Secondary alkali-metal salts in supporting electrolytes for lithium polysulfide flow batteries

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Supplementary Information

Contents

1. Crystallographic Data

1.1. General fitting and refinement data

Table S1: Selected crystallographic and refinement parameters

Compound	***1 (TFSINa·DME)***	***2 (RbTFSI)***
CCDC ref. no.	2529359	2529360
Formula	$C_6H_{10}F_6NNaO_6S_2$	$C_2F_6NO_4RbS_2$
Formula Weight	393.26	365.62
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	P-1
Temp. (K)	100(2)	100(2)
a (Å)	11.7450(6)	8.1792(5)
b (Å)	9.8155(5)	10.6823(5)
c (Å)	13.1950(6)	11.4178(7)
α (°)	90	101.302(5)
β (°)	104.079(5)	101.707(6)
γ (°)	90	90.023(4)
Volume (Å³)	1475.47(13)	957.07(10)
Z	4	4
Collected Reflections	10839	11581
Independent Reflections	4216	3603
Observed Reflections	3481	3217
Rint	0.0463	0.0402
2Θmax (°)	144.702	143.268
No. Parameters	402	289
S	1.145	1.071
R [on F, obs refs only]	0.0478	0.0523
ωR [on F², all data]	0.1421	0.1500
Flack	0.50(4)	n.a.

1.2 TFSINa·DME

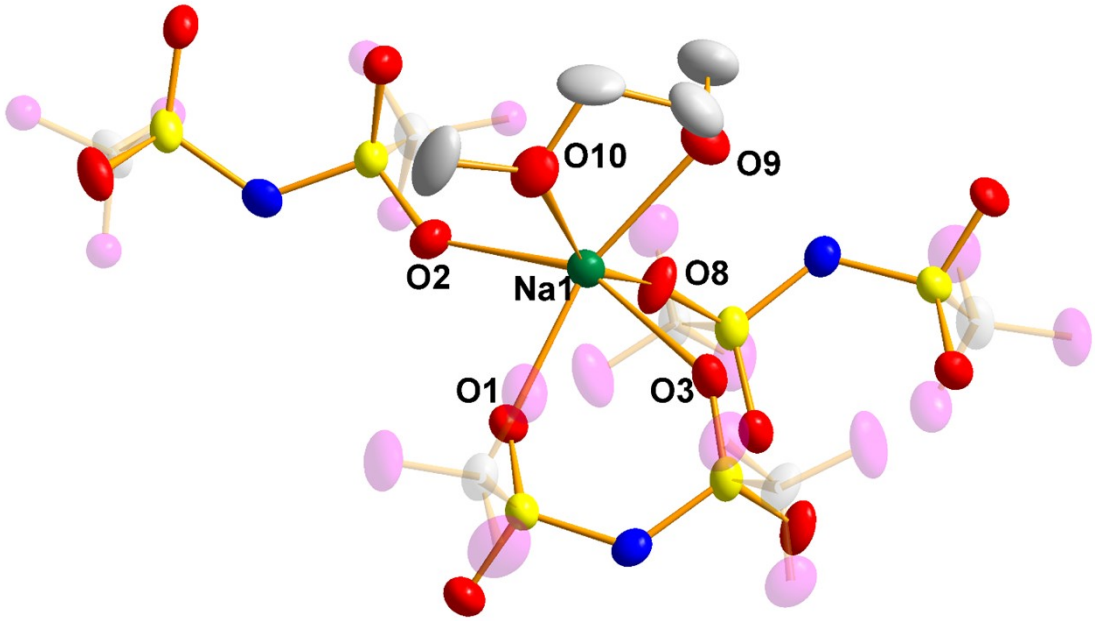

Fig. S1 Part of the structure of TFSINa·DME complex showing coordination sphere at Na1, with hydrogen atoms omitted and thermal ellipsoids drawn at 50% probability level.

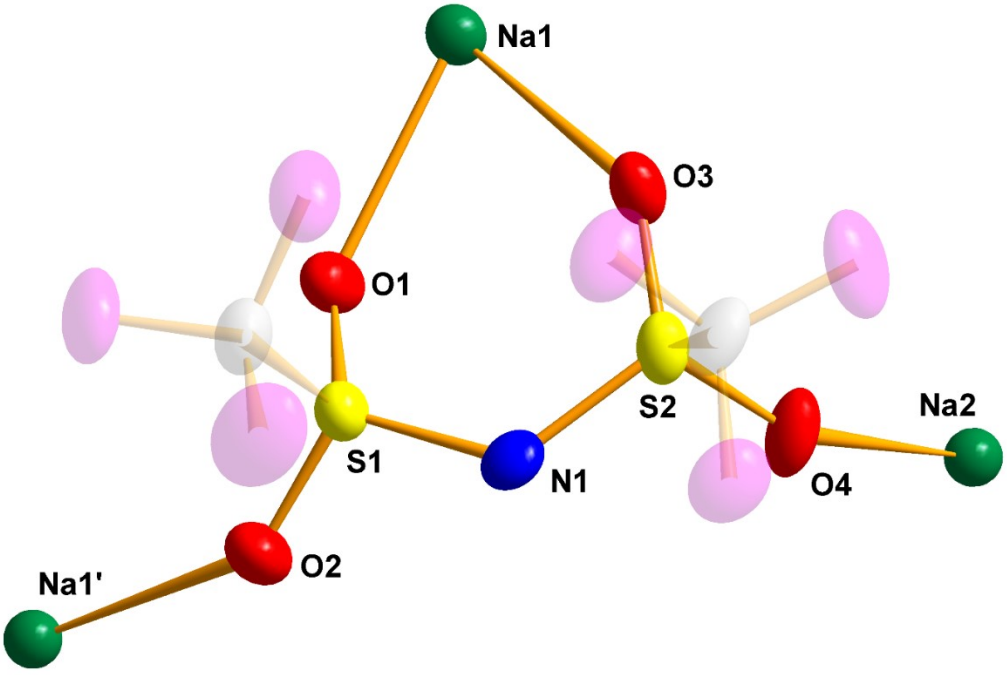

Fig. S2 Part of the structure of TFSINa·DME showing TFSI ligand and its different interactions with Na cations to propagate polymer, with hydrogen atoms omitted and thermal ellipsoids drawn at 50% probability level.

Table S2: Selected bond lengths for TFSINa·DME

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Na1-O1	2.355(7)	Na2-O5	2.349(7)	S1-N1	1.568(6)
Na1-O3	2.383(7)	Na2-O7	2.435(6)	S2-N1	1.578(7)
Na1-O8	2.327(6)	Na2-O4	2.367(5)	S1-O2	1.425(6)
Na1-O9	2.377(7)	Na2-O11	2.367(7)	S2-O4	1.429(6)
Na1-O10	2.397(6)	Na2-O12	2.383(6)	S3-N2	1.566(6)
Na1-O2’	2.379(6)	Na2-O6’	2.376(6)	S4-N2	1.567(7)
O1-S1	1.428(7)	O5-S3	1.434(6)	S3-O6	1.426(6)
O3-S2	1.415(7)	O7-S4	1.441(7)	S4-O8	1.433(6)

Table S3: Selected bond angles for TFSINa·DME

Bonds	Angle (˚)	Bonds	Angle (˚)	Bonds	Angle (˚)	Bonds	Angle (˚)
O1-Na1-O3	74.2(2)	O5-Na2-O7	73.5(2)	O3-Na1-O2’	151.9(3)	O7-Na2-O6’	153.3(3)
O1-Na1-O8	101.2(3)	O5-Na2-O4	108.3(3)	O8-Na1-O9	86.3(2)	O4-Na2-O11	95.2(3)
O1-Na1-O9	157.3(2)	O5-Na2-O11	146.3(2)	O8-Na1-O10	152.3(3)	O4-Na2-O12	155.2(3)
O1-Na1-O10	105.7(2)	O5-Na2-O12	94.1(2)	O8-Na1-O2’	88.9(2)	O4-Na2-O6’	84.3(2)
O1-Na1-O2’	78.6(2)	O5-Na2-O6’	84.8(2)	O9-Na1-O10	71.2(2)	O11-Na2-O12	69.9(2)
O3-Na1-O8	89.3(2)	O7-Na2-O4	87.8(2)	O9-Na1-O2’	123.3(3)	O11-Na2-O6’	122.3(3)
O3-Na1-O9	84.5(2)	O7-Na2-O11	83.8(2)	O10-Na1-O2’	90.2(2)	O12-Na2-O6’	87.3(2)
O3-Na1-O10	103.9(2)	O7-Na2-O12	109.3(2)	S1-N1-S2	124.9(5)	S3-N2-S4	126.0(5)

1.3 RbTFSI

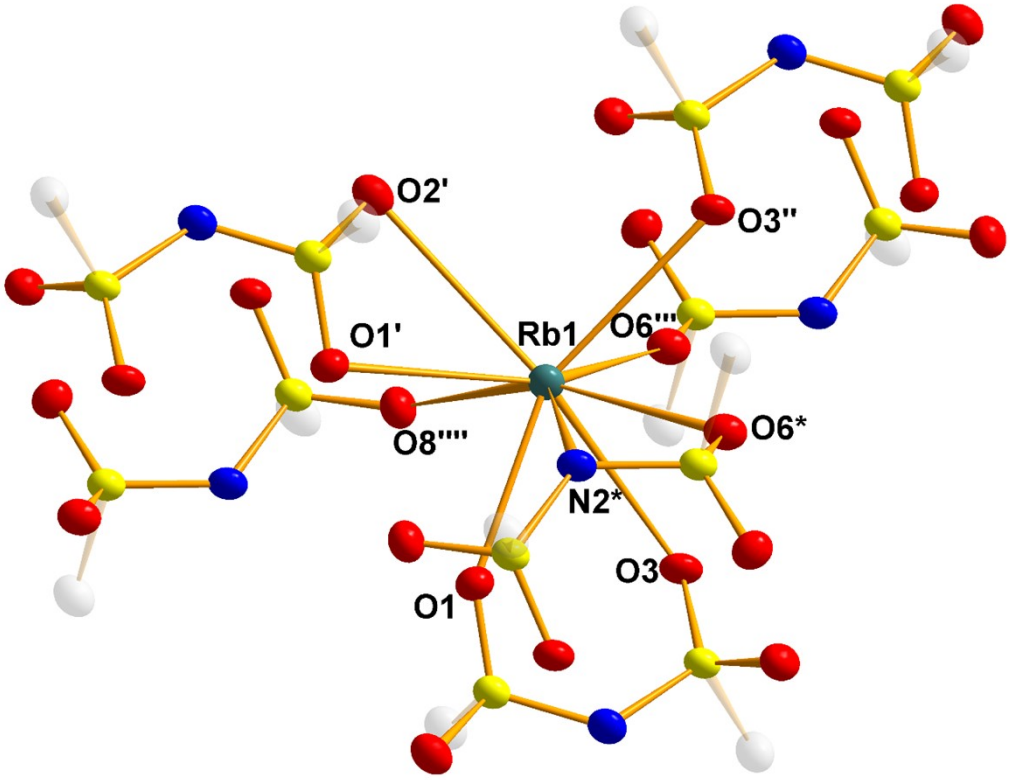

Fig. S3 Part of the structure of RbTFSI showing coordination sphere at Rb1, with hydrogen and fluorine atoms omitted and thermal ellipsoids drawn at 50% probability level.

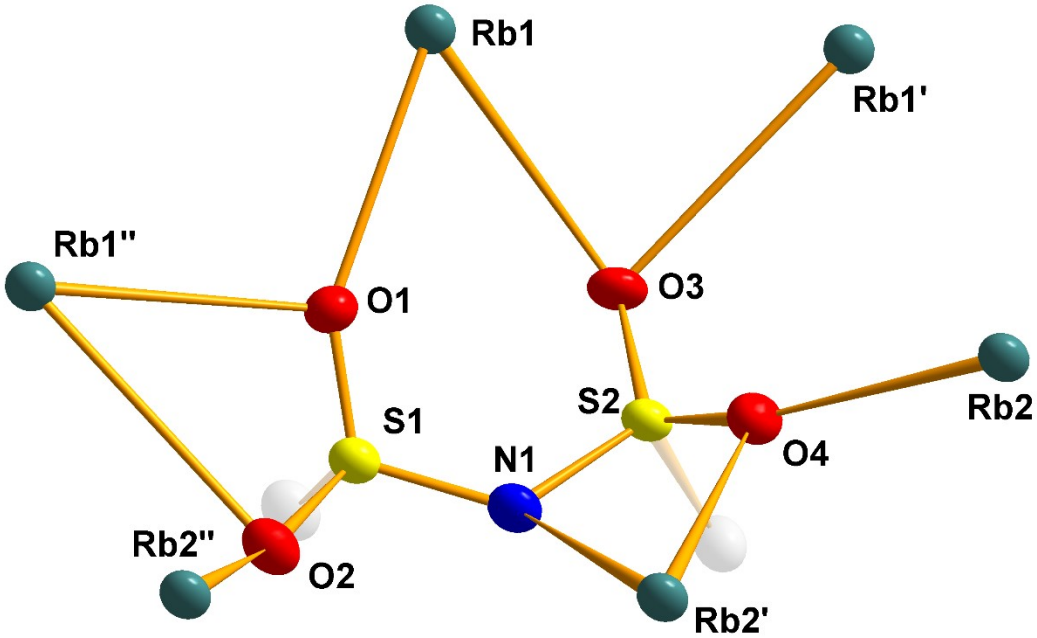

Fig. S4 Part of the structure of RbTFSI showing TFSI ligand and its different interactions with Rb cations to propagate polymer, with hydrogen and fluorine atoms omitted and thermal ellipsoids drawn at 50% probability level.

Table S4: Selected bond lengths for complex 2

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Rb1-O1	2.794(3)	Rb2-O7	2.789(3)	O3-S2	1.430(3)
Rb1-O3	3.161(3)	Rb2-O5	3.226(3)	S1-N1	1.572(4)
Rb1-O1’	2.966(3)	Rb2-O7’	2.977(3)	S2-N1	1.584(4)
Rb1-O2’	3.327(3)	Rb2-O8’	3.305(3)	S1-O2	1.432(3)
Rb1-O3’’	3.149(3)	Rb2-O5’’	3.163(3)	S2-O4	1.438(3)
Rb1-O6’’’	2.834(3)	Rb2-O4’’’	2.813(3)	O7-S4	1.440(3)
Rb1-O6*	2.946(3)	Rb2-O4*	2.964(3)	S3-N2	1.590(4)
Rb1-N2*	3.314(4)	Rb2-N1*	3.212(4)	S4-N2	1.565(3)
Rb1-O8’’’’	2.969(3)	Rb2-O2’’’’	2.970(3)	S3-O6	1.433(3)
O1-S1	1.435(3)	O5-S3	1.432(3)	S4-O8	1.433(3)

1.4 Bond Valence Sum Calculations

The bond valence sums for each metal centre in RbTFSI and TFSINa·DME are calculated using:

$$V = \sum v_i = \sum exp\left(\frac{R_0 - R_i}{B}\right)$$

Where v_i is the individual bond valence, R_0 = 2.263 Å for Rb-O, 2.37 Å for Rb-N, and 1.803 Å for Na-O, R_i is the observed bond distance and B = 0.37 Å.

Table S5: Bond valence values for Rb1 from RbTFSI giving a bond valence sum of 1.22

Bond	R_i	R_0	$[R_0-R]/B$	ν_i
Rb1-O1	2.794(3)	2.263	-1.435	0.238
Rb1-O3	3.161(3)	2.263	-2.427	0.088
Rb1-O1'	2.966(3)	2.263	-1.900	0.150
Rb1-O2'	3.327(3)	2.263	-2.876	0.056
Rb1-O3''	3.149(3)	2.263	-2.395	0.091
Rb1-O6'''	2.834(3)	2.263	-1.543	0.214
Rb1-O6*	2.946(3)	2.263	-1.846	0.158
Rb1-N2*	3.314(4)	2.37	-2.551	0.078
Rb1-O8''''	2.969(3)	2.263	-1.908	0.148

Table S6: Bond valence values for Rb2 from RbTFSI giving a bond valence sum of 1.23

Bond	R_i	R_0	$[R_0-R]/B$	ν_i
Rb2-O7	2.789(3)	2.263	-1.422	0.241
Rb2-O5	3.226(3)	2.263	-2.603	0.074
Rb2-O7'	2.977(3)	2.263	-1.930	0.145
Rb2-O8'	3.305(3)	2.263	-2.816	0.060
Rb2-O5''	3.163(3)	2.263	-2.432	0.088
Rb2-O4'''	2.813(3)	2.263	-1.486	0.226
Rb2-O4*	2.964(3)	2.263	-1.895	0.150
Rb2-N1*	3.212(4)	2.370	-2.276	0.103
Rb2-O2''''	2.970(3)	2.263	-1.911	0.148

Table S7: Bond valence values for Na1 from TFSINa·DME giving a bond valence sum of 1.30

Bond	R_i	R_0	$[R_0-R]/B$	ν_i
Na1-O1	2.355(7)	1.803	-1.492	0.225
Na1-O3	2.383(7)	1.803	-1.568	0.209
Na1-O8	2.327(6)	1.803	-1.416	0.243
Na1-O9	2.377(7)	1.803	-1.551	0.212
Na1-O10	2.397(6)	1.803	-1.605	0.201
Na1-O2'	2.379(6)	1.803	-1.557	0.211

Table S8: Bond valence values for Na2 from TFSINa·DME giving a bond valence sum of 1.27

Bond	**R_i**	**R_0**	**$[R_0-R]/B$**	**ν_i**
Na2-O5	2.349(7)	1.803	-1.476	0.229
Na2-O7	2.435(6)	1.803	-1.708	0.181
Na2-O4	2.367(5)	1.803	-1.524	0.218
Na2-O11	2.367(7)	1.803	-1.524	0.218
Na2-O12	2.383(6)	1.803	-1.568	0.209
Na2-O6'	2.376(6)	1.803	-1.549	0.213

2. NMR spectra of synthesised MTFSI salts

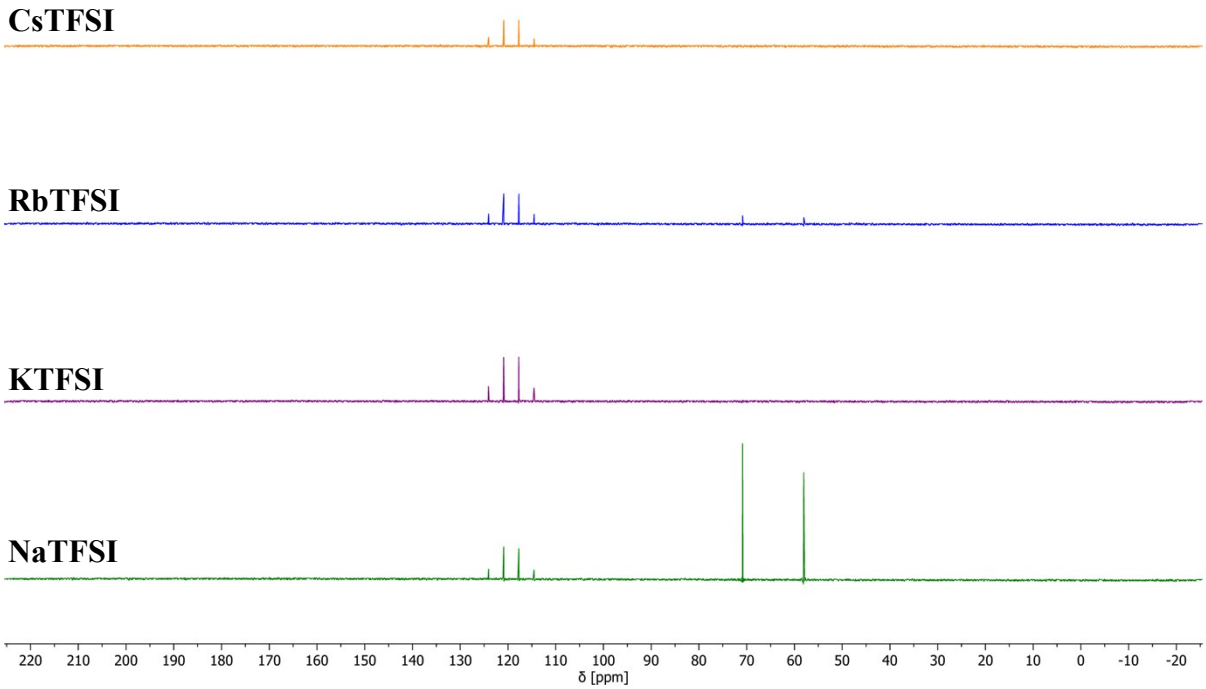

Fig. S5 $^{13}C\{^{1}H\}$ NMR spectrum (100.62 MHz, D_2O) of synthesized MTFSI salts

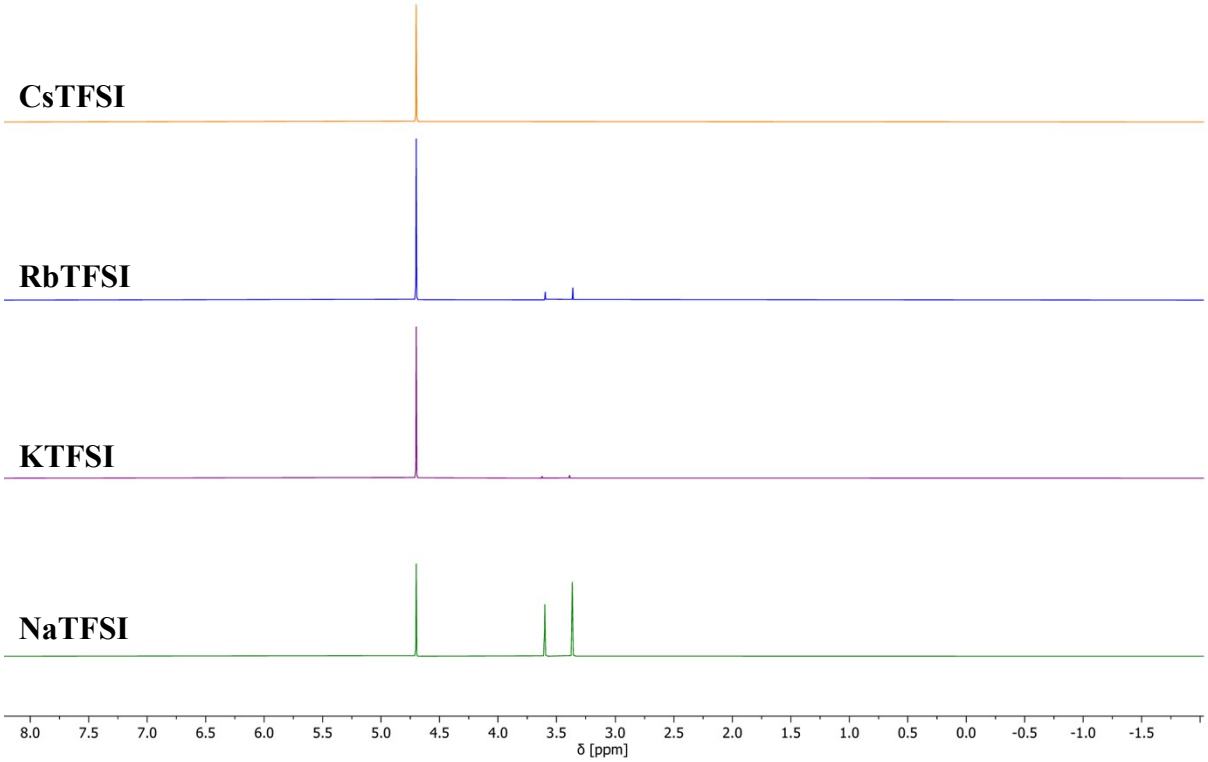

Fig. S6 ^{1}H NMR spectrum (400.13 MHz, D_2O) of synthesized MTFSI salts

NMR Spectra Asssignments:

NaTFSI:^{13}C NMR (101 MHz, D_2O): δ = 118.77 (q, $^1J_{C\text{-}F}$ = 323.2 Hz, CF_3), 70.78 (RCH_2-OR), 58.05 (RO-CH_3).
^{1}H NMR (400 MHz, D2O): δ = 3.60 (s, 2H, RCH_2-OR), 3.37 (s, 3H, RO-CH_3).

KTFSI:^{13}C NMR (101 MHz, D_2O): δ = 119.32 (q, $^1J_{C\text{-}F}$ = 319.7 Hz, CF_3).
^{1}H NMR (400 MHz, D2O): δ = 3.62 (s, 2H, RCH_2-OR), 3.39 (s, 3H, RO-CH_3).

RbTFSI:^{13}C NMR (101 MHz, D_2O): δ = 119.29 (q, $^1J_{C\text{-}F}$ = 319.6 Hz, CF_3), 70.85 (RCH_2-OR), 58.04 (RO-CH_3).
^{1}H NMR (400 MHz, D2O): δ = 3.60 (s, 2H, RCH_2-OR), 3.36 (s, 3H, RO-CH_3).

CsTFSI:^{13}C NMR (101 MHz, D_2O): δ = 119.30 (q, $^1J_{C\text{-}F}$ = 319.5 Hz, CF_3).
^{1}H NMR (400 MHz, D_2O): Only solvent peak observed

3. ATR-IR spectra of MTFSI salts

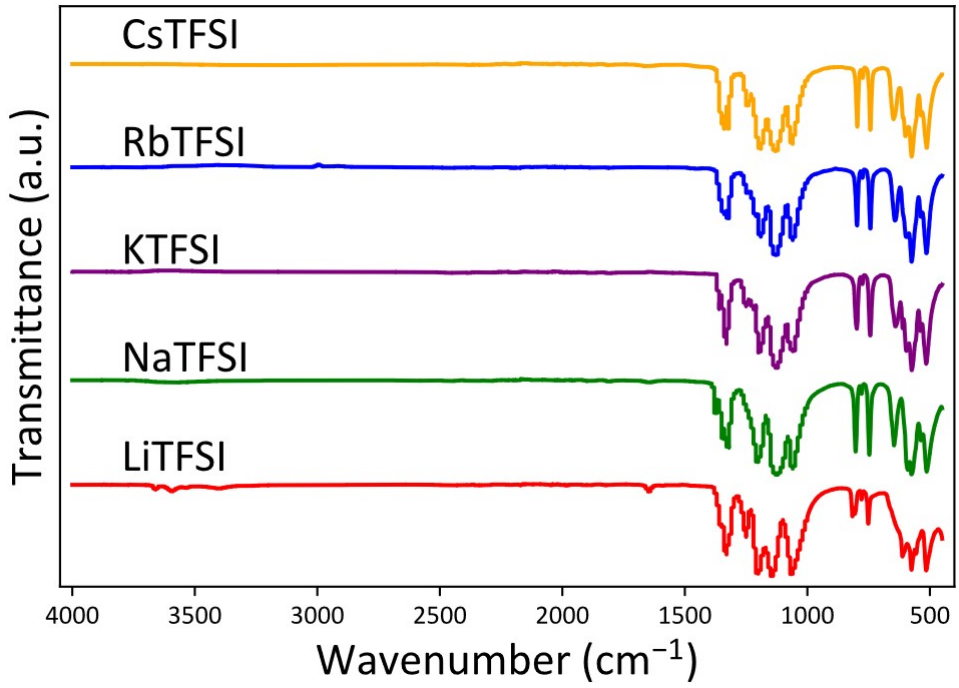

Fig. S7 Stacked ATR-IR spectra of MTFSI salts

4. Cyclic Voltammetry

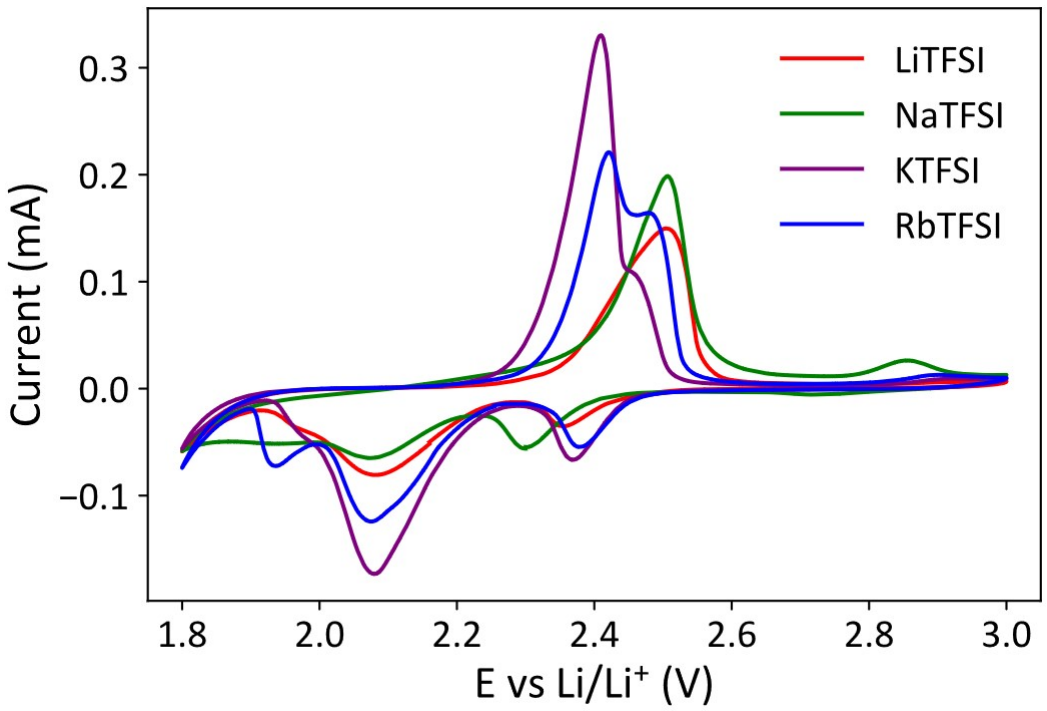

Fig. S8 CVs of different MTFSI salts at 0.05 mV s^{-1} on shared axes. Data represented as a stacked plot (Fig. 2a) in full text

5. Equivalent Circuit Model

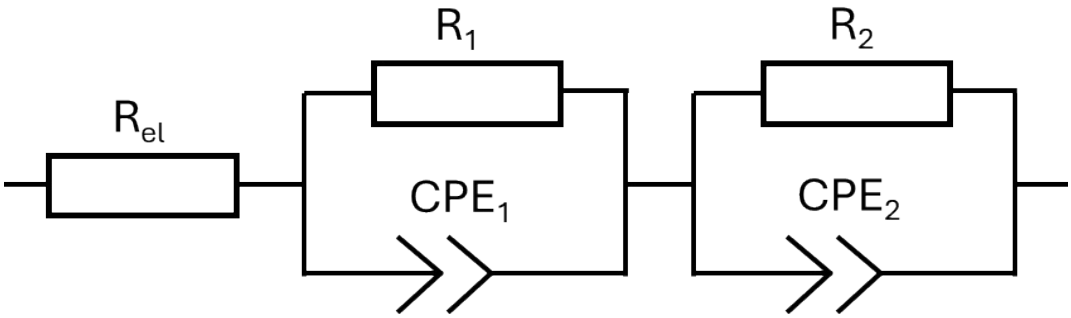

Fig. S9 Equivalent circuit model used for EIS data fitting in ZView4 software (R_{el} = Electrolyte Resistance, R_1 = SEI layer charge transfer resistance, CPE_1 = Constant Phase Element for modelling capacitance of SEI charge transfer process, R_2 = LiPS charge transfer resistance, CPE_2 = Constant Phase Element for modelling capacitance of LiPS charge transfer)

6. Li Anode - SEM-EDX Images & Spectra

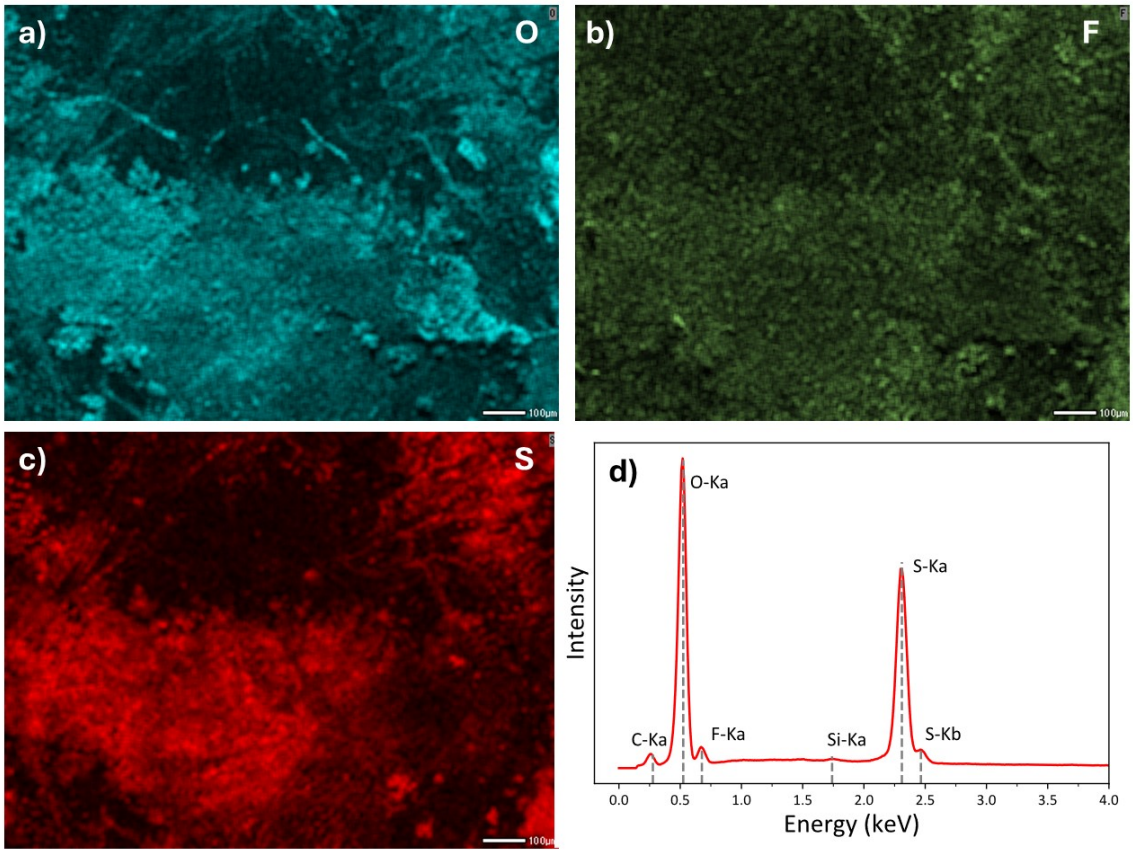

Fig. S10 (a-c) Elemental maps of Li anode from a cell containing no MTFSI (Fig. 4a): (a) Oxygen; (b) Fluorine; (c) Sulfur. (d) EDX spectrum from sample shown in Fig. 4a

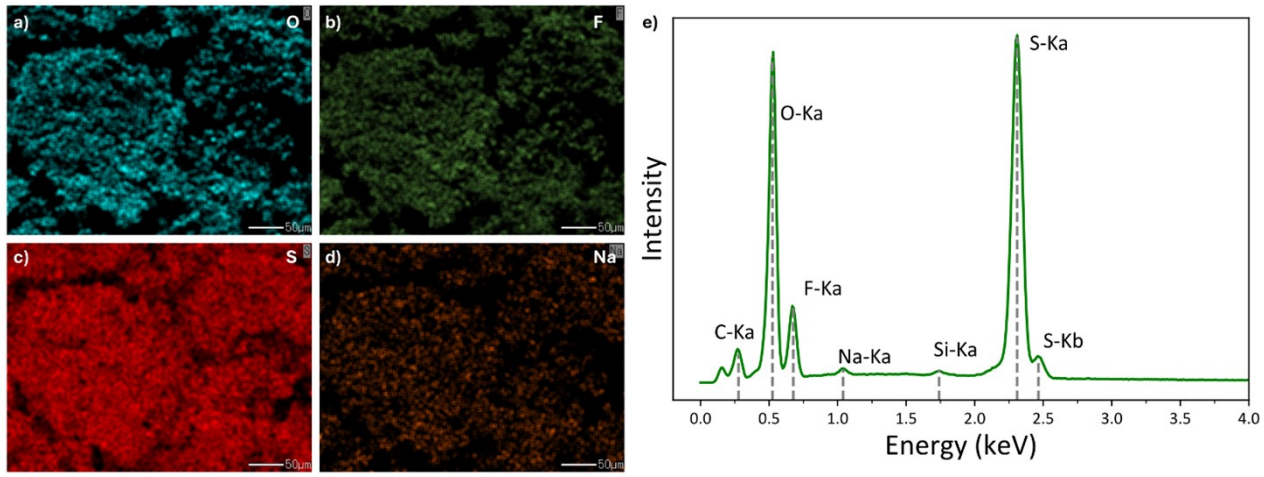

Fig. S11 (a-d) Elemental maps of Li anode from a cell containing NaTFSI (Fig. 4b): (a) Oxygen; (b) Fluorine; (c) Sulfur; (d) Sodium. (e) EDX spectrum from sample shown in Fig. 4b

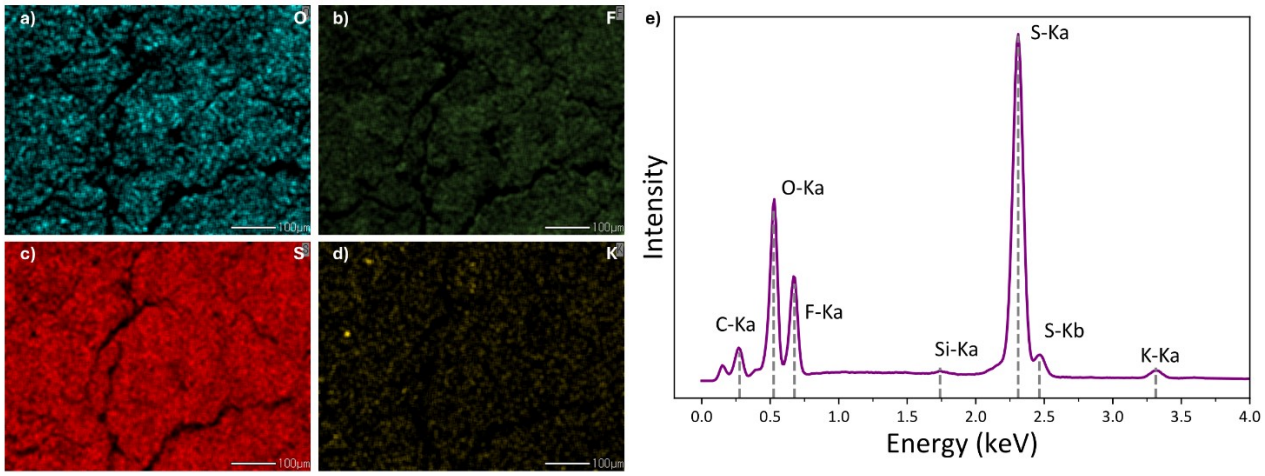

Fig. S12 (a-d) Elemental maps of Li anode from a cell containing KTFSI (Fig. 4c): (a) Oxygen; (b) Fluorine; (c) Sulfur; (d) Potassium. (e) EDX spectrum from sample shown in Fig. 4c

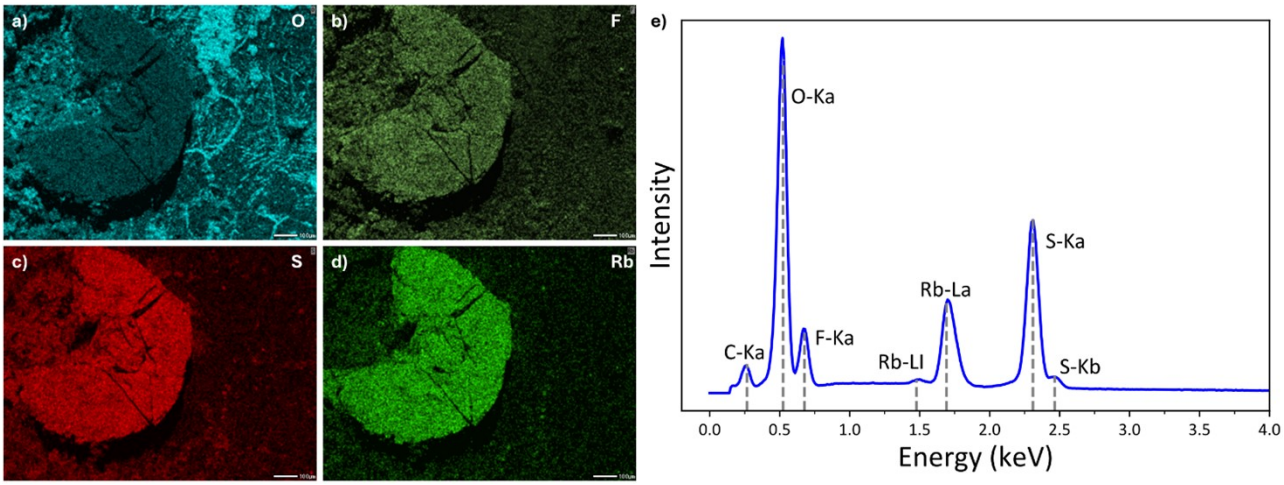

Fig. S13 (a-d) Elemental maps of Li anode from a cell containing RbTFSI (Fig. 4d): (a) Oxygen; (b) Fluorine; (c) Sulfur; (d) Rubidium. (e) EDX spectrum from sample shown in Fig. 4d

7. Carbon Felt Cathode - SEM-EDX Images & Spectra

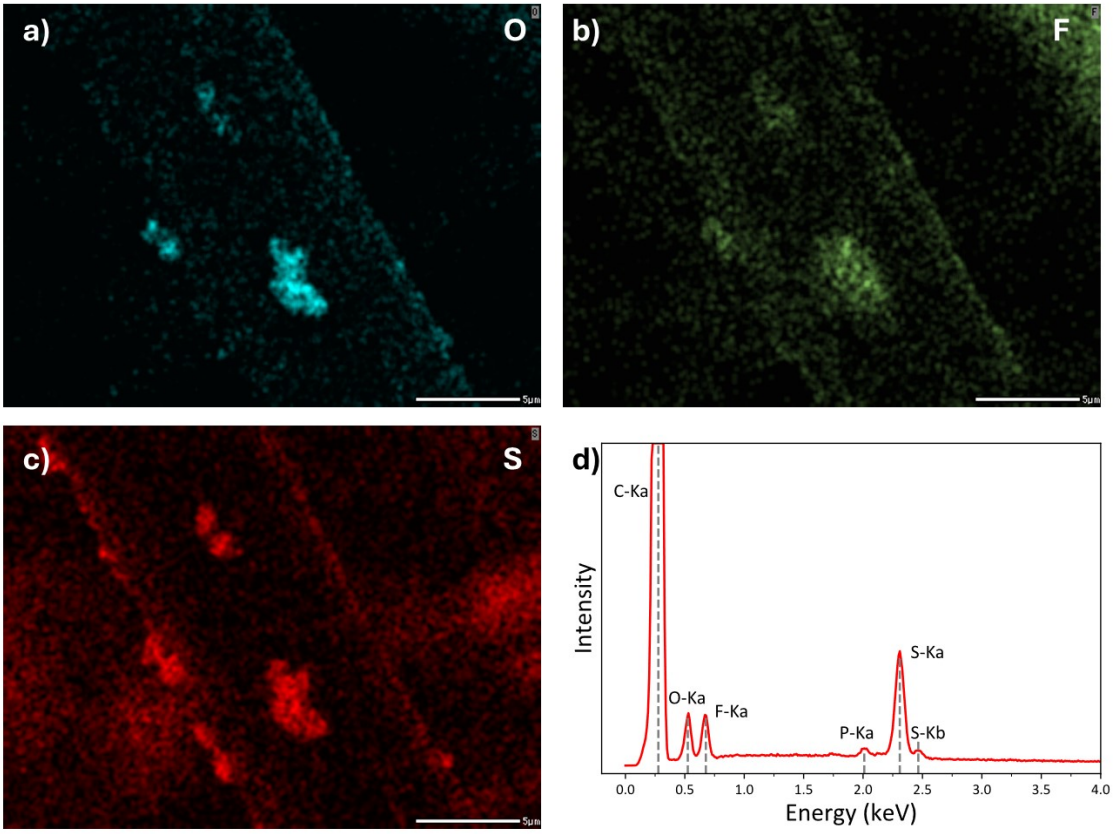

Fig. S14 (a-c) Elemental maps of C Cathode from a cell containing no MTFSI (Fig. 5a): (a) Oxygen; (b) Fluorine; (c) Sulfur. (d) EDX spectrum from sample shown in Fig. 5a

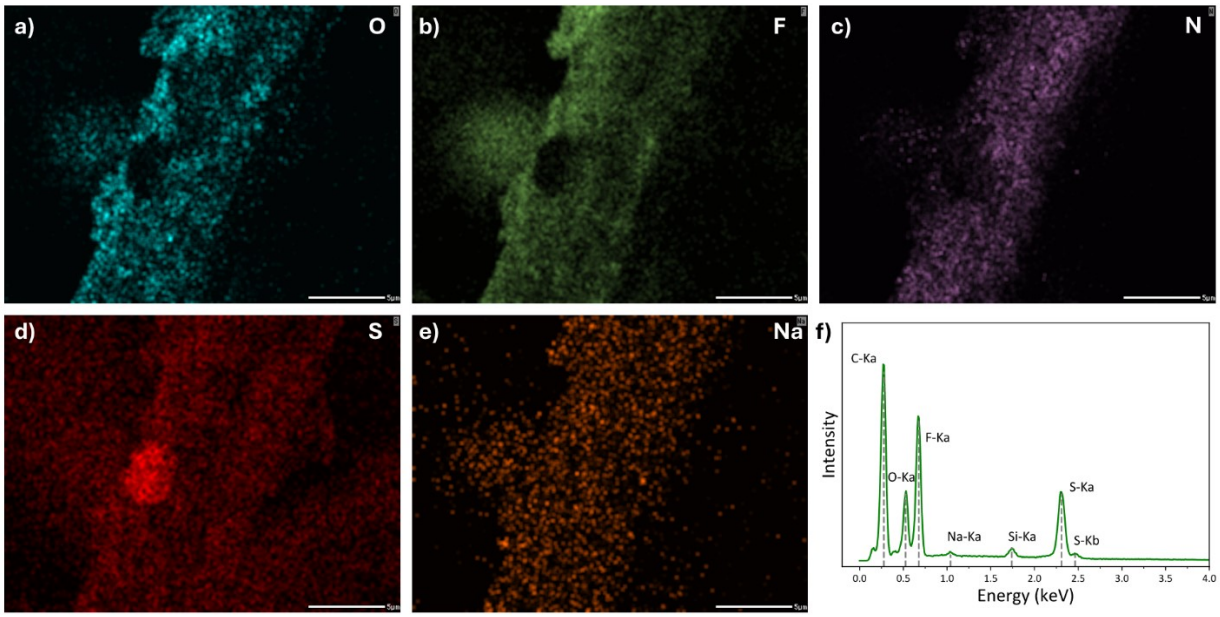

Fig. S15 (a-e) Elemental maps of C Cathode from a cell containing NaTFSI (Fig. 5b): (a) Oxygen; (b) Fluorine; (c) Nitrogen; (d) Sulfur; (e) Sodium. (f) EDX spectrum from sample shown in Fig. 5b

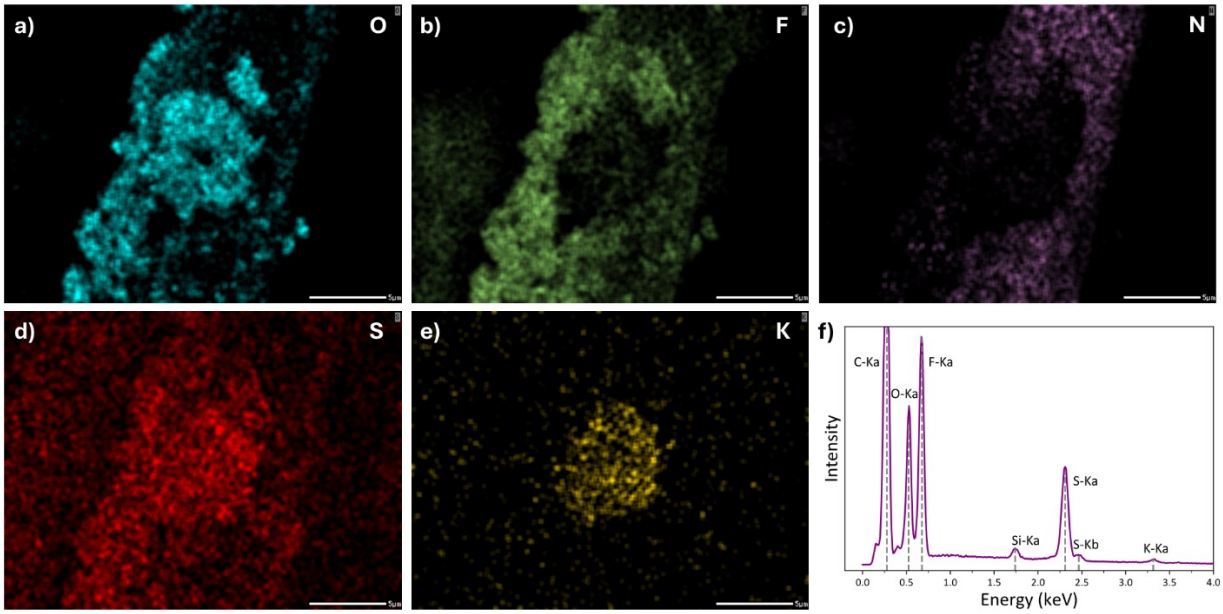

Fig. S16 (a-e) Elemental maps of C Cathode from a cell containing KTFSI (Fig. 5c): (a) Oxygen; (b) Fluorine; (c) Nitrogen; (d) Sulfur; (e) Potassium. (f) EDX spectrum from sample shown in Fig. 5c

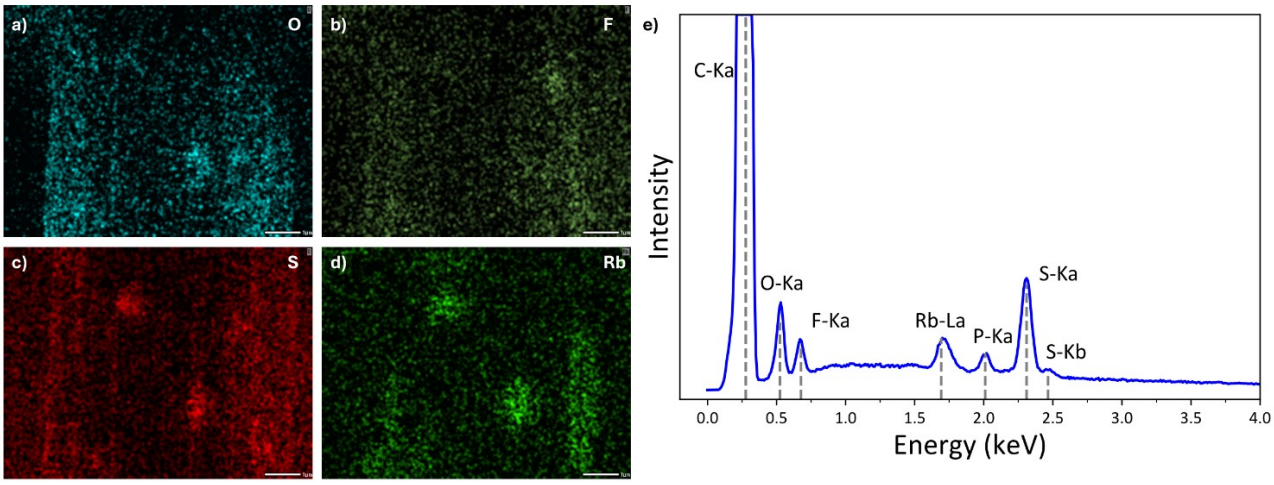

Fig. S17 (a-d) Elemental maps of C Cathode from a cell containing RbTFSI (Fig. 5d): (a) Oxygen; (b) Fluorine; (c) Sulfur; (d) Rubidium. (e) EDX spectrum from sample shown in Fig. 5d