

## Fluorosulfonamide-type Electrolyte Additives for Long-Life K-Ion Batteries

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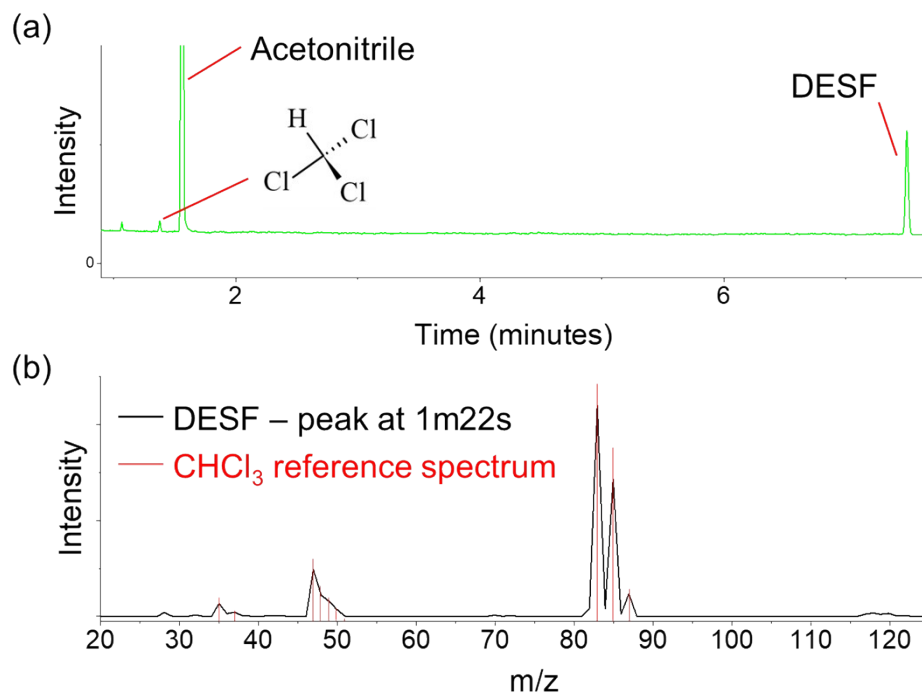
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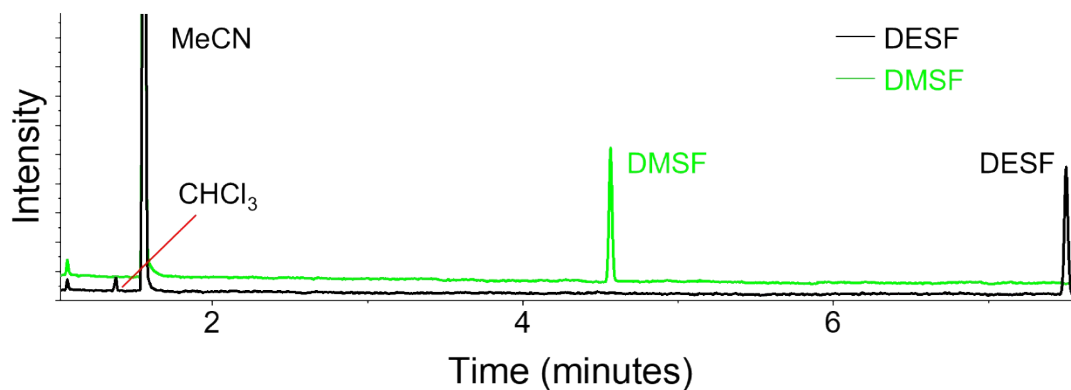
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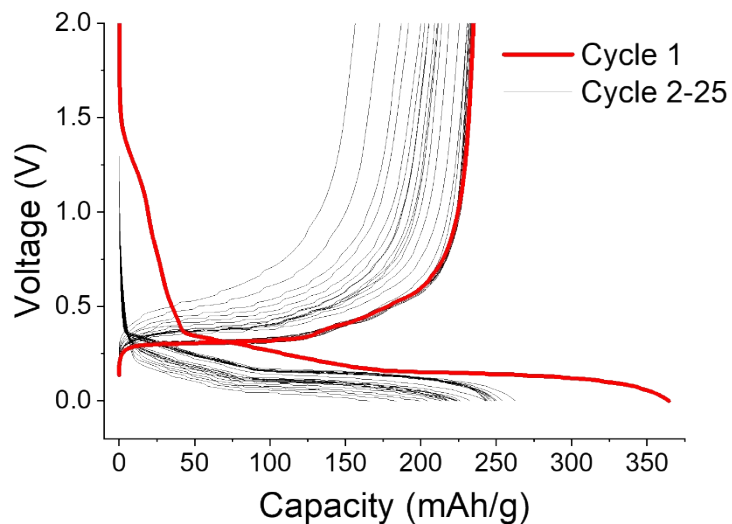
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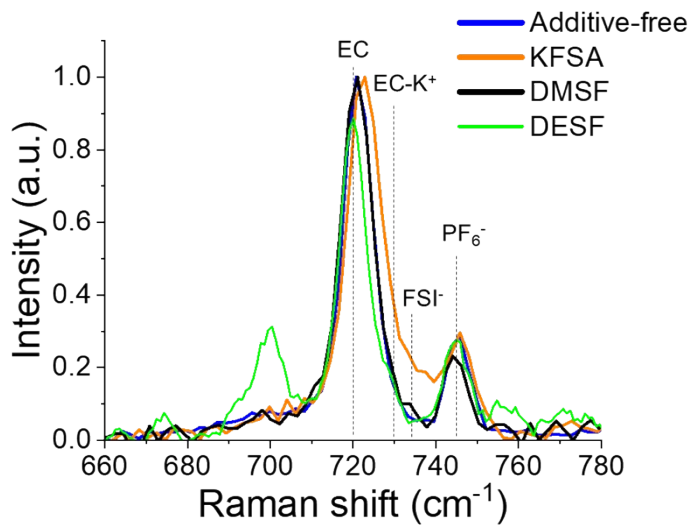
**Figure S1.** Gas-chromatography mass spectrometry analysis of as-purchased DESF used in this study. (a) Gas chromatogram of DESF (20  $\mu$ L) dissolved in MeCN (180  $\mu$ L). (b) Mass spectrum of peak eluted at ~1 min 22 seconds.



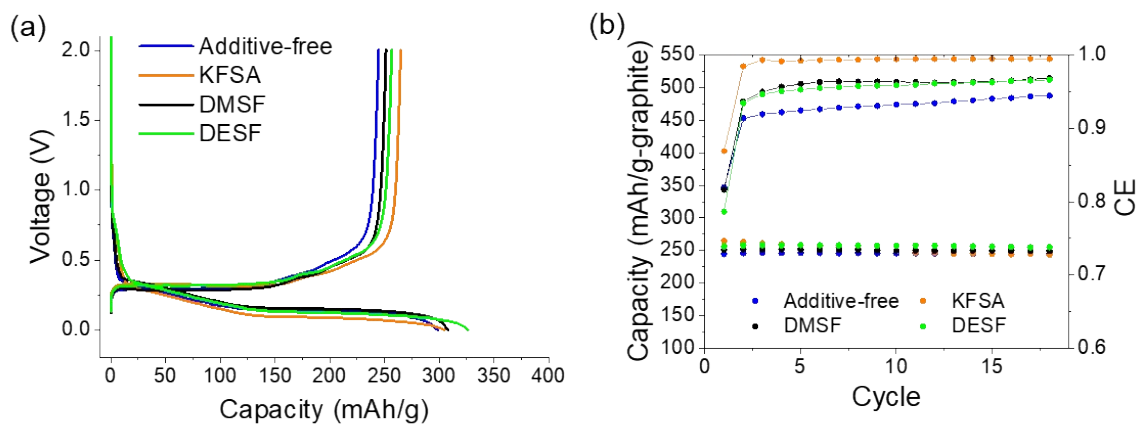
**Figure S2.** Gas-chromatography mass spectrometry analysis of as-purchased DMSF used in this study. (a) Gas chromatogram of DMSF (20  $\mu$ L) dissolved in MeCN (180  $\mu$ L). The GC results for DESF from Figure S1 are added for reference.



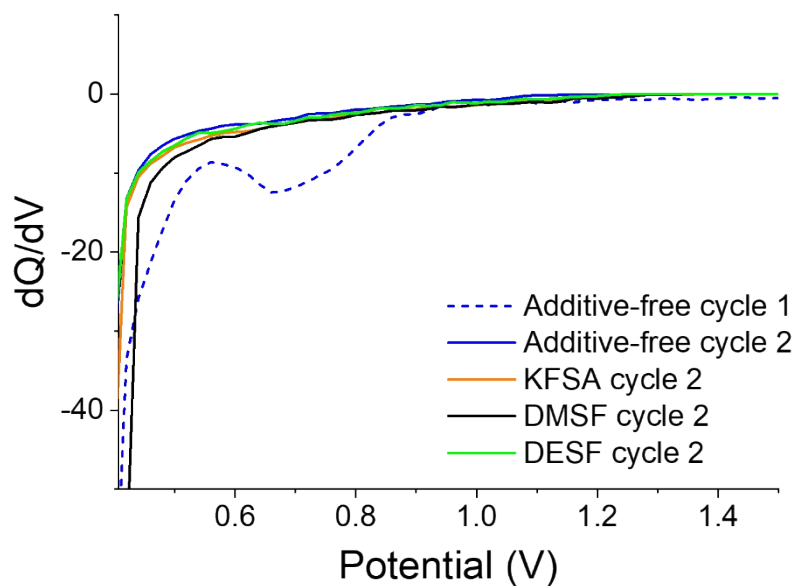
**Figure S3.** Cycling of half-cell (graphite||K) with 10 wt.% DESF at 0.1 C.



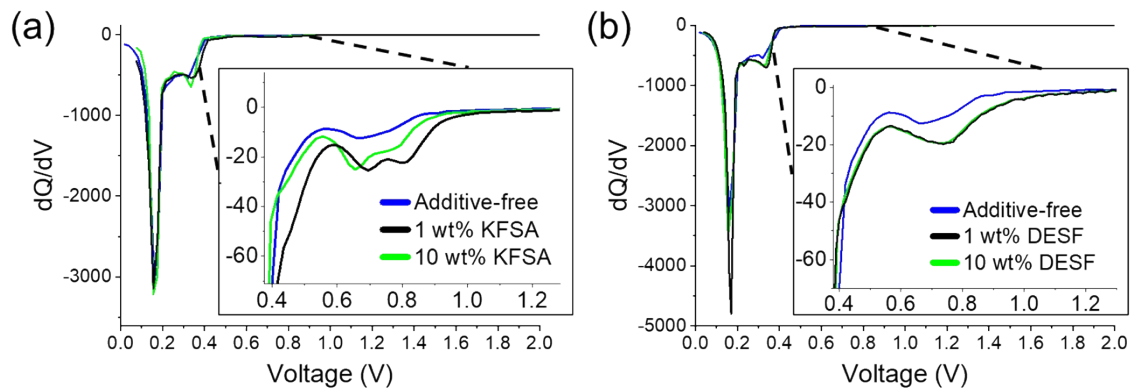
**Figure S4.** Raman analysis of the EC-K<sup>+</sup> region for KPF<sub>6</sub> in EC:DEC and with each additive at 10 wt.%.



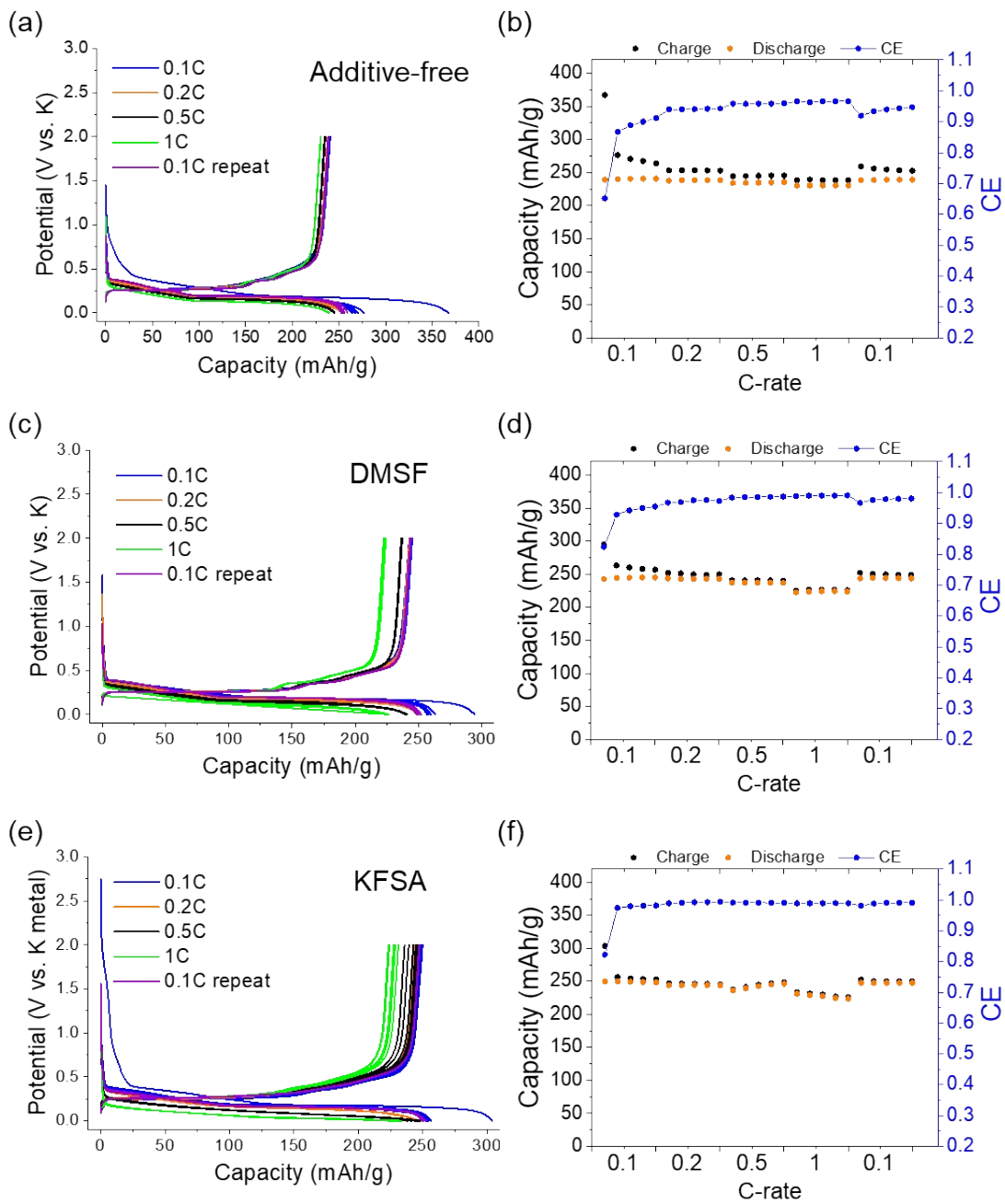
**Figure S5.** Cycling results with 1 wt.% additives in graphite||K cells. (a) First charge-discharge curves for each additive. (b) Extracted discharge capacities and CE during further cycling.



**Figure S6.** dQ/dV curves of the half-cell measurements during the second cycle for each additive at 10 wt.%.

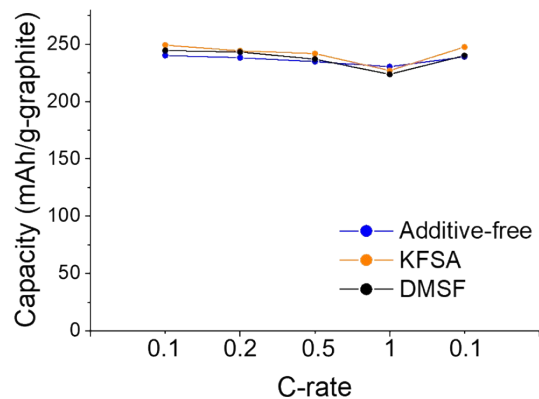


**Figure S7.**  $dQ/dV$  curves of half-cell containing 1 or 10 wt.% additives during the first charging.  $dQ/dV$  results for (a) KFSAs and (b) DESFs compared with additive-free cells.

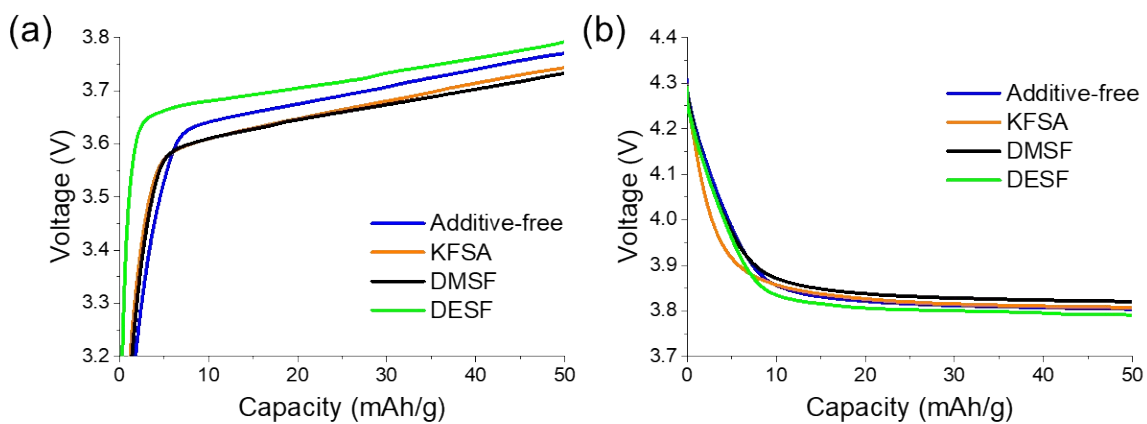


**Figure S8.** Charge-discharge curves and extracted results during rate test with (a) additive-free, (b) 10 wt.% DMSF and (c) 10 wt.% KFSA additives.

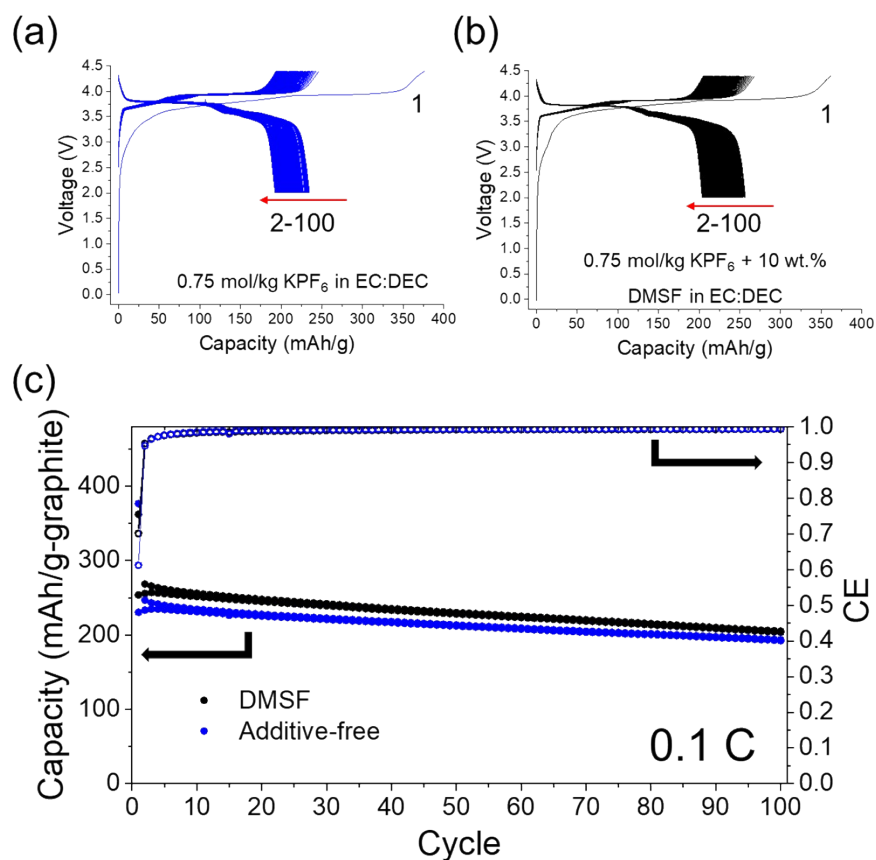




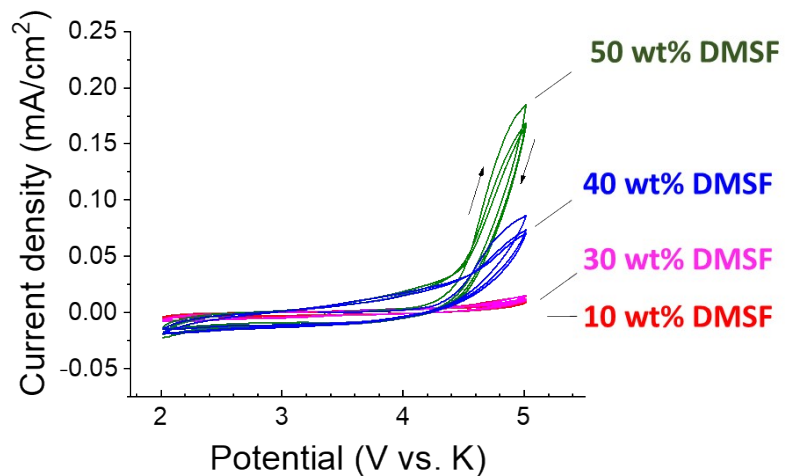
**Figure S9.** Average discharge capacity for 5 cycles during rate testing.



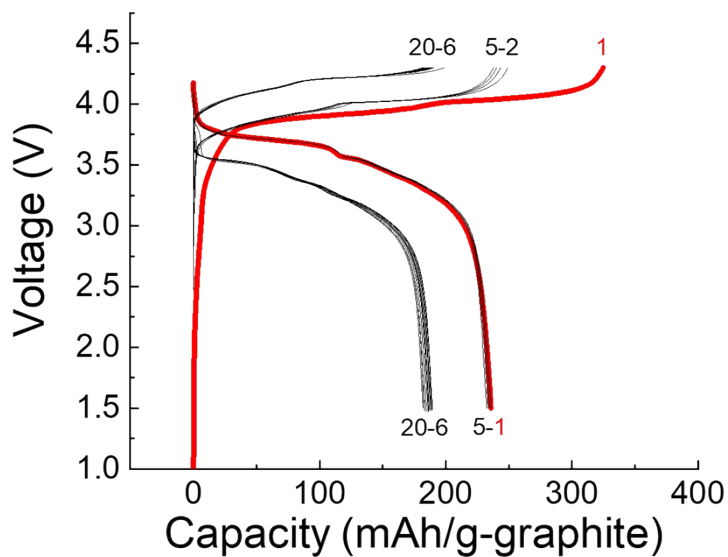
**Figure S10.** Close-up of (a) charge and (b) discharge curves in full cell measurements at 0.1 C.



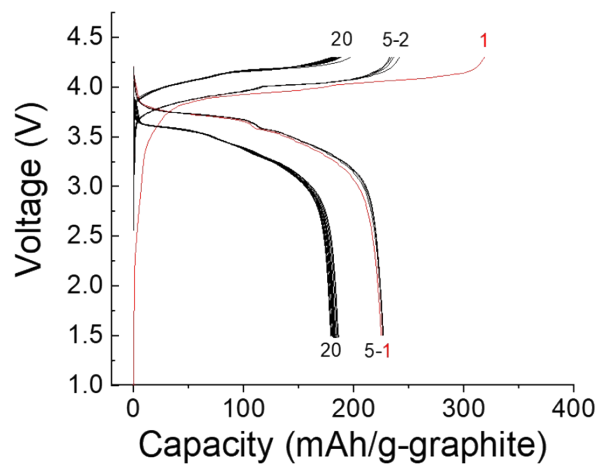
**Figure S11.** Full cell measurements at 0.1 C with and without DMSF. (a) Full cell measurements in 0.75 mol/kg  $\text{KPF}_6$  in EC:DEC. (b) Full cell measurements in 0.75 mol/kg  $\text{KPF}_6$  in EC:DEC with 10 wt.% DMSF. (c) Extracted charge/discharge and CE for the cycling measurements.



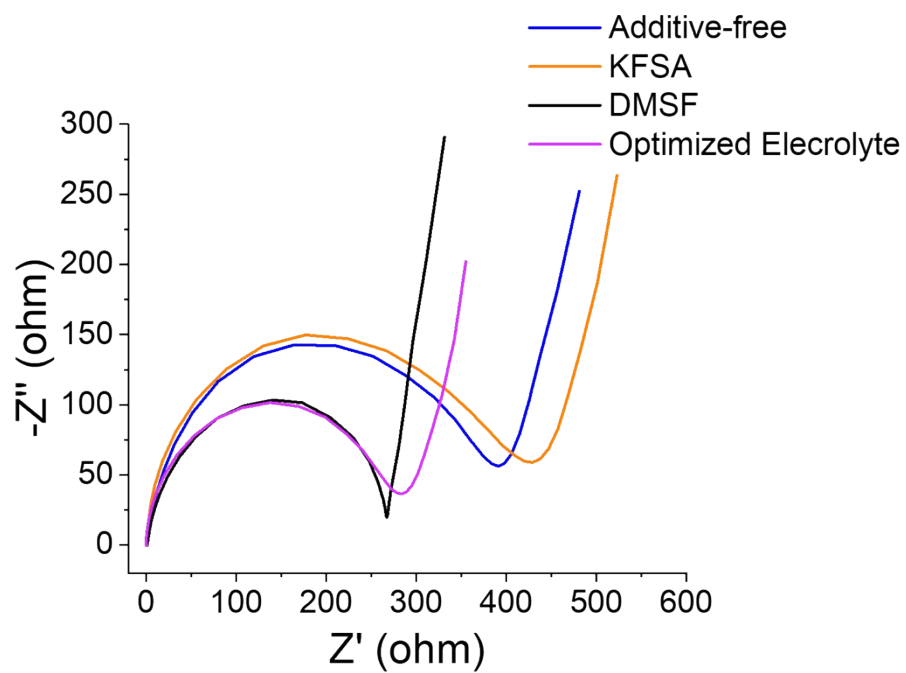
**Figure S12.** Test of oxidative stability of DMSF on an Al working electrode. For the measurement, the electrolyte was 0.75 mol/kg KPF<sub>6</sub> + 10–50 wt% DMSF and the scan rate was 0.5 mV/s.



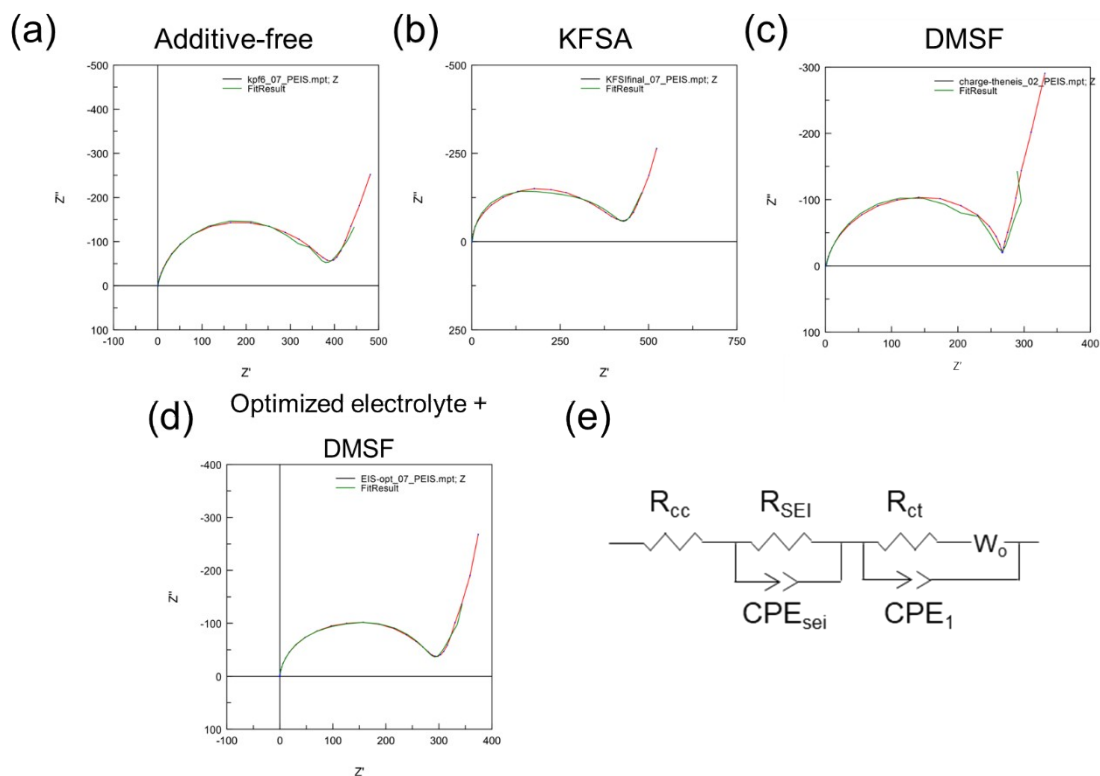
**Figure S13.** Full cell measurements with 10 wt.% DMSF. Cycle 1-5 are at a rate of 0.1 C and the remaining cycles are at 1 C.



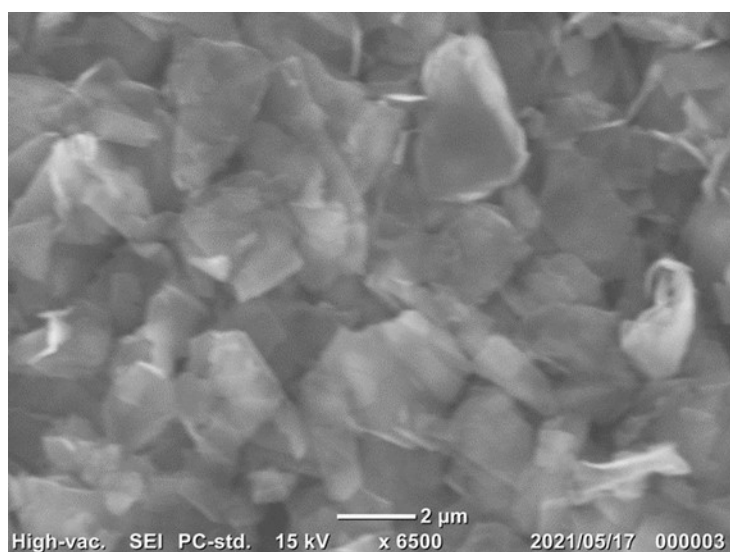
**Figure S14.** Full cell measurements of an optimized  $\text{KPF}_6$ -FSA electrolyte with 10 wt.% DMSF. Cycle 1-5 are at a rate of 0.1 C and the remaining cycles are at 1 C.



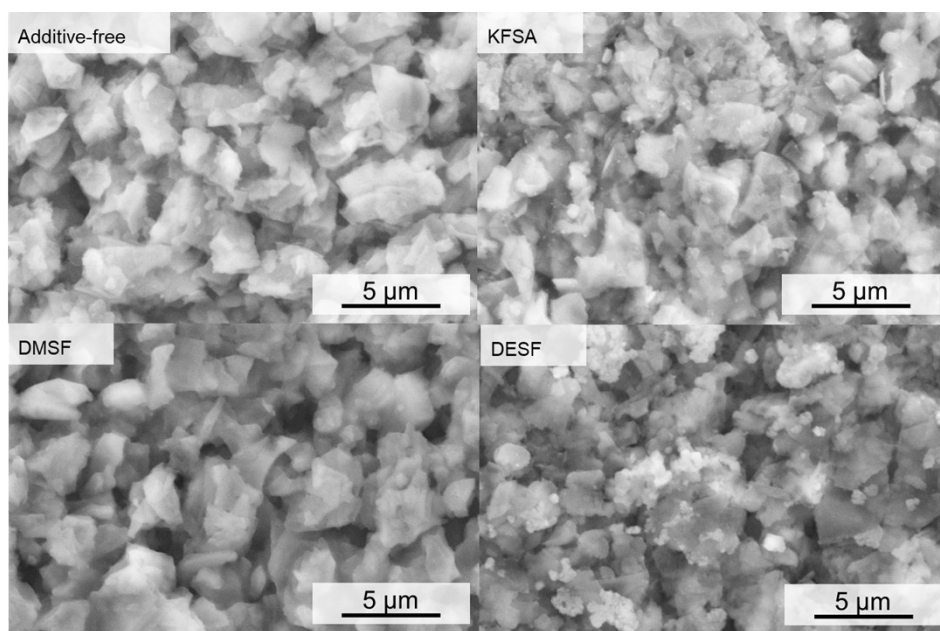
**Figure S15.** Nyquist plots of the graphite electrodes after a few charge-discharge cycles.



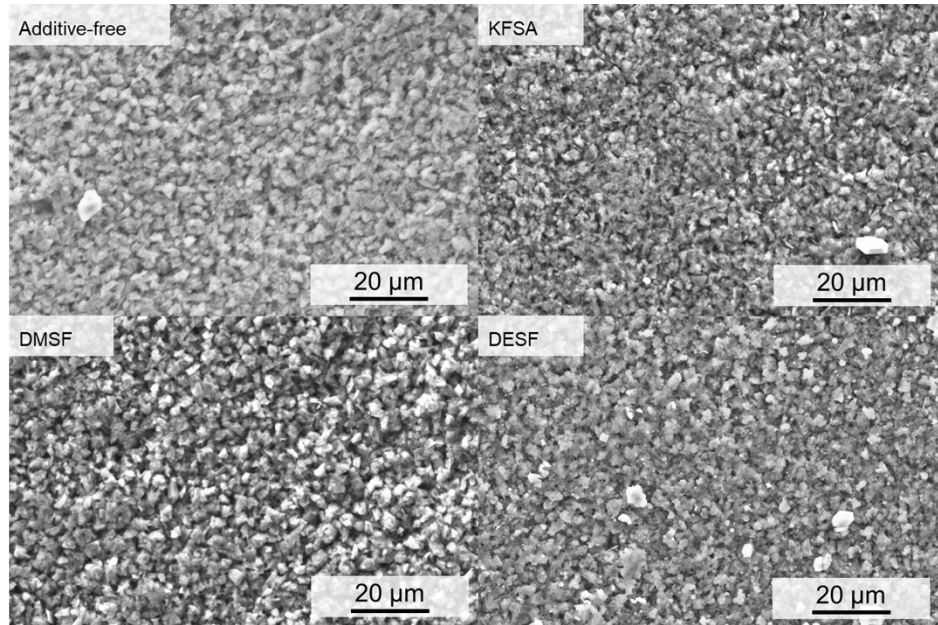
**Figure S16.** Fitting of the impedance data for (a) additive-free, (b) 10 wt.% KFSA, (c) 10 wt.% DMSF in EC:DEC and the optimized electrolyte (d) 10 wt.% DMSF + 0.25 mol/kg KFSA in EC:PC. (e) Equivalent circuit diagram for fittings.



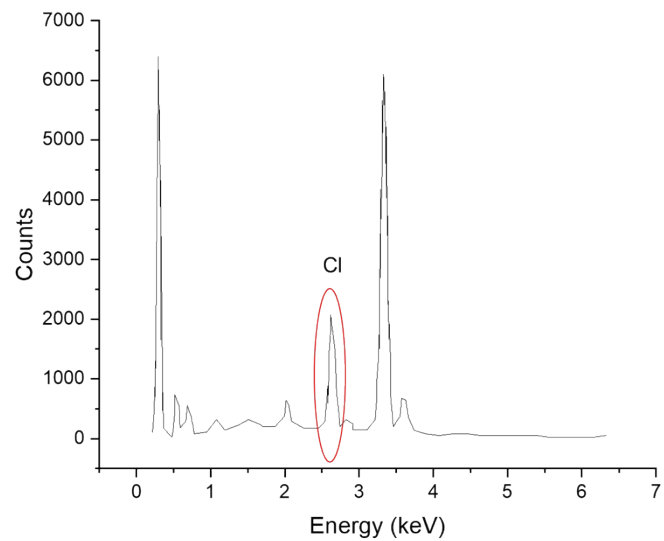
**Figure S17.** SEM image of unused graphite composite electrode.



**Figure S18.** SEM images of cycled graphite composite electrodes at 5000X magnification.

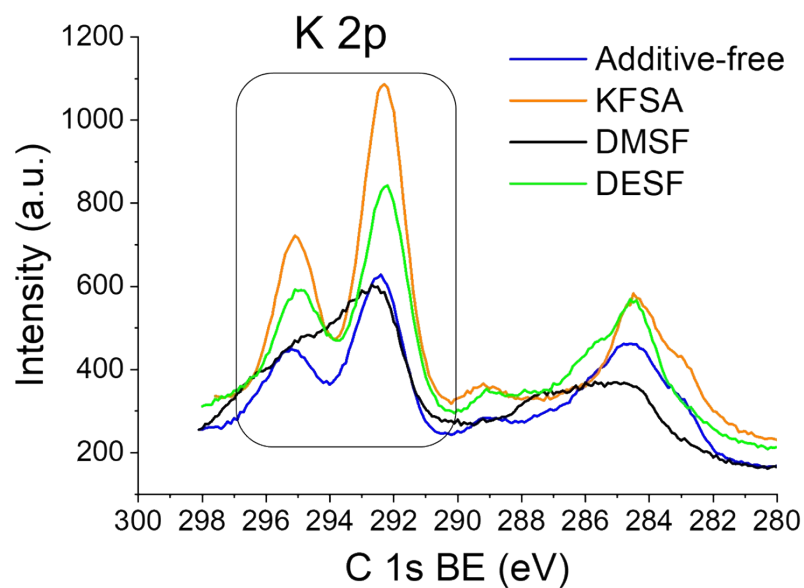


**Figure S19.** SEM images of cycled graphite composite electrodes at 1000X magnification.

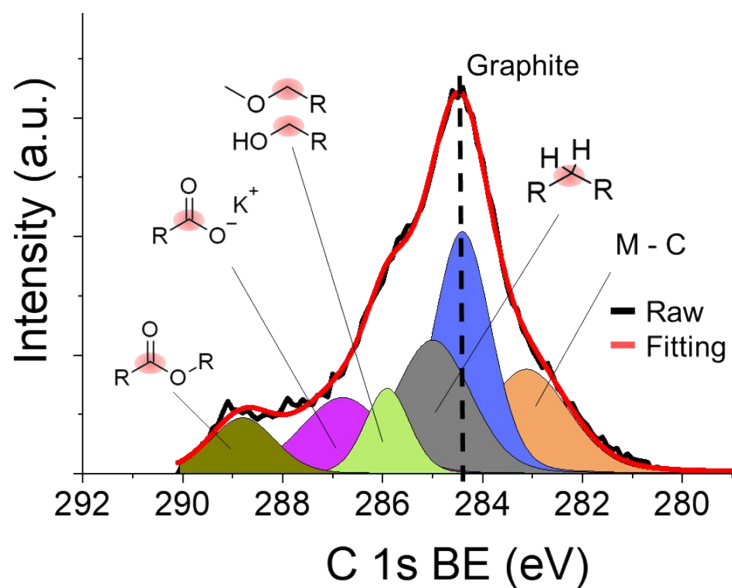


**Figure S20.** EDS results of the graphite electrode cycle with 10 wt.% DESF.

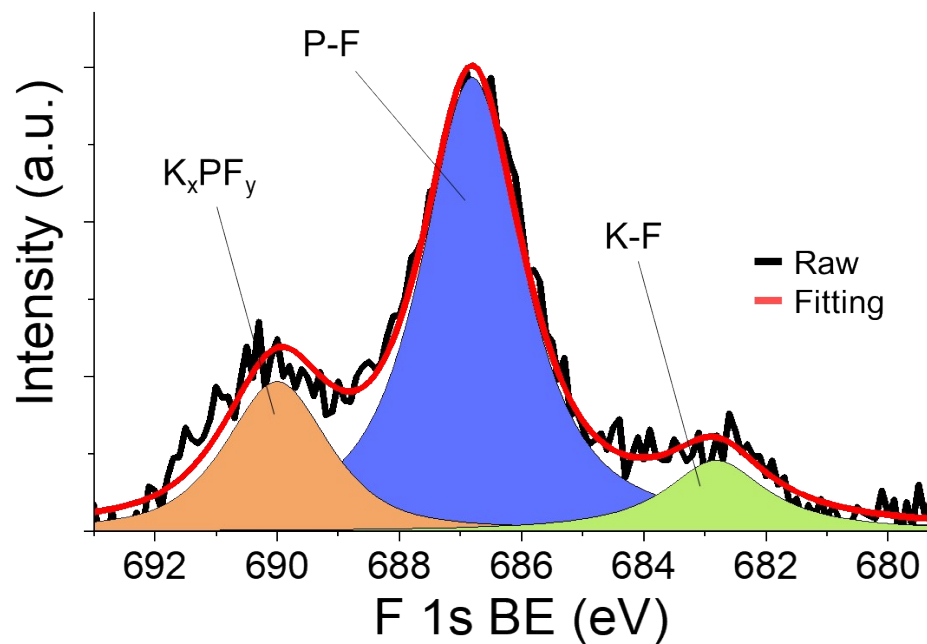




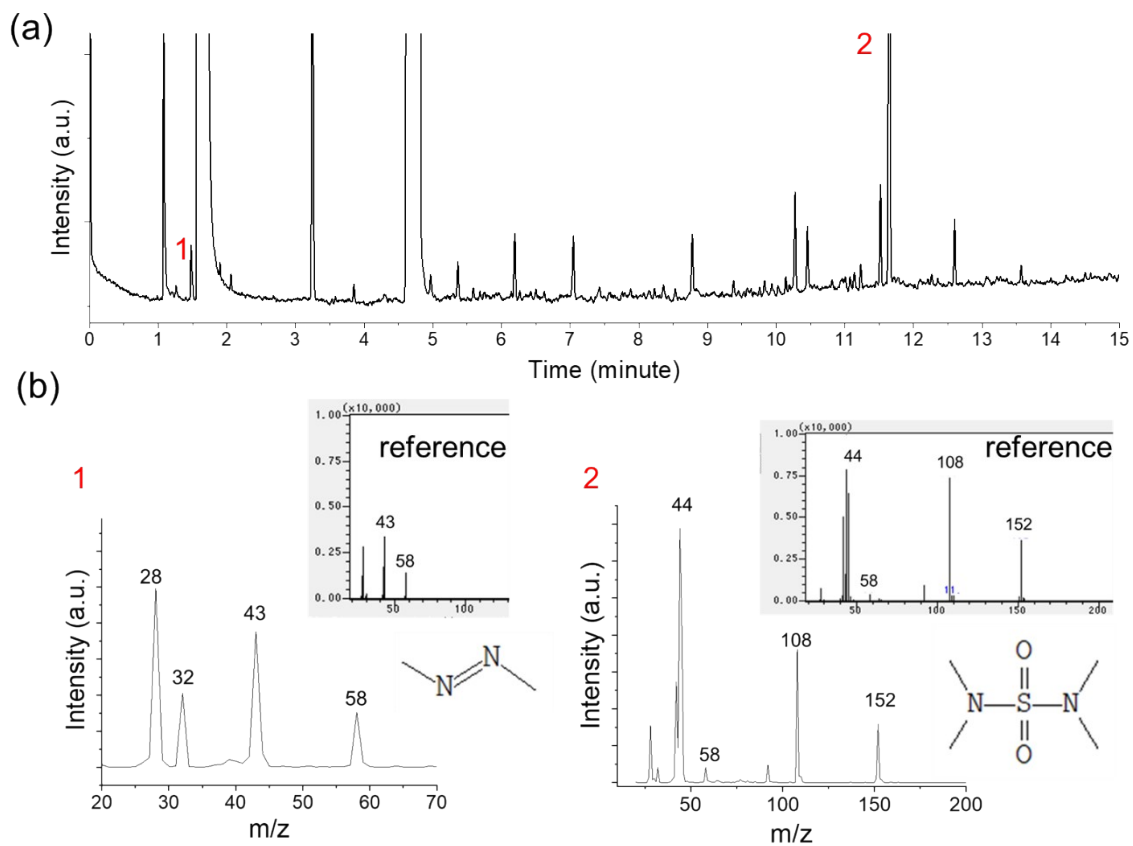
**Figure S21.** XPS spectrum including C 1s and K 2p regions.



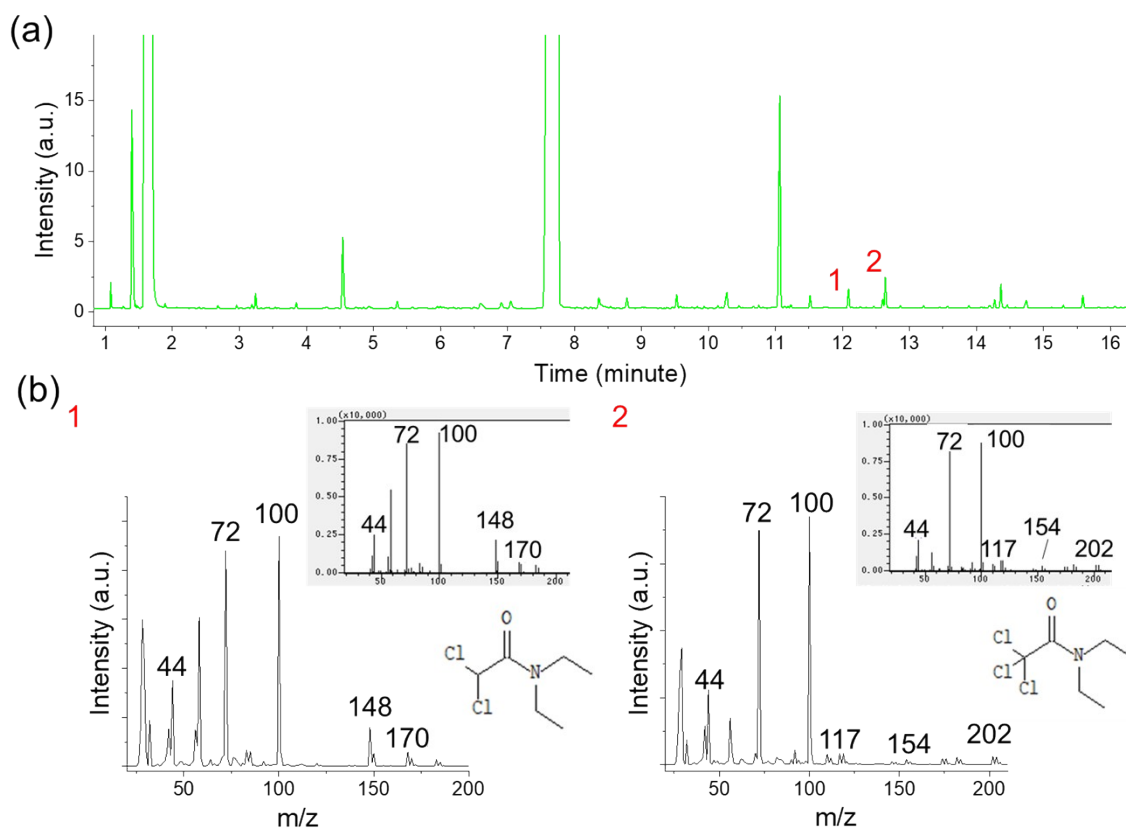
**Figure S22.** Deconvoluted XPS spectrum of the C 1s region for graphite electrode cycled with 10 wt.% DESF.



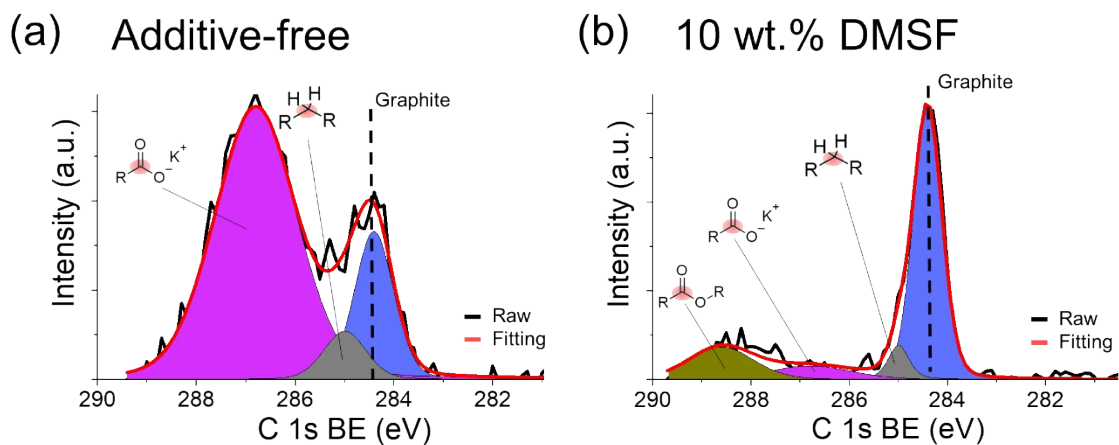
**Figure S23.** Deconvoluted XPS spectrum of the F 1s region for graphite electrode cycled with 10 wt.% DESF.



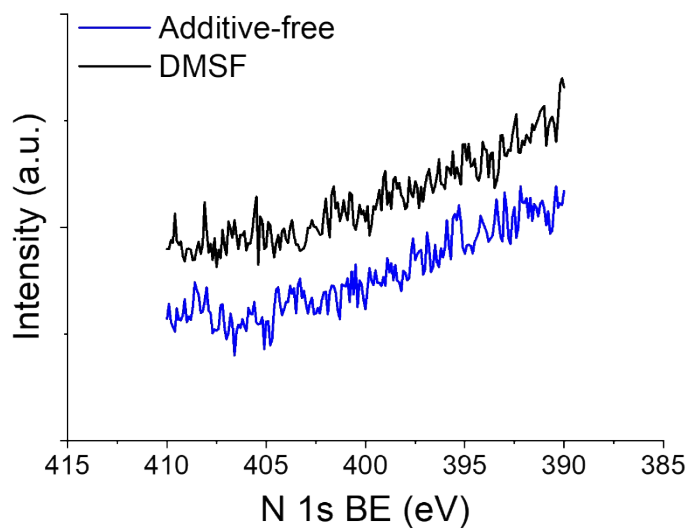
**Figure S24.** GC/MS analysis of DMSF after reaction with K metal. Chromin (a) and (b) with an added 10 wt.% DMSF.



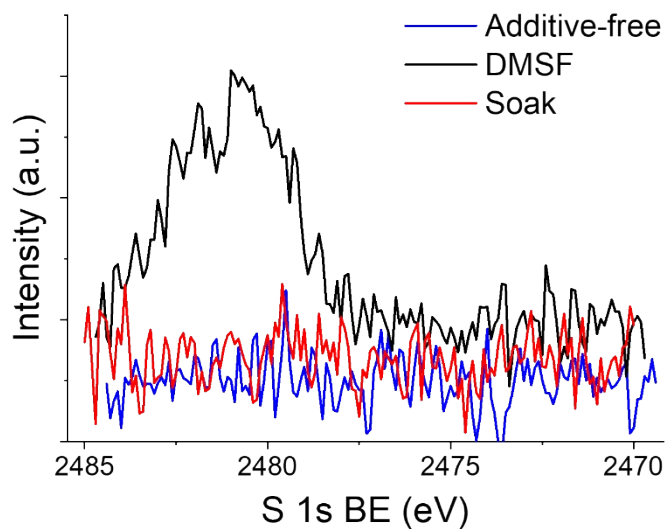
**Figure S25.** GC/MS analysis of DESF after reaction with K metal. in (a) additive-free electrolytes and (b) with DMSF.



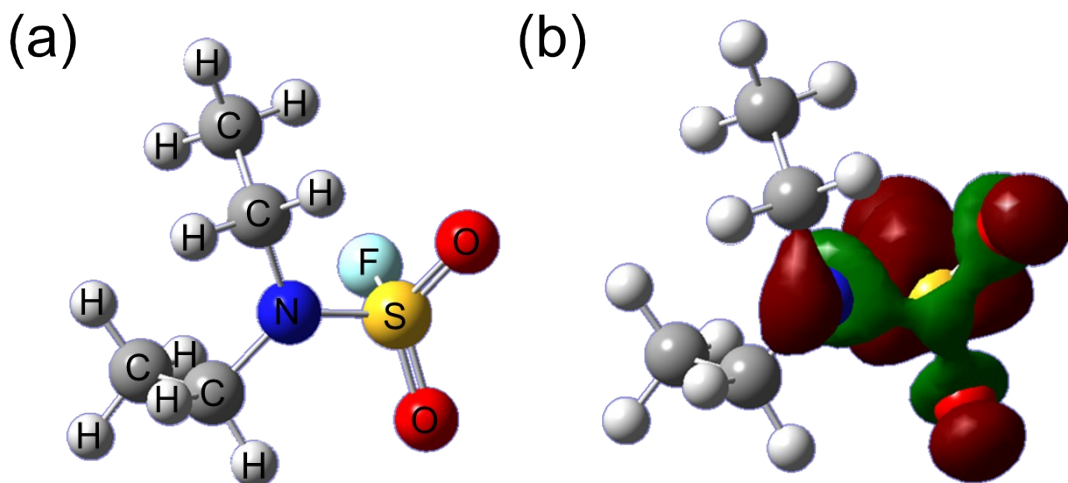
**Figure S26.** HAXPES spectrum of the C 1s region for graphite electrode cycled in (a) additive-free electrolytes and (b) with an added 10 wt.% DMSF.



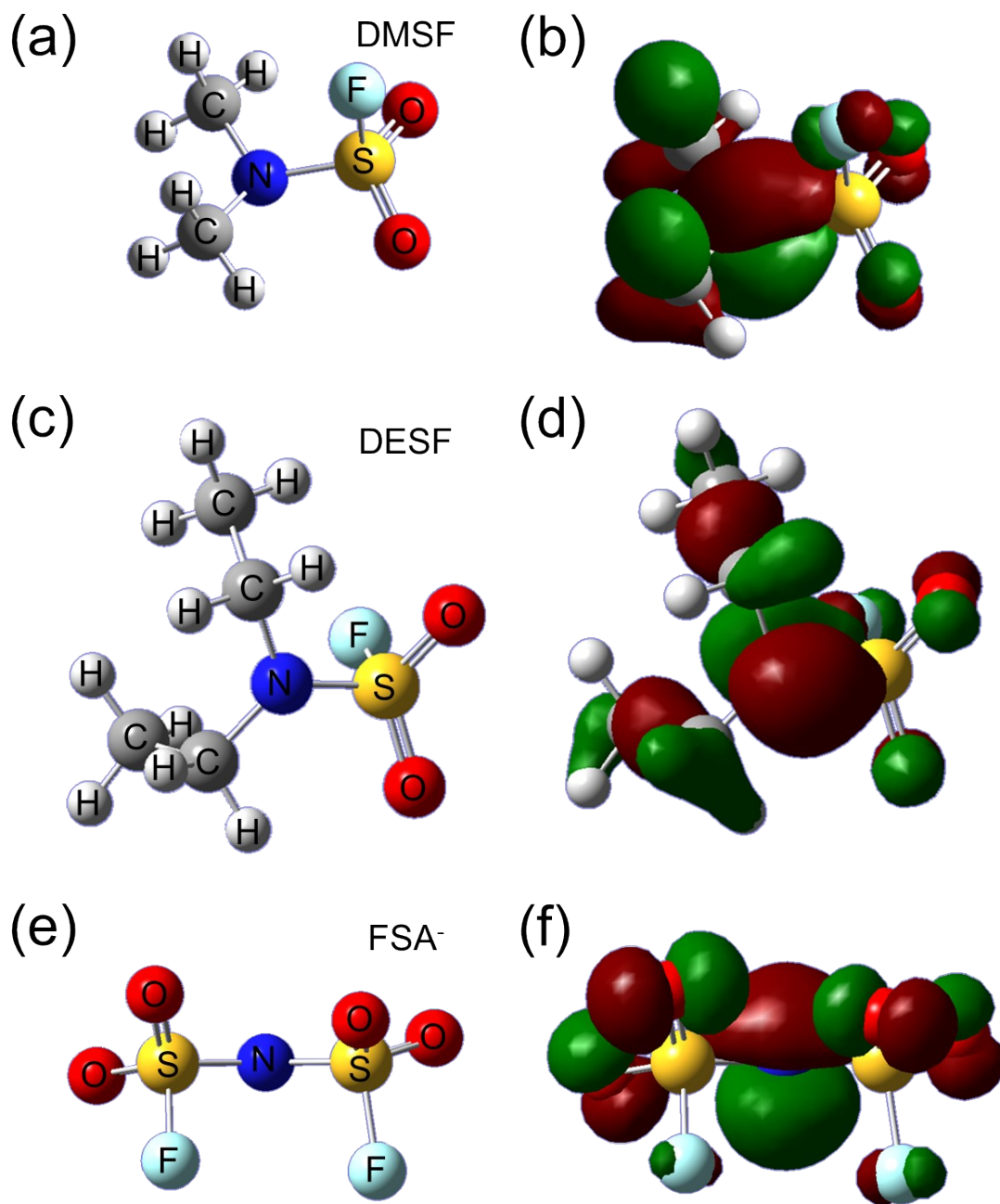
**Figure S27.** HAXPES results of additive-free and DMSF samples in the N 1s region.



**Figure S28.** HAXPES results of cycled electrodes in additive-free and electrolytes containing DMSF, and samples soaked in the electrolyte containing DMSF in the S 1s region.



**Figure S29.** Visualization of the LUMO molecular orbitals for DESF. (a) Molecular structure and (b) LUMO molecular orbitals for DESF using an isovalue of 0.04.



**Figure S30.** Visualization of the HOMO molecular orbitals for each additive. (a) Molecular structure and (b) HOMO molecular orbitals for DMSF. (c) Molecular structure and (d) HOMO molecular orbitals for DESF. (e) Molecular structure and (f) HOMO molecular orbitals for FSA<sup>-</sup>. The isovalues are maintained at 0.04 for all additives.

Table S1. Ionic conductivity and viscosity of the additive-containing electrolytes.

<b>Electrolyte</b>	<b>Ionic conductivity (mS/cm)</b>	<b>Viscosity (mPa·s)</b>
0.75 mol/kg KPF <sub>6</sub> in EC:DEC	7.03	3.798
0.75 mol/kg KPF <sub>6</sub> + 10 wt.% KFSI in EC:DEC	8.33	5.683
0.75 mol/kg KPF <sub>6</sub> + 10 wt.% DMSF in EC:DEC	5.95	3.396
0.75 mol/kg KPF <sub>6</sub> + 10 wt.% DESF in EC:DEC	5.81	3.336
0.75 mol/kg KPF <sub>6</sub> + 10 wt.% DMSF + 0.25 mol/kg KFSI in EC:PC	6.64	8.189

Table S2. Charge transfer resistances after cycling evaluated with EIS.

<b>Electrolyte</b>	<b>R<sub>ct</sub> (Ω)</b>	<b>R<sub>SEI</sub> (Ω)</b>
0.75 mol/kg KPF <sub>6</sub> in EC:DEC	360.5	14.99
0.75 mol/kg KPF <sub>6</sub> + 10 wt.% KFSI in EC:DEC	306.8	132.8
0.75 mol/kg KPF <sub>6</sub> + 10 wt.% DMSF in EC:DEC	254.5	11.6
0.75 mol/kg KPF <sub>6</sub> + 10 wt.% DMSF + 0.25 mol/kg KFSI in EC:PC	195.1	97.22