSI binary mixtures. All spectra were individually, vertically scaled to equal intensity of the largest signal.

Table S3. System composition, equilibrated box length, and density for molecular dynamics simulations of the two electrolyte solutions at 298.15 K.

Electrolyte solution	THF / MeTHF	KFSI	Box length *a* (Å)	$\rho_{calc.}$ at 298.15 K (g cm^{-3})
THF-KFSI 3:1	750	250	53.13	1.21
MeTHF-KFSI 4:1	800	200	55.42	1.10

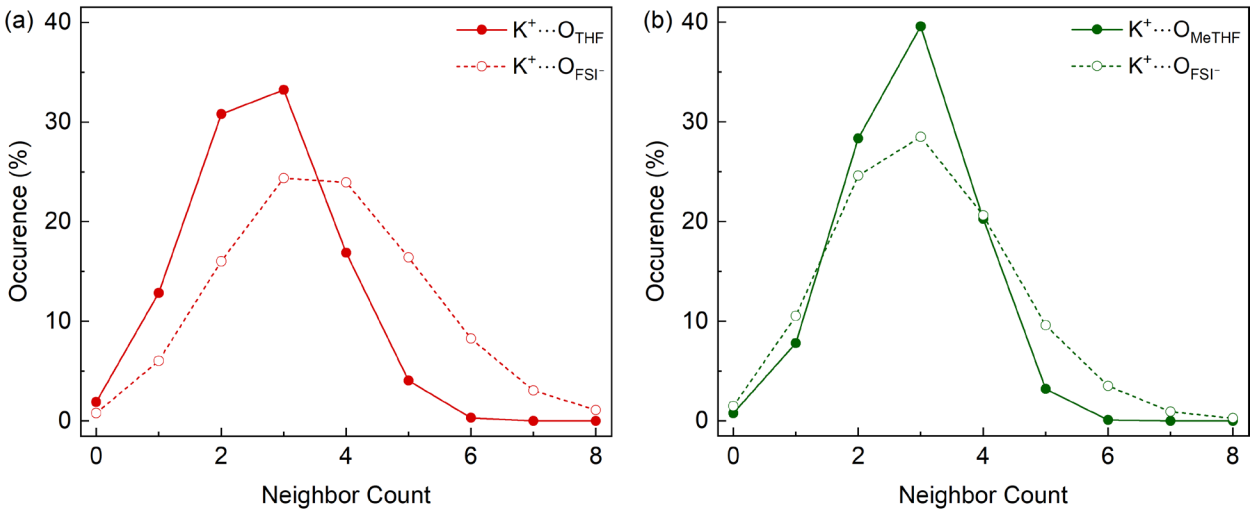

Figure S4. Neighbor count histogram for the cation's first solvation shell in (a) THF-KFSI 3:1 and (b) MeTHF-KFSI 4:1.

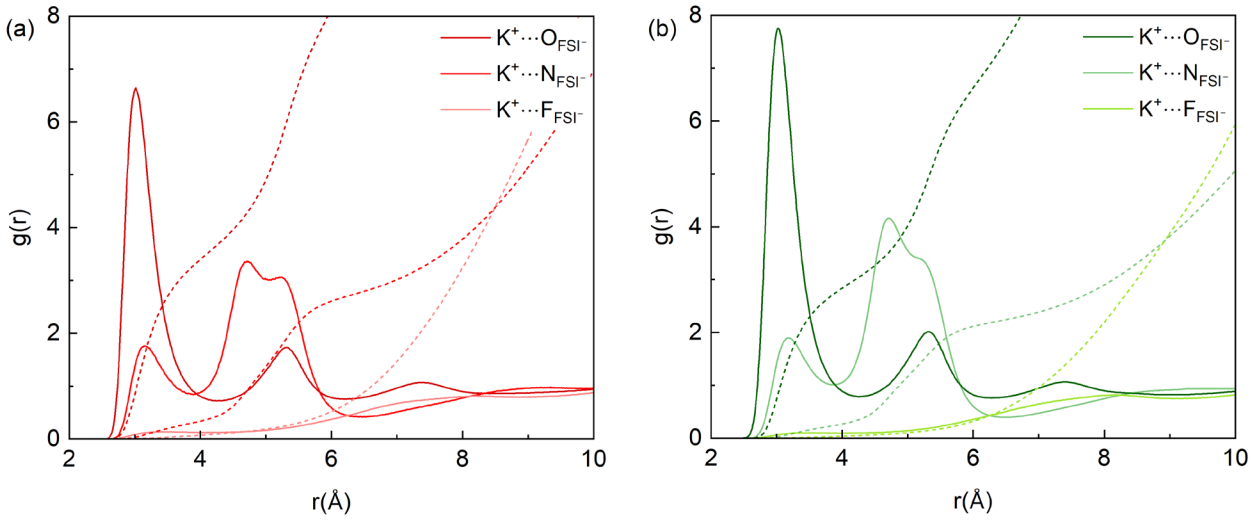

Figure S5. Radial distribution functions (solid lines) and number integrals (dashed lines) of the K^+ cation interacting with different atoms of the FSI^- anion in (a) THF-KFSI 3:1 and (b) MeTHF-KFSI 4:1.

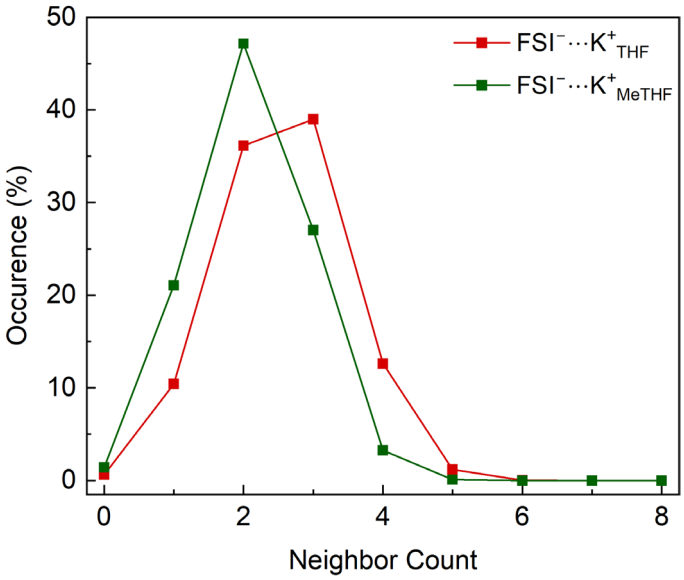

Figure S6. Neighbor count histogram for the anion's first solvation shell in THF-KFSI 3:1 and MeTHF-KFSI 4:1.

Table S4. Overview of the galvanostatic cycling experiments conducted in K||Al half-cells cycled in THF-KFSI 3:1 and in MeTHF-KFSI 4:1, with two coin cells tested for each cycling condition.

Cell configuration	Electrolyte solution	Coin cell	Cycling conditions	$CE_{Initial}$ (%)	Cycle number	η First cycle (V)
K||Al	THF-KFSI 3:1	1	0.5 mA cm^{-2} 1 mAh cm^{-2}	95.4	> 500	0.142
		2		93.6	> 500	0.139
	MeTHF-KFSI 4:1	1		88.7	> 500	0.188
		2		91.6	> 500	0.194
	THF-KFSI 3:1	1	1.0 mA cm^{-2} 1 mAh cm^{-2}	94.9	> 350	0.196
		2		93.0	> 350	0.192
	MeTHF-KFSI 4:1	1		75.7	> 350	0.274
		2		89.0	> 350	0.249
	THF-KFSI 3:1	1	2.0 mA cm^{-2} 1 mAh cm^{-2}	93.2	> 200	0.249
		2		97.5	> 200	0.252
	MeTHF-KFSI 4:1	1		74.8	> 150	0.346
		2		82.9	36	0.333
	THF-KFSI 3:1	1	4.0 mA cm^{-2} 1 mAh cm^{-2}	90.8	104	0.327
		2		98.5	96	0.328
	MeTHF-KFSI 4:1	1		72.5	35	0.422
		2		74.5	29	0.414

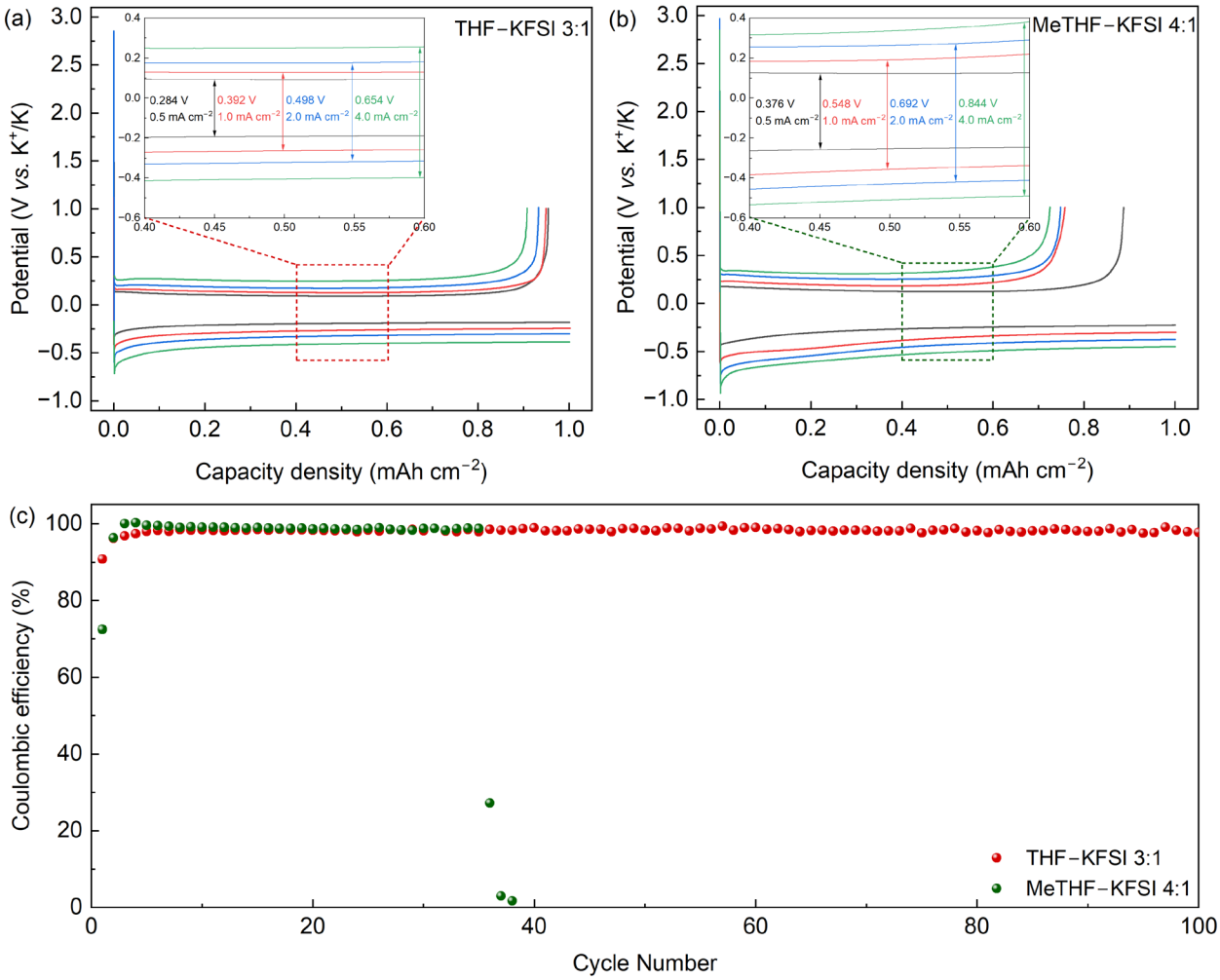

Figure S7. Potassium metal plating/stripping behavior in THF/MeTHF-KFSI electrolyte solutions. Polarization profiles of the K||Al half-cell configuration cycled in (a) THF-KFSI 3:1 and in (b) MeTHF-KFSI 4:1 at different current densities with a cutoff capacity of 1 mAh cm^{-2}. (c) Potassium metal plating/stripping CE of the K||Al half-cell cycled in different electrolyte solutions at a current density of 4.0 mA cm^{-2} with a cutoff capacity of 1 mAh cm^{-2}.

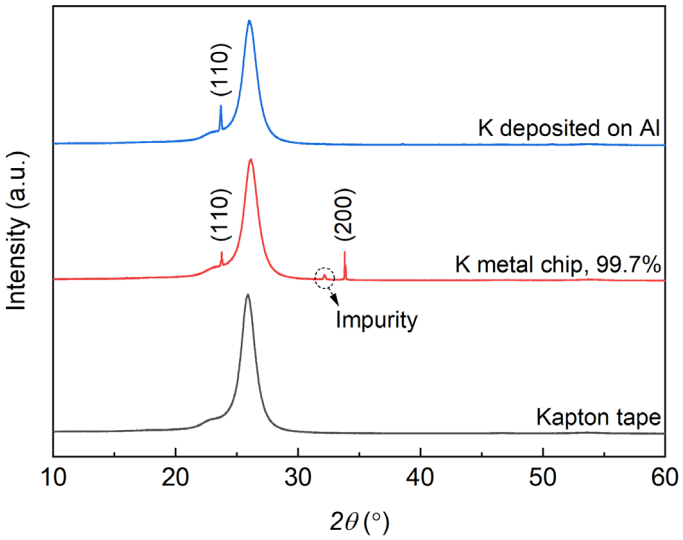

Figure S8. X-ray diffraction (XRD) pattern of Kapton tape, potassium metal chip with a purity of 99.7% and potassium metal electrochemically deposited on aluminum foil (0.5 mA cm^{-2}; 1 mAh cm^{-2} – during discharge).

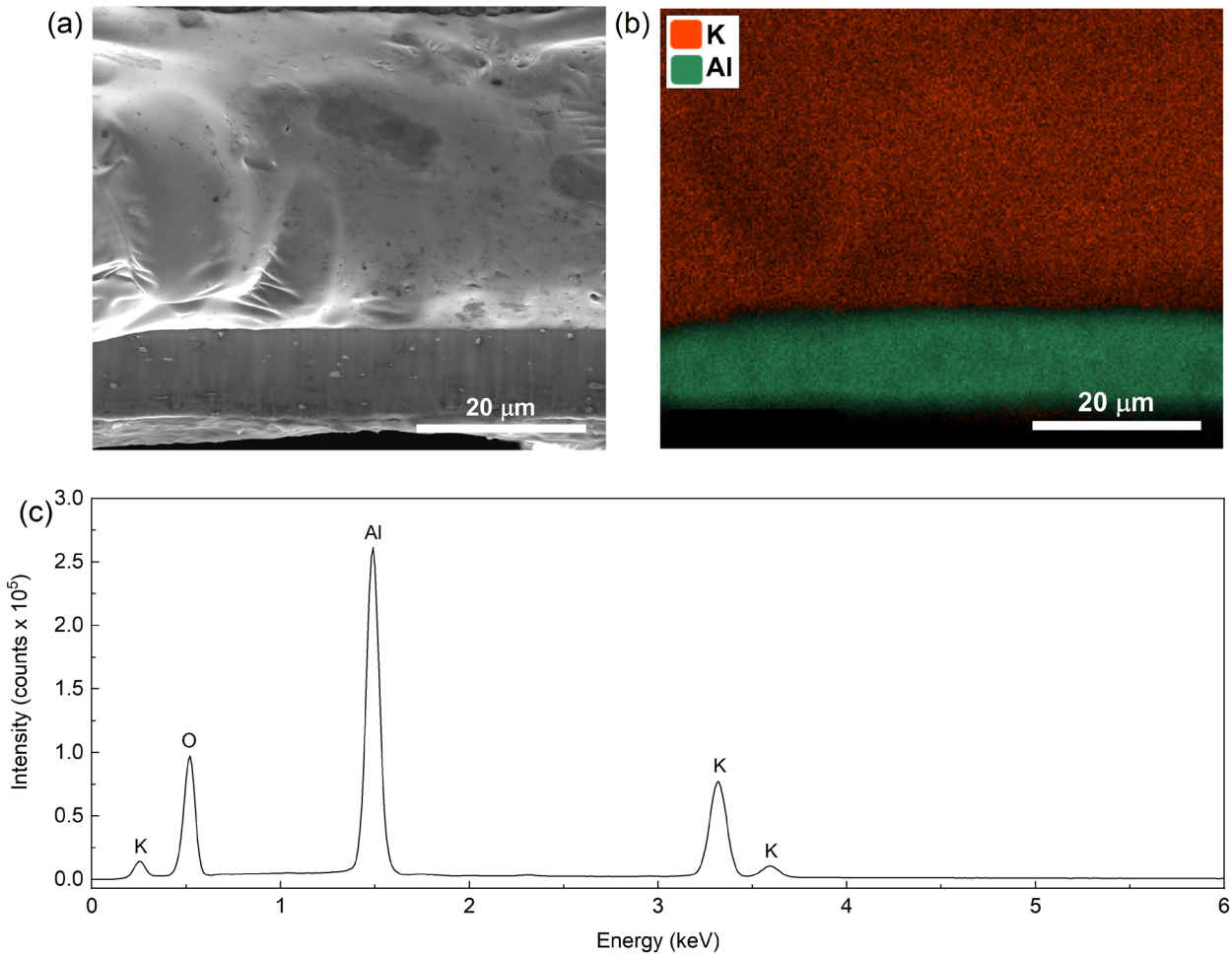

Figure S9. (a) SEM cross section image of the deposited potassium metal on the aluminum current collector after discharging of the first cycle at 0.5 mA cm^{-2} under 1 mAh cm^{-2} in THF-KFSI 3:1. (b) EDX elemental mapping and (c) EDX spectrum of the cross section.

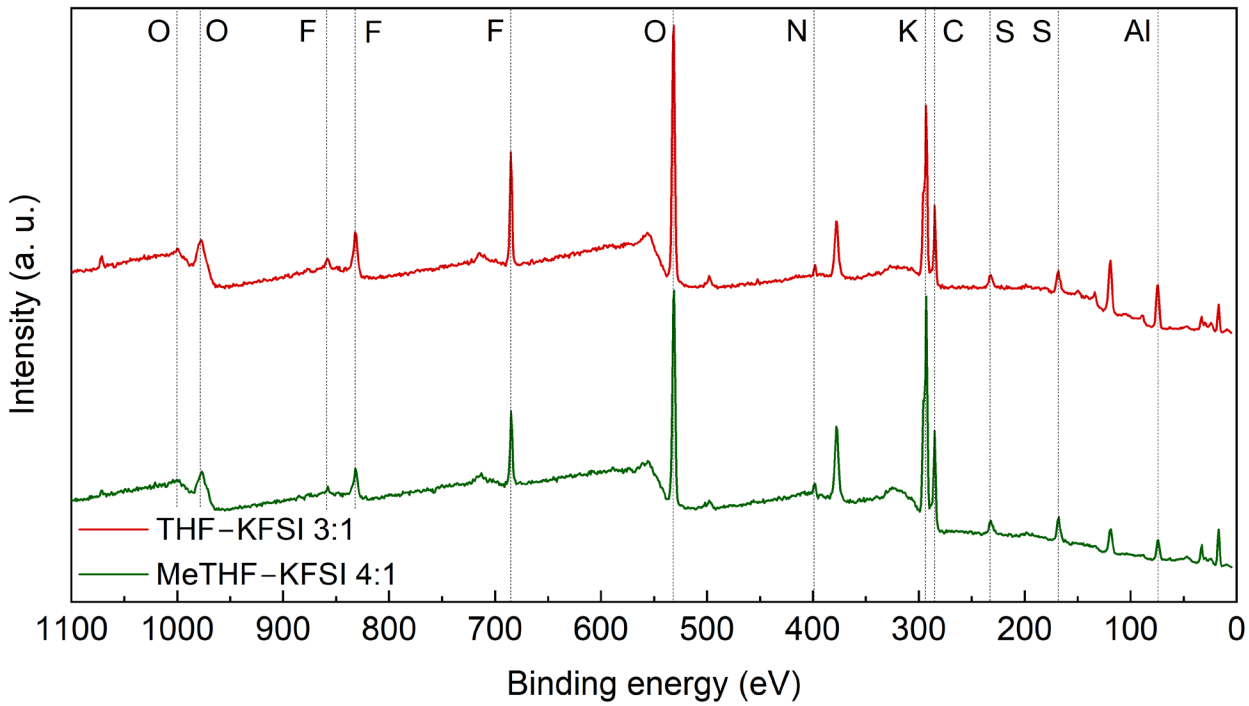

Figure S10. XPS profiles of the SEIs formed on the aluminum electrode after the first cycle in THF-KFSI 3:1 and MeTHF-KFSI 4:1.

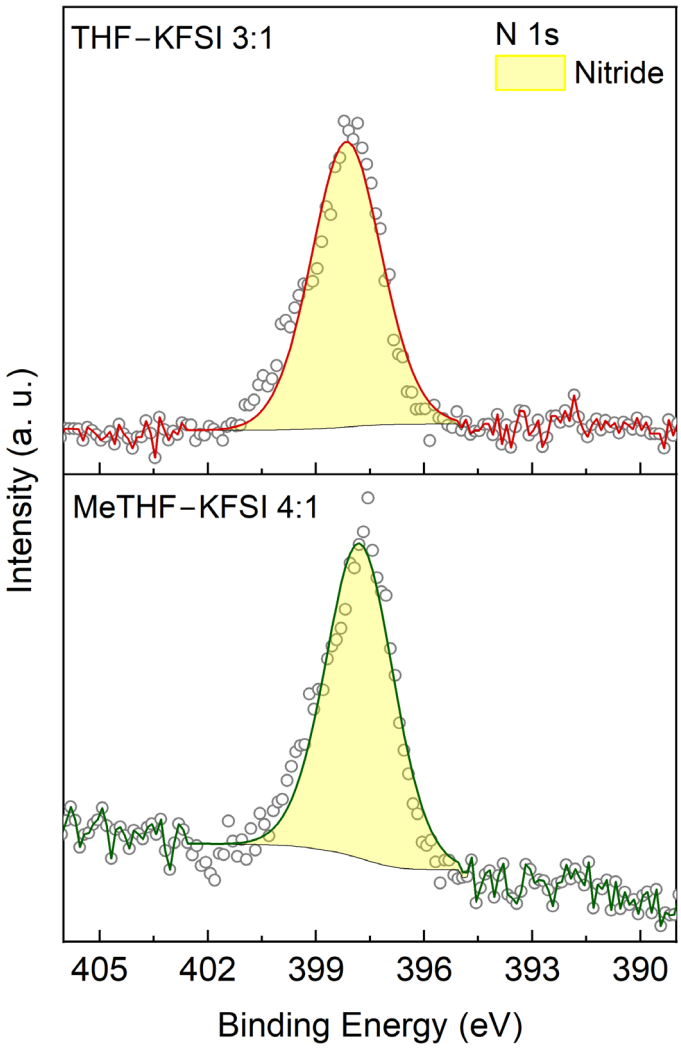

Figure S11. N 1s XPS spectra of the SEI layers formed on the aluminum current collector after the first cycle in THF-KFSI 3:1 and MeTHF-KFSI 4:1.

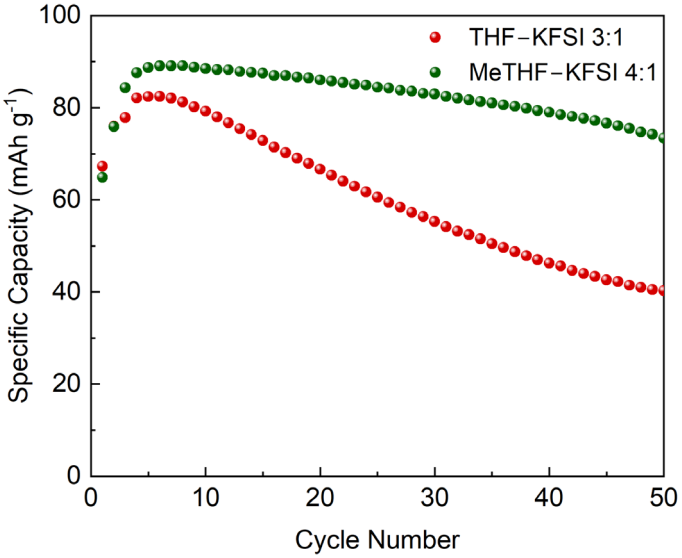

Figure S12. Cycling performance of AC||K_2-Co-PTtSA cells in THF-KFSI 3:1 and MeTHF-KFSI 4:1 at a rate of 0.1C.