Electronic Supplementary Material (ESI) for Chemical Science.

Impact of electrolyte decomposition products on electrochemical performance of 4 V class K-ion batteries

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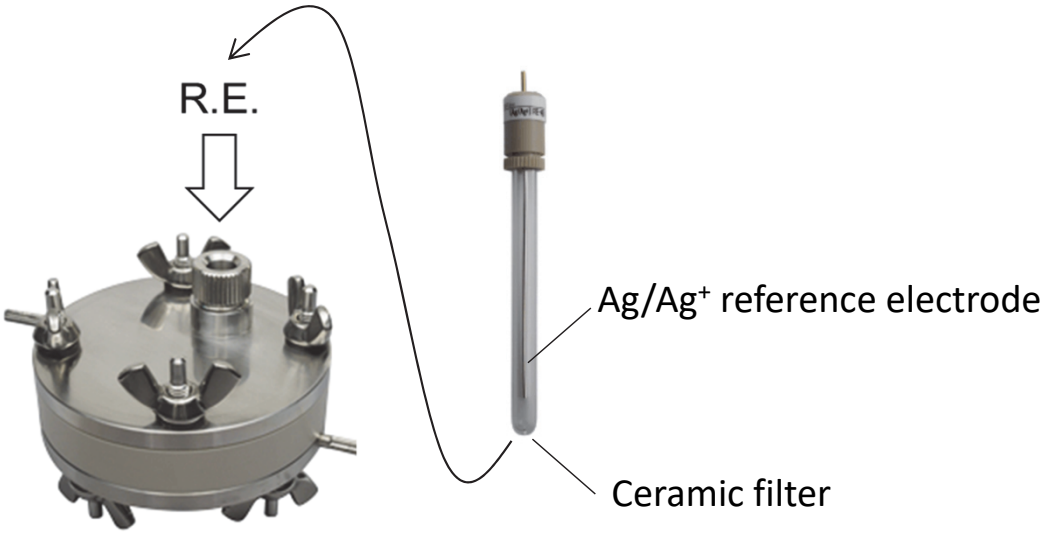


Fig. S1 Photograph of the three-electrode cell.

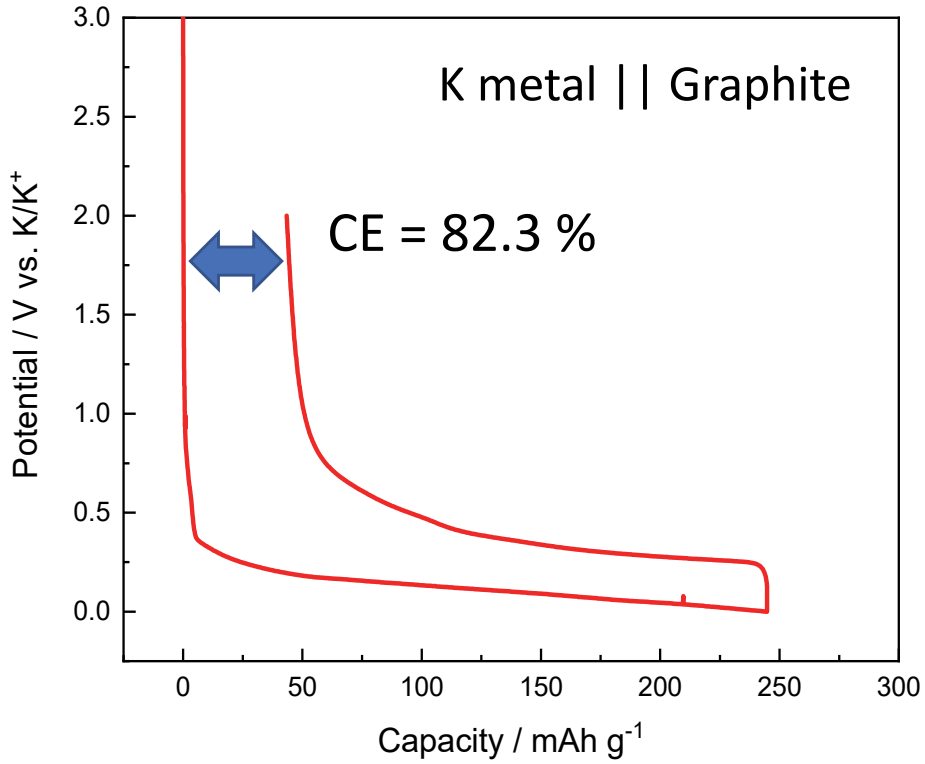


Fig. S2 Initial charge/discharge curve of graphite in a three-electrode cell with K metal counter electrode and filled with 1 mol kg^{-1} $K(PF_6)_{0.75}(FSA)_{0.25}$/EC/DEC.

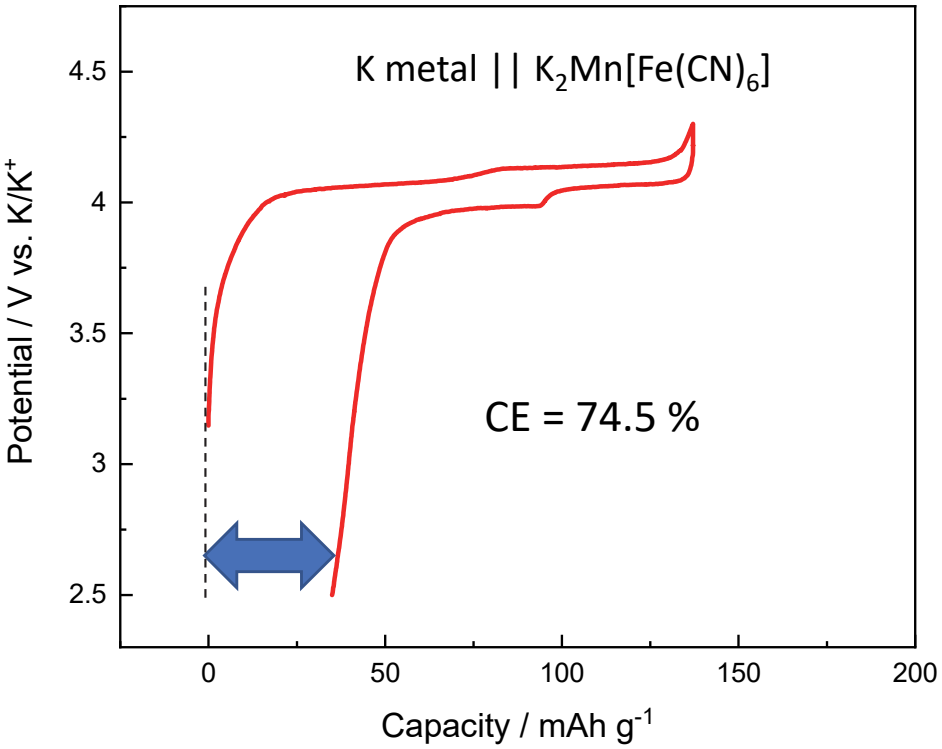


Fig. S3 Initial charge/discharge curve of the $K_2Mn[Fe(CN)_6]$ electrodes in a three-electrode cell with a K metal counter electrode and filled with 1 mol kg^{-1} $K(PF_6)_{0.75}(FSA)_{0.25}$/EC/DEC.

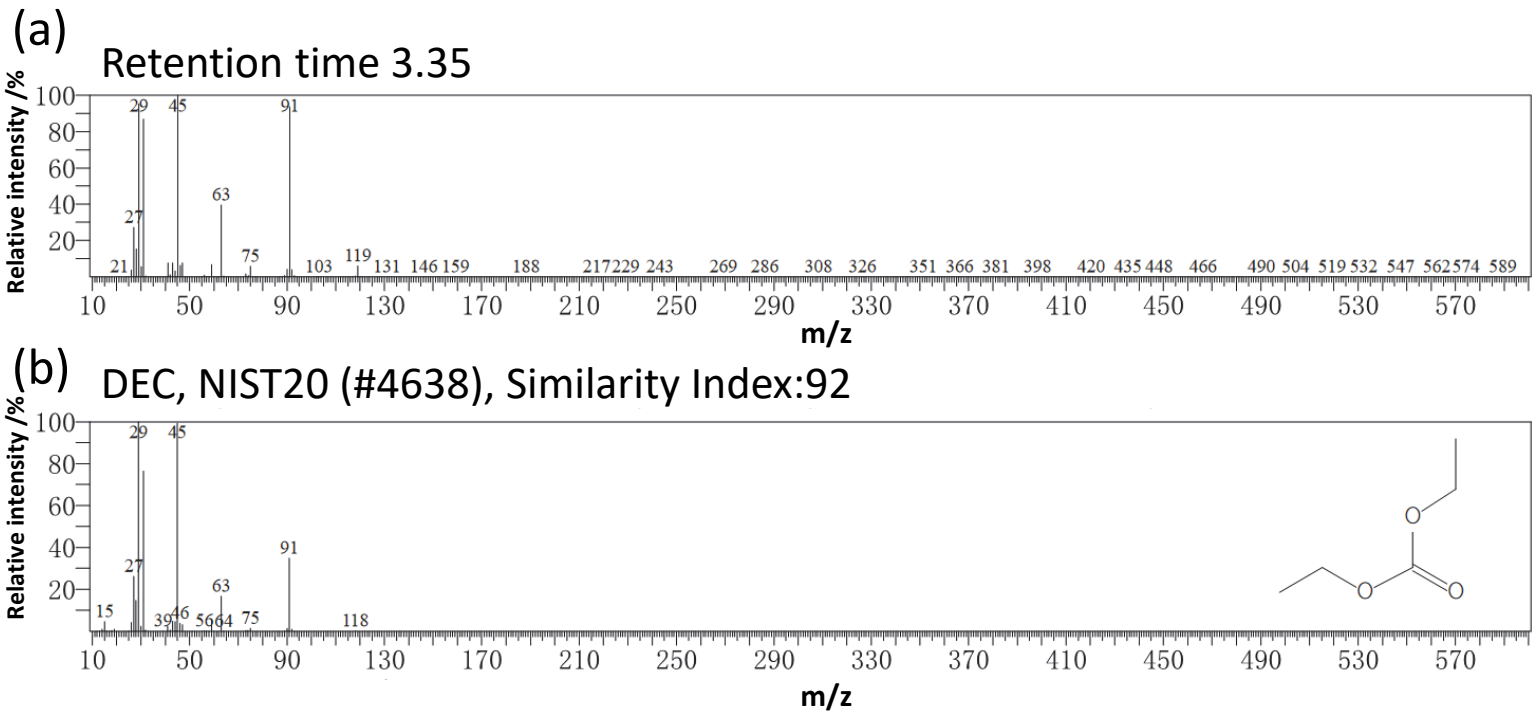


Figure S4 (a) EI-MS spectra at a retention time 3.35 min. (b) Reference EI-MS spectra of DEC from National Institute of Standards and Technology (NIST) library.

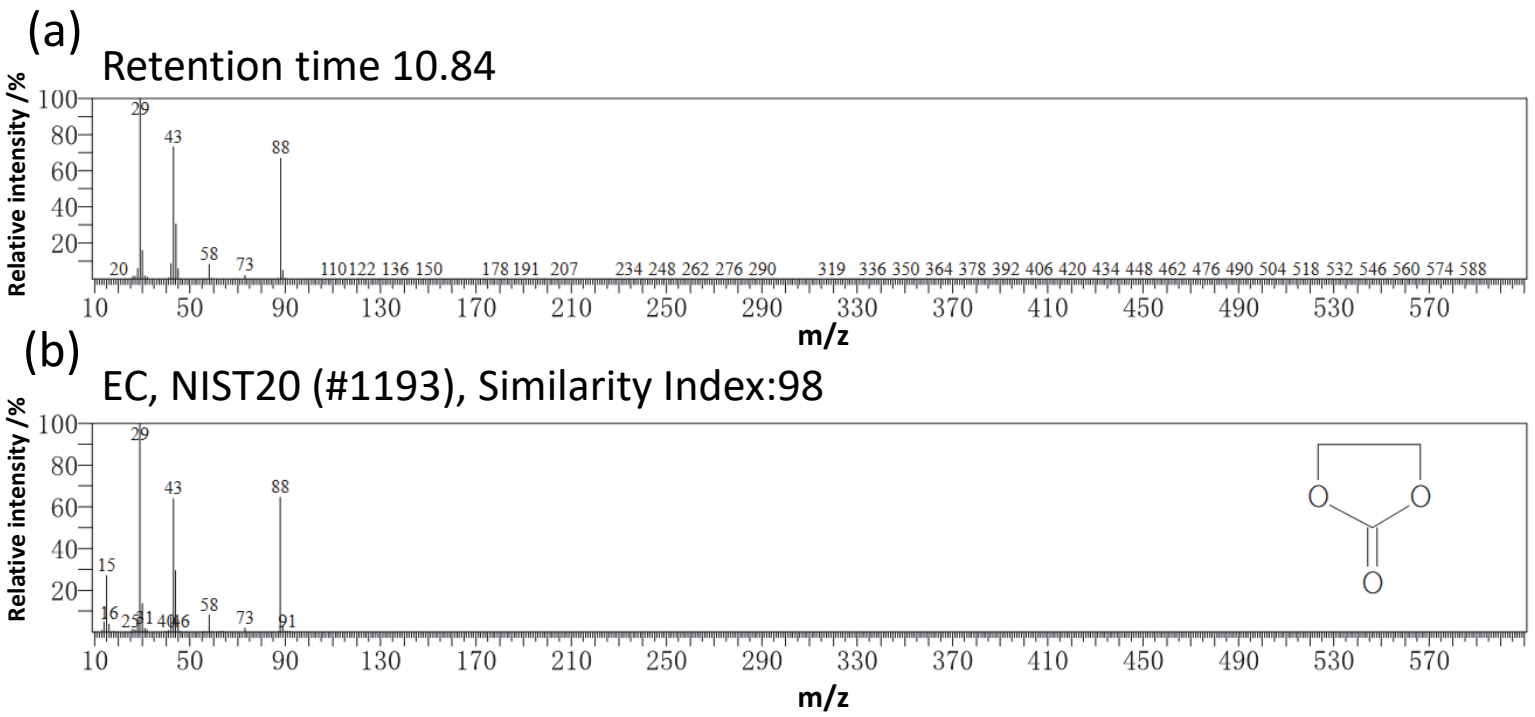
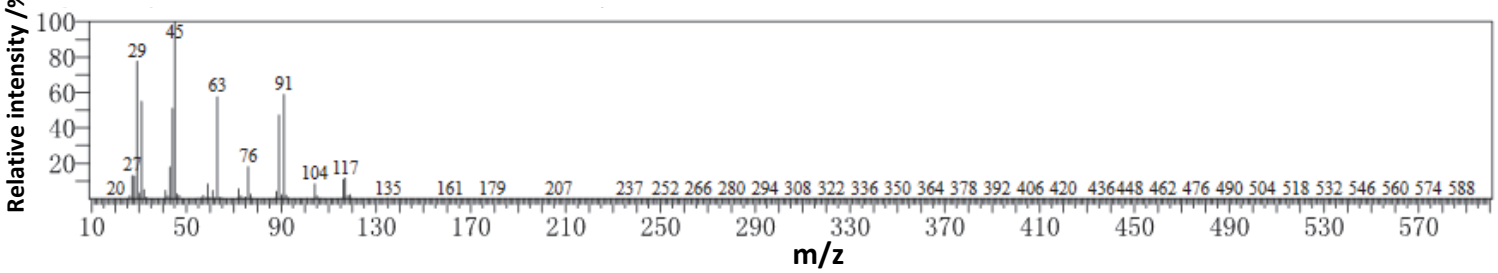
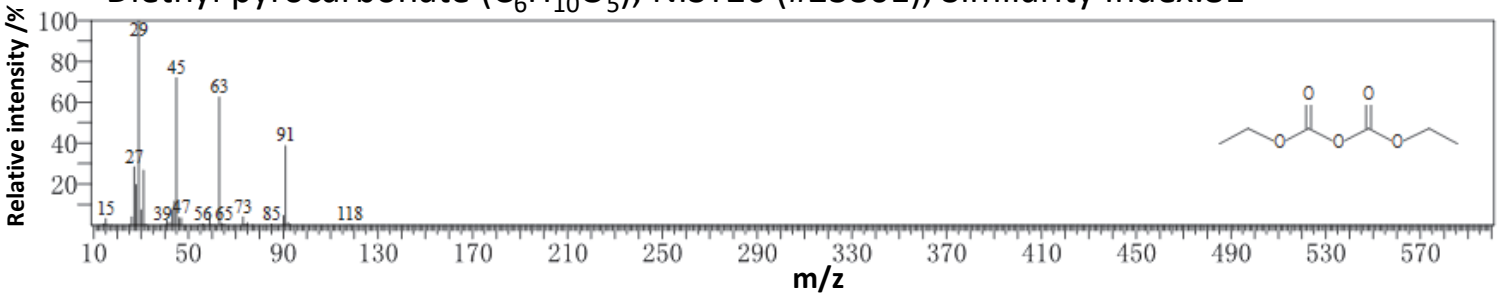


Figure S5 (a) EI-MS spectra at a retention time 3.35 min. (b) Reference EI-MS spectra of DEC from NIST library.

(a) #1, Retention time 13.16



(b) Diethyl pyrocarbonate ($C_6H_{10}O_5$), NIST20 (#23801), Similarity Index:81



(c) Ethane-1,2-diyl diethyl biscarbonate ($C_8H_{14}O_6$), NIST20 (#58189), Similarity Index:77

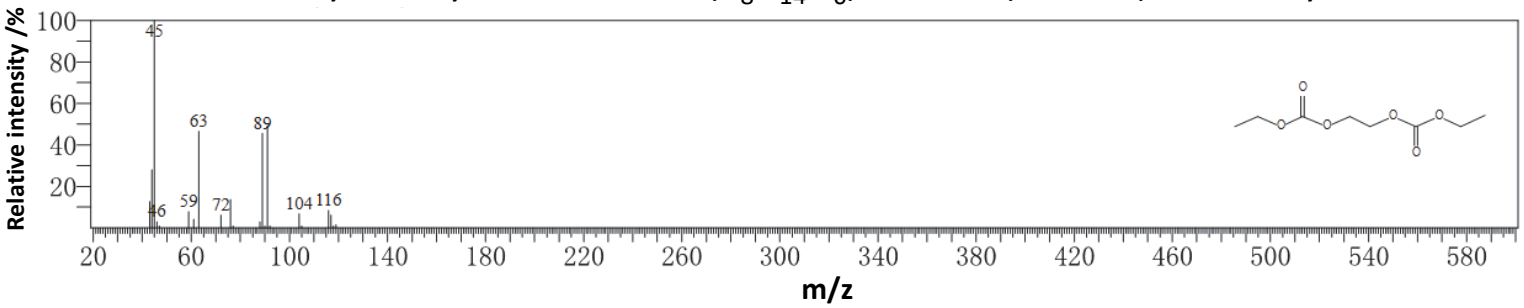
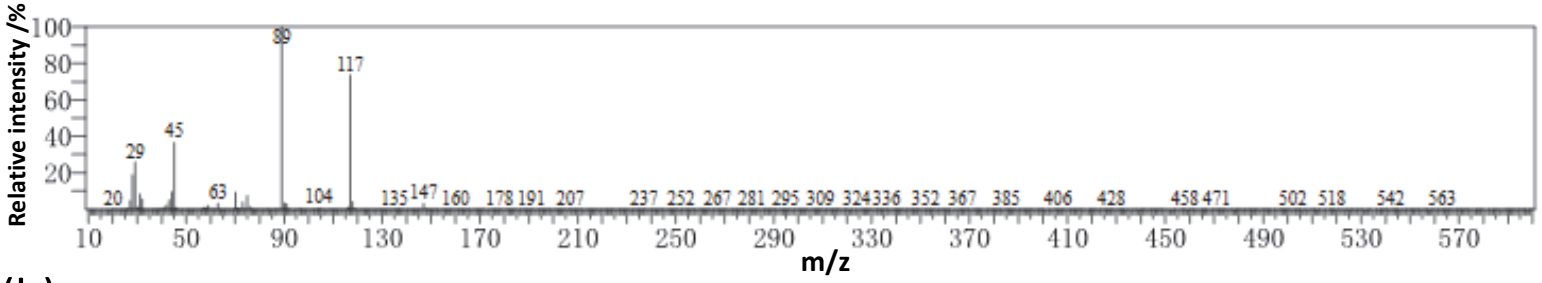
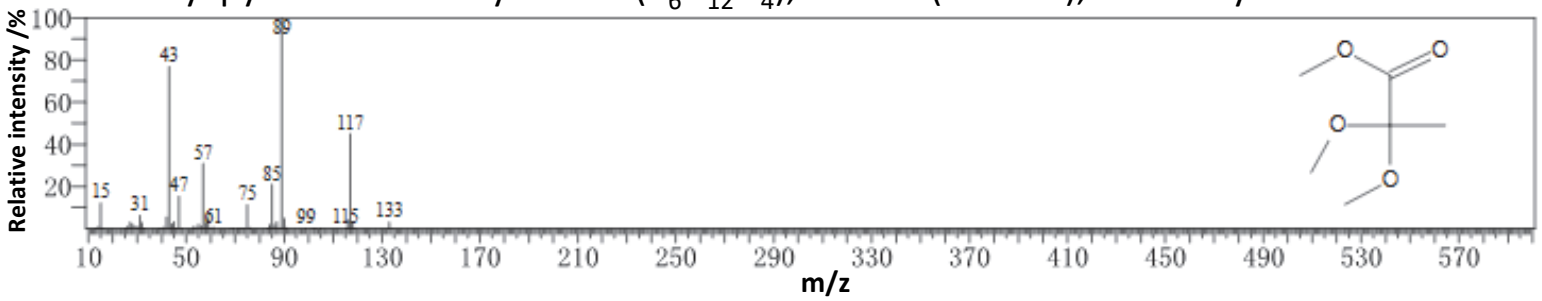


Figure S6 (a) EI-MS spectra at a retention time 13.16 min. Reference EI-MS spectra of (b) diethyl pyrocarbonate and (c) ethane-1,2-diyl diethyl biscarbonate from NIST library.

(a) #2, Retention time 16.085



(b) Methyl pyruvate dimethyl acetal ($C_6H_{12}O_4$), NIST20 (#15949), Similarity Index:74



(c) Dimethyl 2,2'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))diacetate ($C_{10}H_{18}O_7$)
NIST20 (#104339), Similarity Index:74

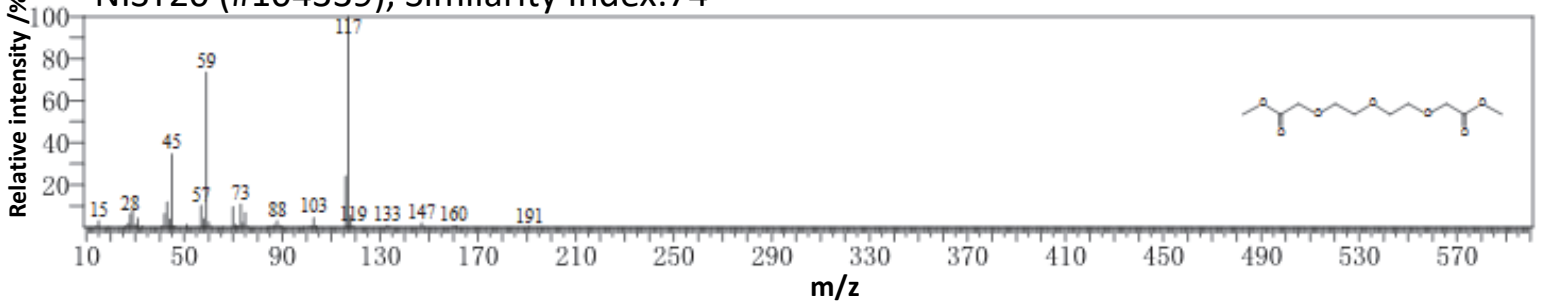
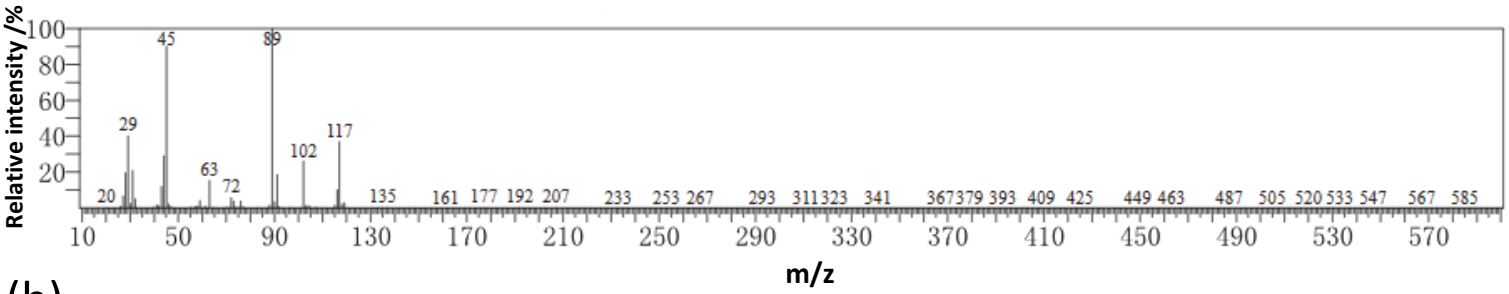
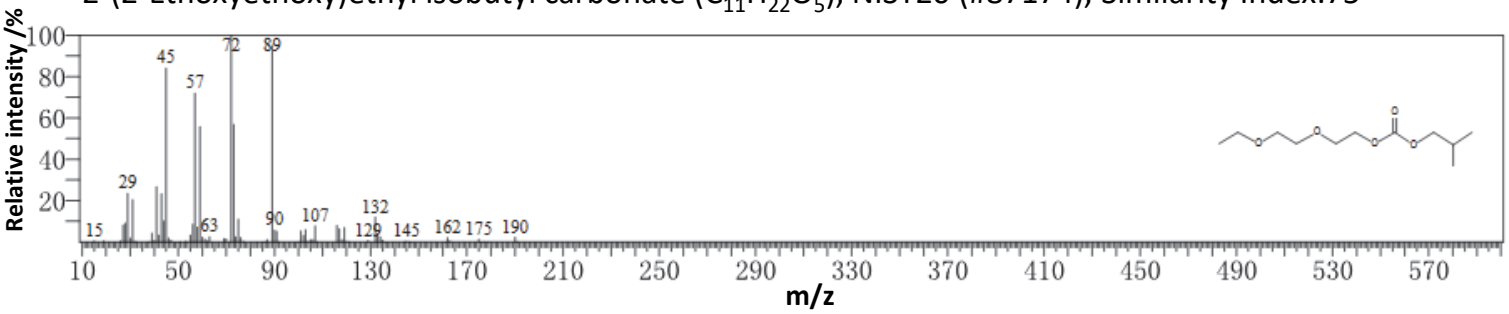


Figure S7 (a) EI-MS spectra at a retention time 16.085 min. Reference EI-MS spectra of (b) methyl pyruvate dimethyl acetal and (c) dimethyl 2,2'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))diacetate from NIST library.

(a) #3, Retention time 18.555



(b) 2-(2-Ethoxyethoxy)ethyl isobutyl carbonate ($C_{11}H_{22}O_5$), NIST20 (#87174), Similarity Index:75



(c) Methoxytriethylene glycol ($C_7H_{16}O_4$), NIST20 (#14408), Similarity Index:75

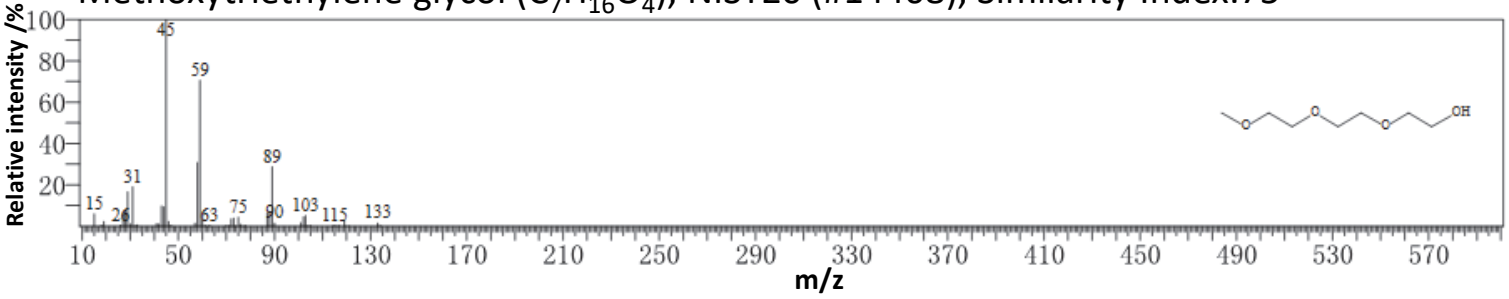


Figure S8 (a) EI-MS spectra at a retention time 18.555 min. Reference EI-MS spectra of (b) 2-(2-Ehoxyethoxy)ethyl isobutyl carbonate and (c) methoxytriethylene glycol from NIST library.

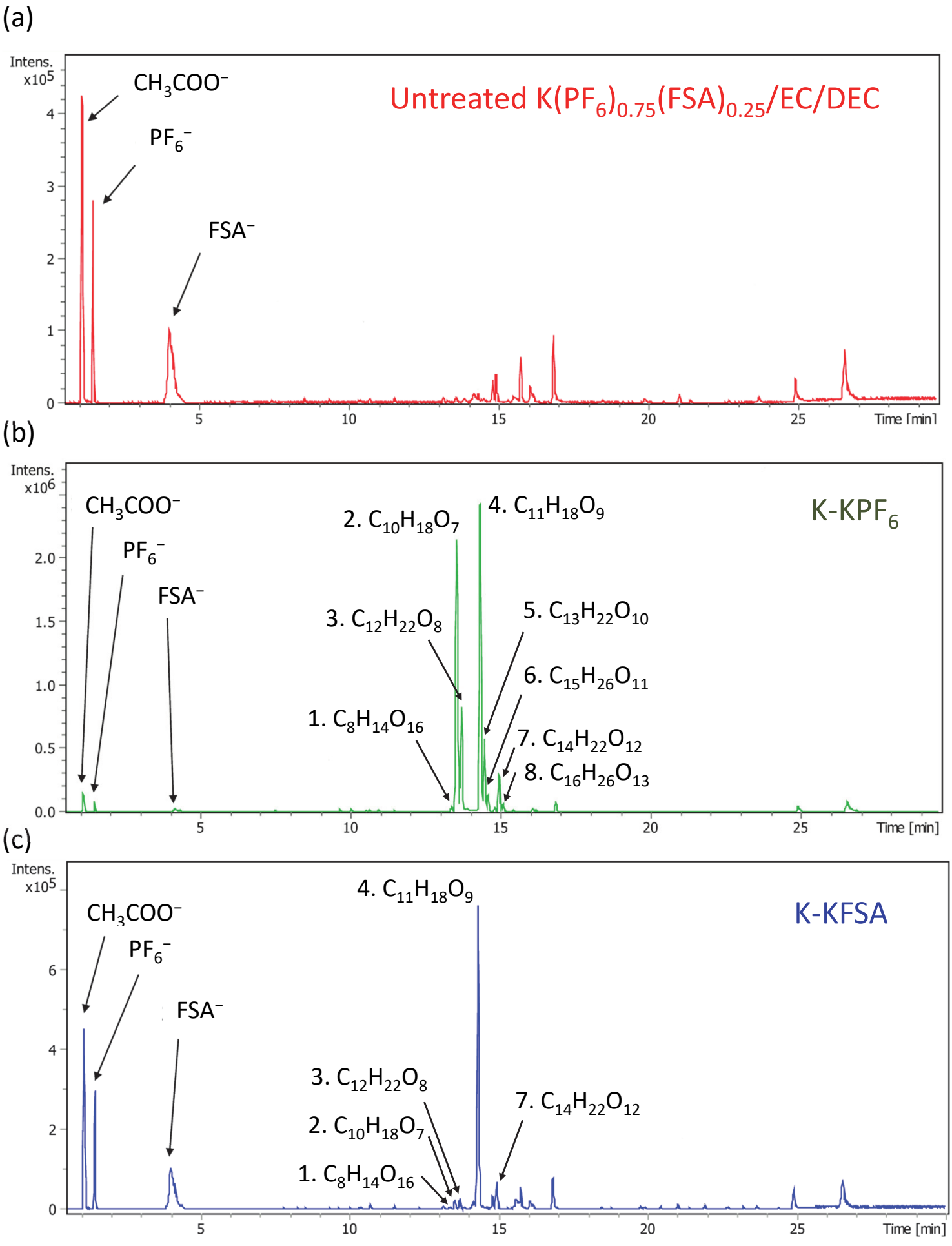
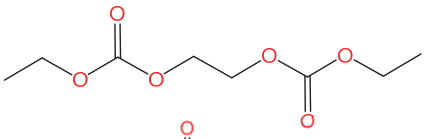
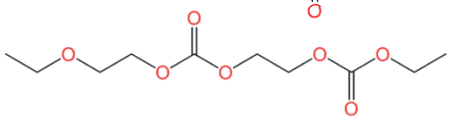
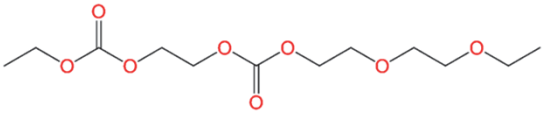
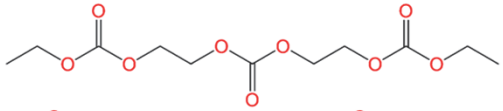
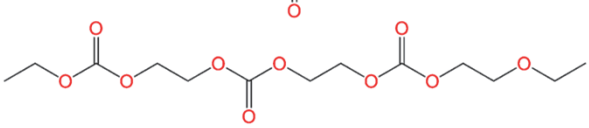
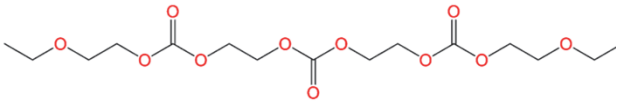
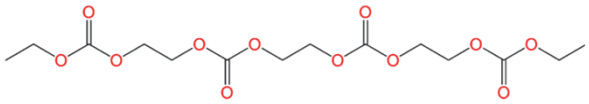
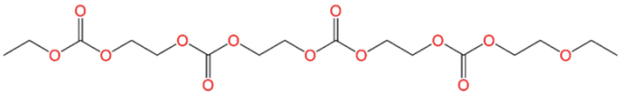
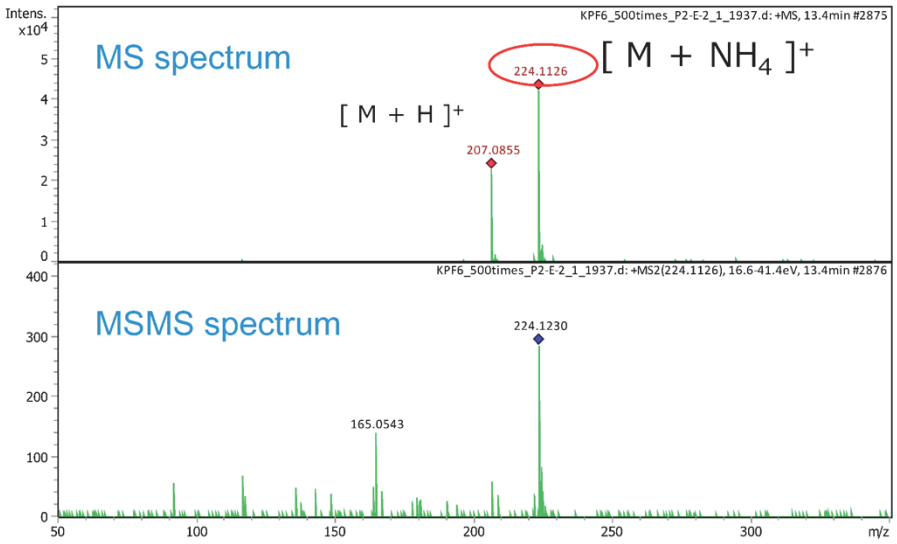


Figure S9. LC-MS analysis of the electrolytes by positive mode: total ion current chromatogram of (a) untreated $K(PF_6)_{0.75}(FSA)_{0.25}$/EC/DEC, (b) K-$KPF_6$, and (c) K-KFSA.

Table S1 Decomposition products in K-KFSA and K-KPF_6 solutions detected by LCMS (positive mode) analysis.

Number	K-KFSA electrolyte	K-KPF_6 electrolyte	Estimated formula	Estimated chemical structure
LCMS Pos. #1	✓	✓	$C_8H_{14}O_6$	
LCMS Pos. #2	✓	✓	$C_{10}H_{18}O_7$	
LCMS Pos. #3	✓	✓	$C_{12}H_{22}O_8$	
LCMS Pos. #4	✓	✓	$C_{11}H_{18}O_9$	
LCMS Pos. #5		✓	$C_{13}H_{22}O_{10}$	
LCMS Pos. #6		✓	$C_{15}H_{26}O_{11}$	
LCMS Pos. #7	✓	✓	$C_{14}H_{22}O_{12}$	
LCMS Pos. #8		✓	$C_{16}H_{26}O_{13}$	

Positive #1 Retention time = 13.4 min



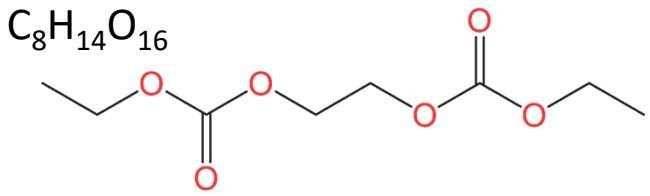
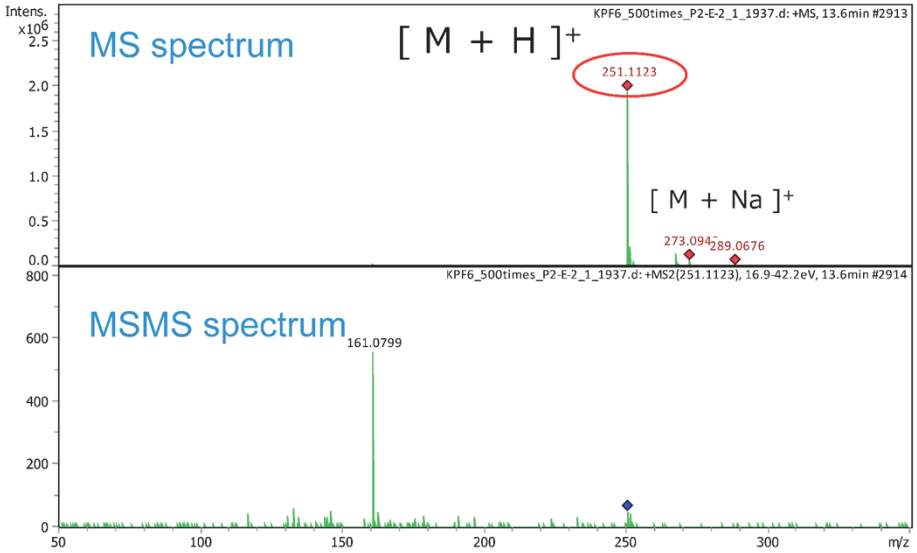


Figure S10. LC-MS and MSMS spectra of peak #1 in positive mode and estimated structure.

Positive #2 Retention time = 13.6 min



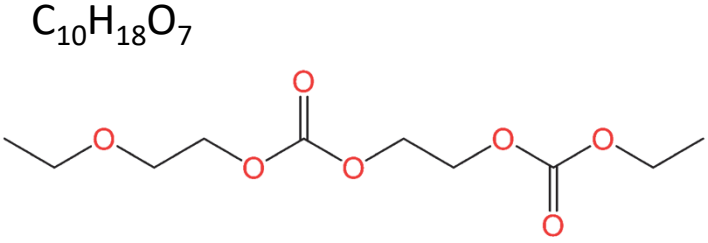
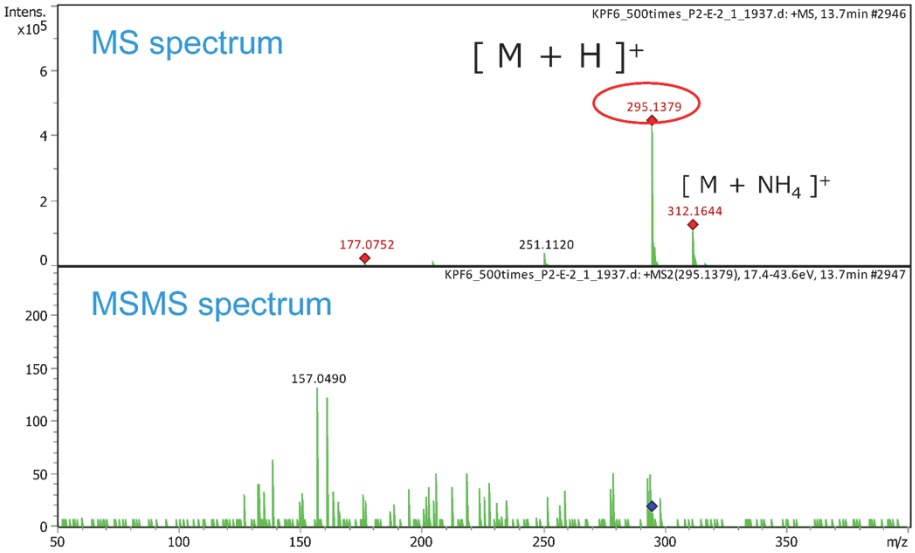


Figure S11. LC-MS and MSMS spectra of peak #2 in positive mode and estimated structure.

Positive #3 Retention time = 13.7 min



$C_{12}H_{22}O_8$

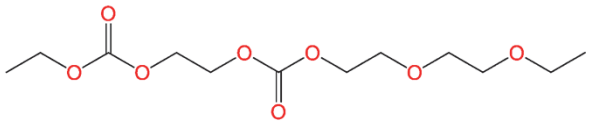
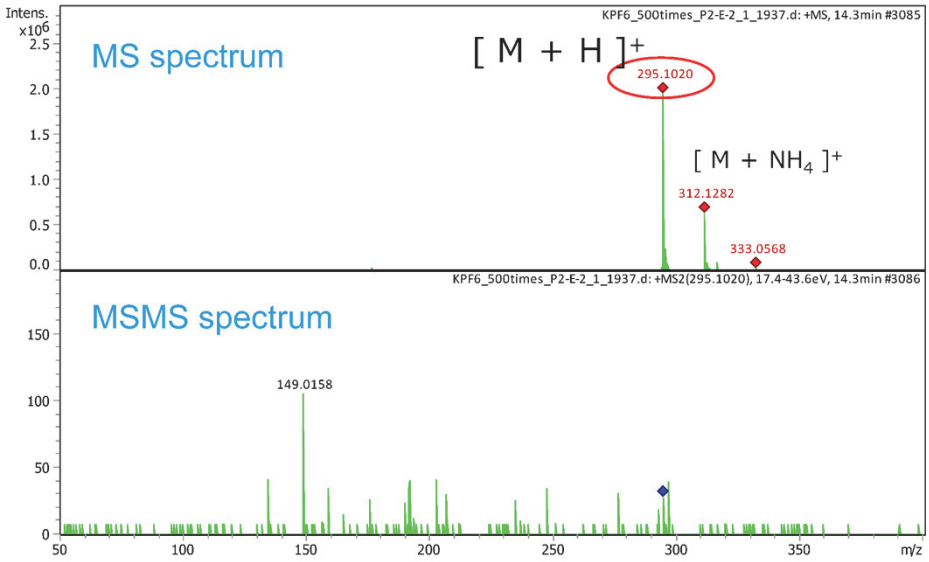


Figure S12. LC-MS and MSMS spectra of peak #3 in positive mode and estimated structure.

Positive #4 Retention time = 14.3 min



$C_{11}H_{18}O_9$

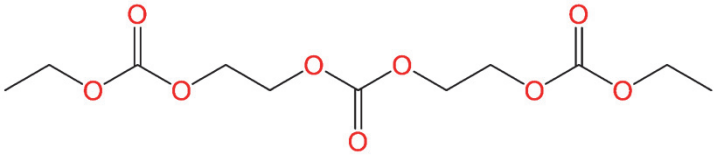
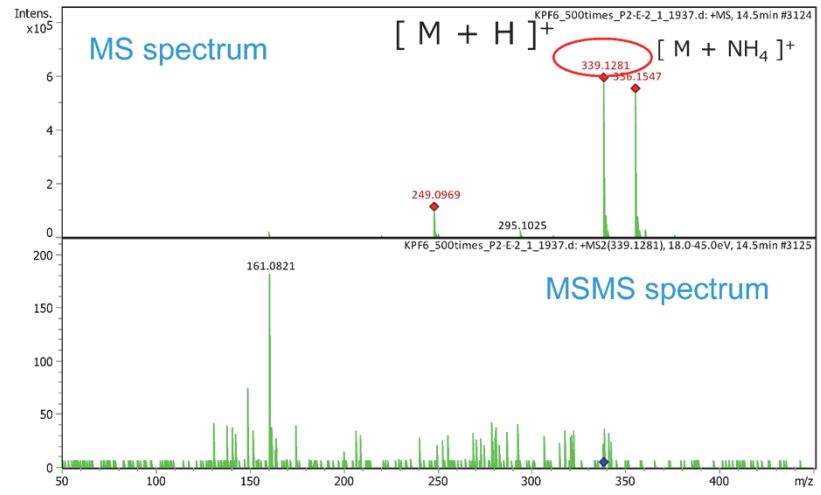


Figure S13. LC-MS and MSMS spectra of peak #4 in positive mode and estimated structure.

Positive #5 Retention time = 14.5 min



$C_{13}H_{22}O_{10}$

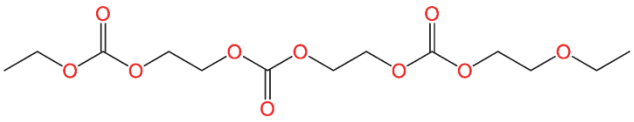
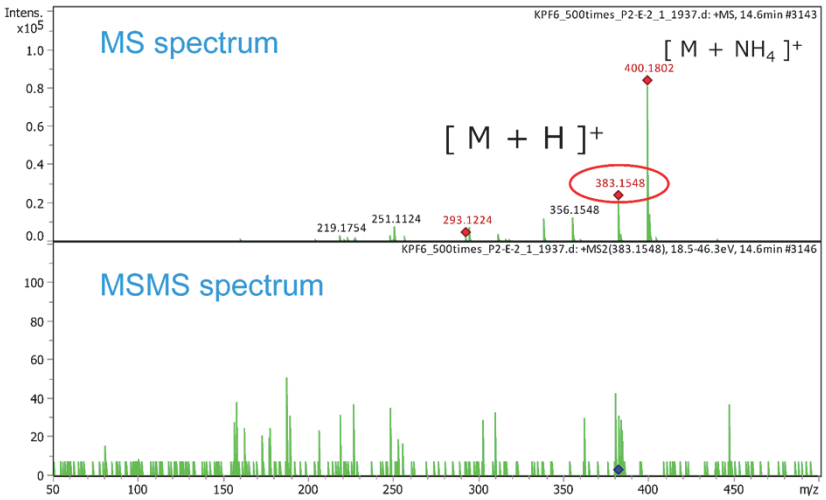


Figure S14. LC-MS and MSMS spectra of peak #5 in positive mode and estimated structure.

Positive #6 Retention time = 14.6 min



$C_{15}H_{26}O_{11}$

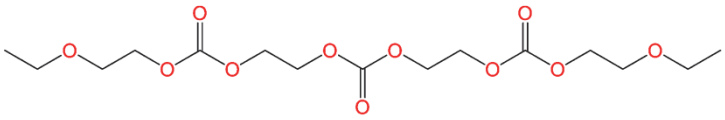
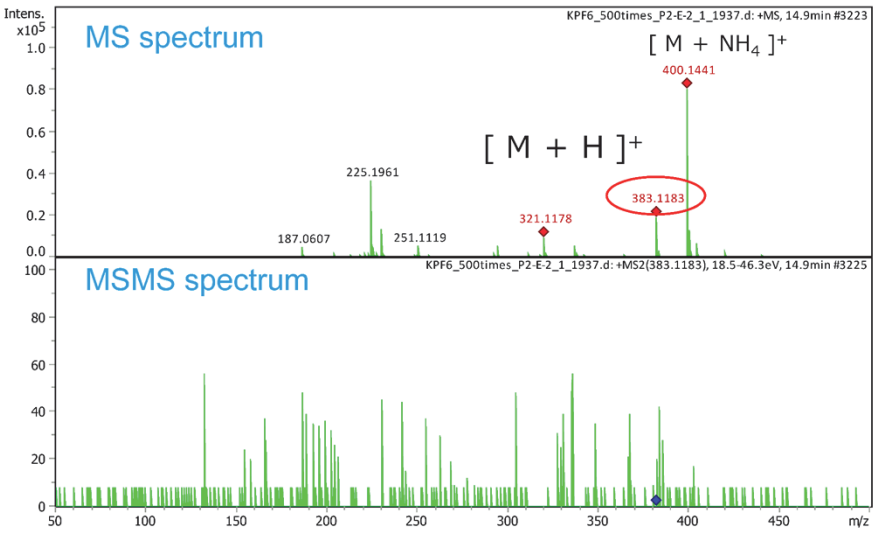


Figure S15. LC-MS and MSMS spectra of peak #6 in positive mode and estimated structure.

Positive #7 Retention time = 14.9 min



$C_{14}H_{22}O_{12}$

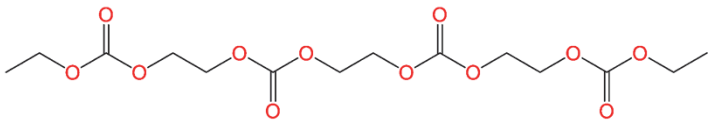
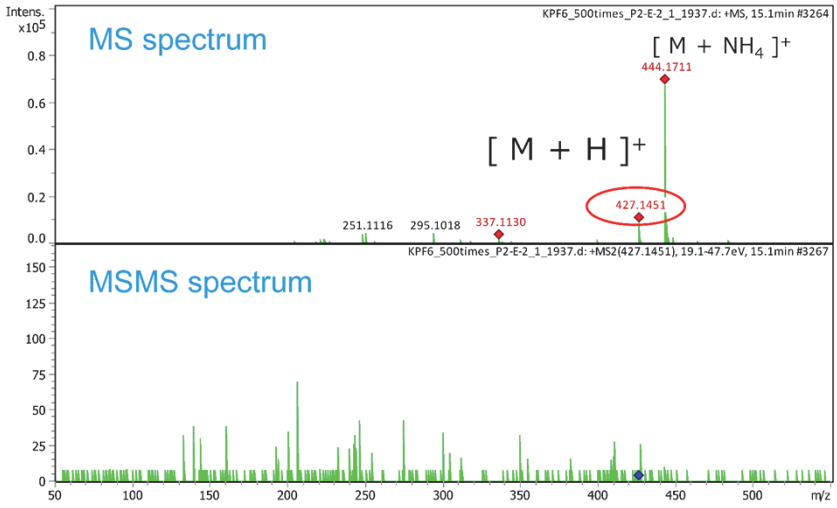


Figure S16. LC-MS and MSMS spectra of peak #7 in positive mode and estimated structure.

Positive #8 Retention time = 15.1 min



$C_{16}H_{26}O_{13}$

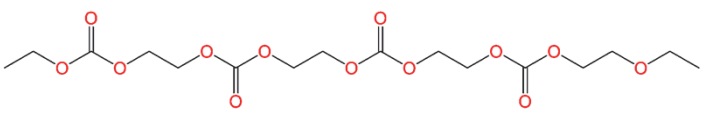


Figure S17. LC-MS and MSMS spectra of peak #8 in positive mode and estimated structure.

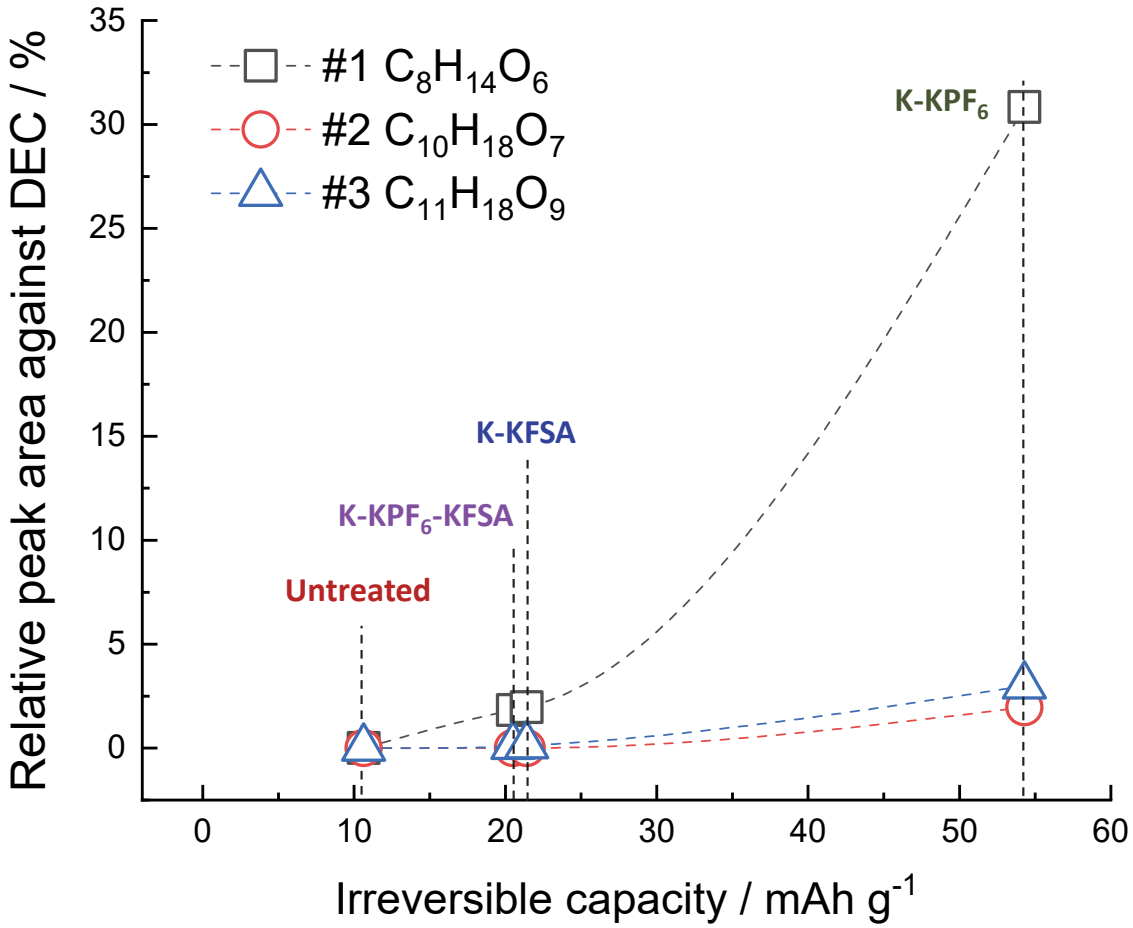
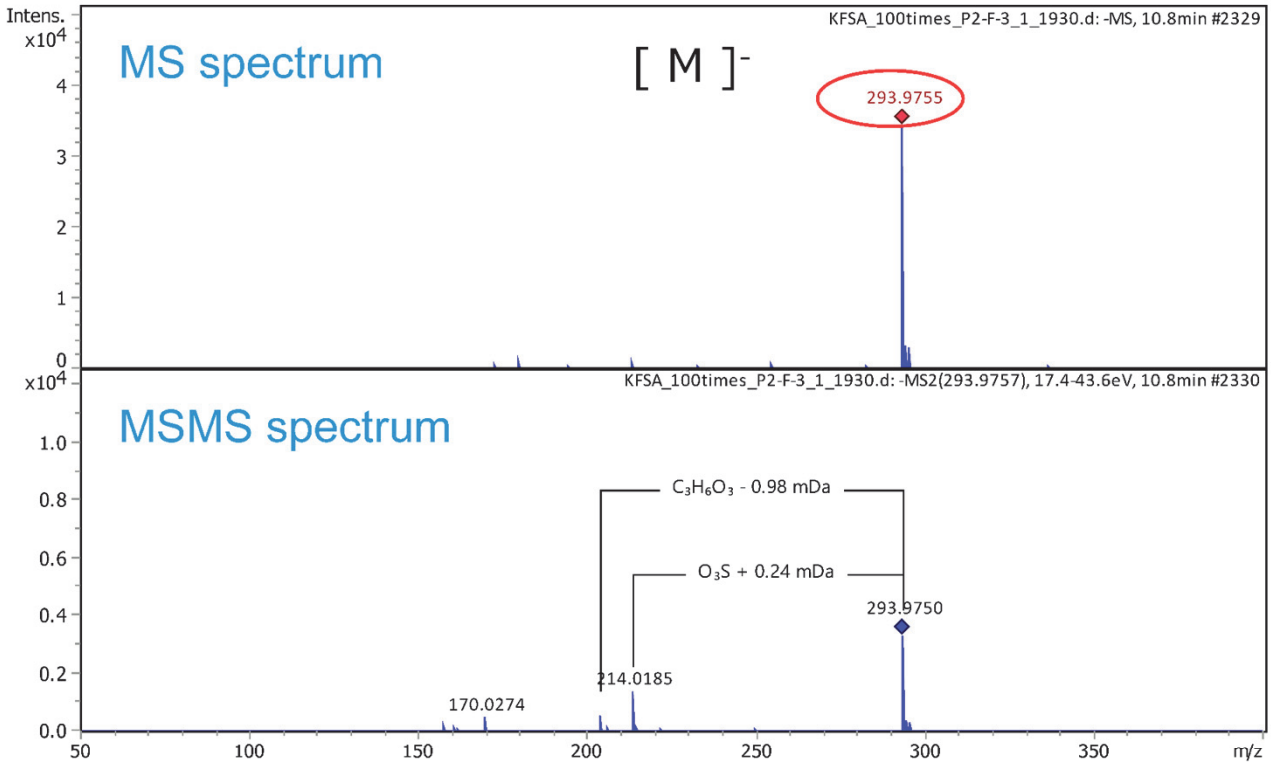


Figure S18. Correlation between the irreversible capacity of the $K_2Mn[Fe(CN)_6]$ electrodes and relative peak area of each oligocarbonate against DEC in the TIC of GC-MS analysis.

Negative #1 Retention time = 10.8 min



$C_5H_9FNO_8S_2^-$

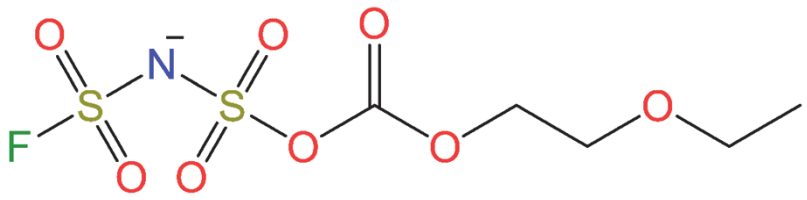
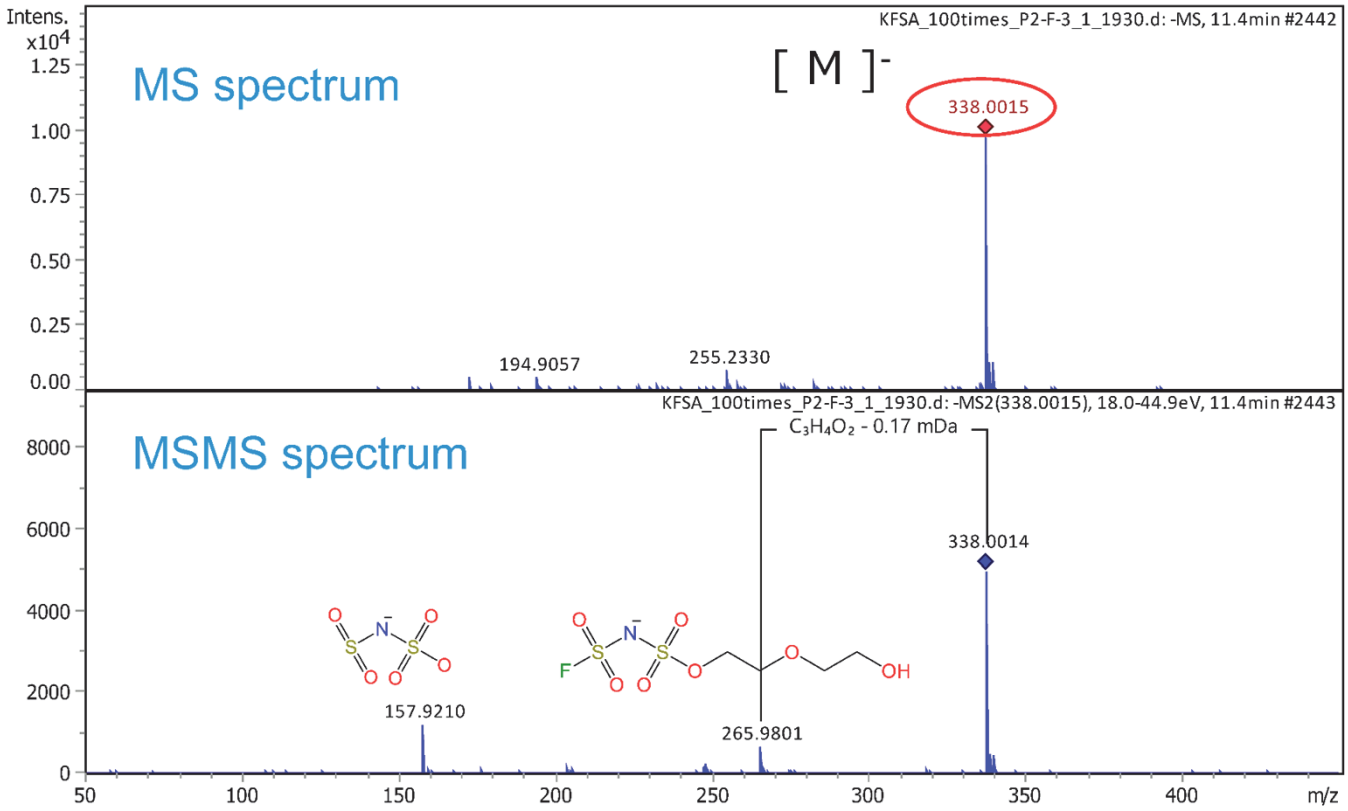


Figure S19. LC-MS and MSMS spectra of peak #1 in negative mode (**Figure 4**) and estimated structure.

Negative #2 Retention time = 11.4 min



$C_7H_{13}FNO_9S_2^-$

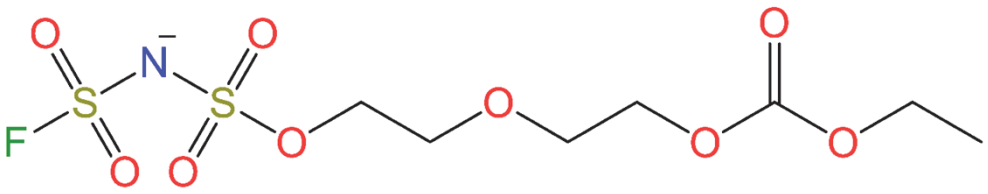
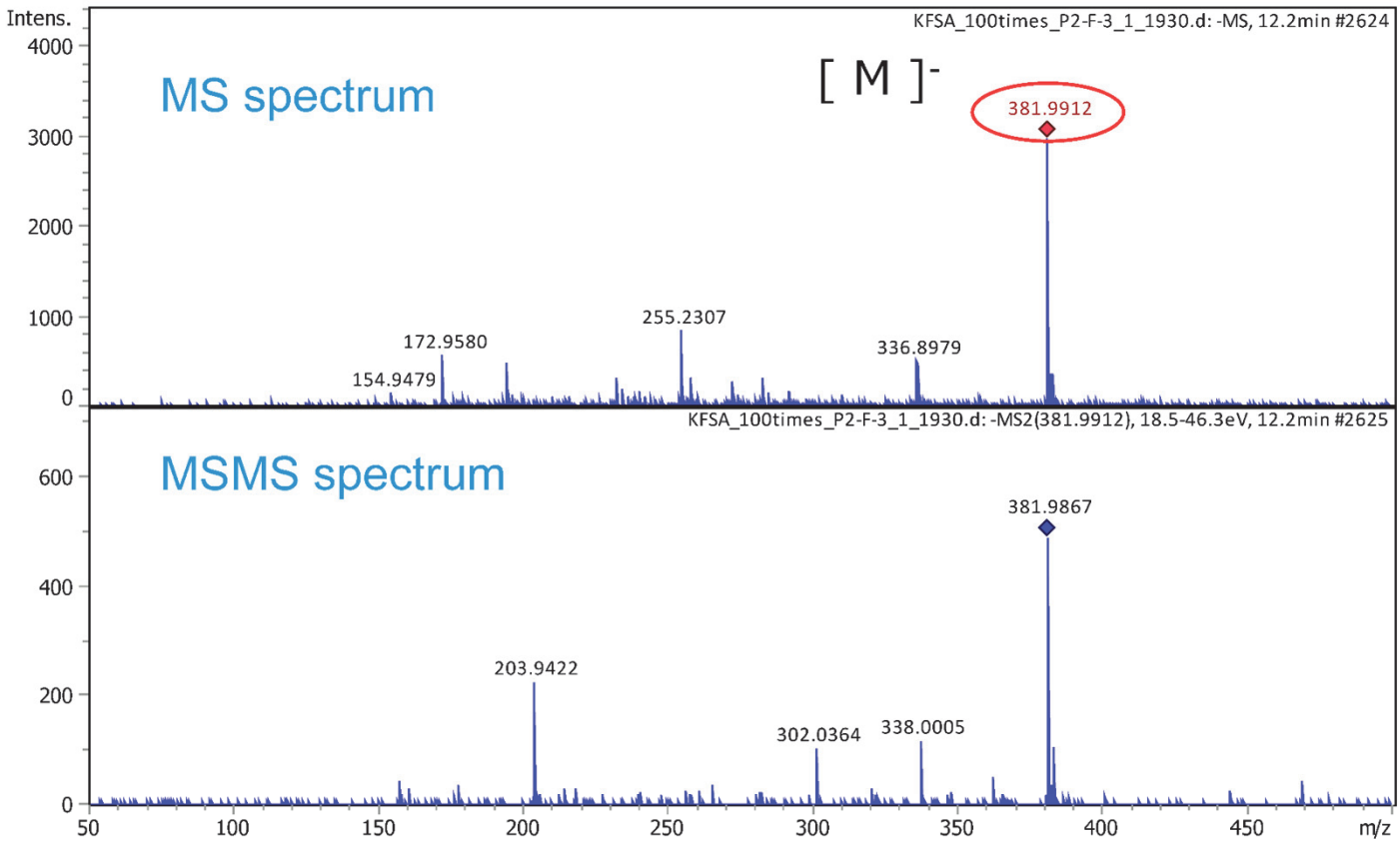


Figure S20. LC-MS and MSMS spectra of peak #2 in negative mode (**Figure 4**) and estimated structure.

Negative #3 Retention time = 13.4 min



$C_8H_{13}FNO_{11}S_2^-$

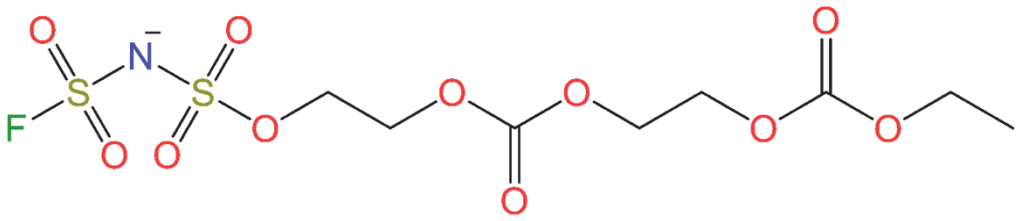


Figure S21. LC-MS and MSMS spectra of peak #3 in negative mode (**Figure 4**) and estimated structure.

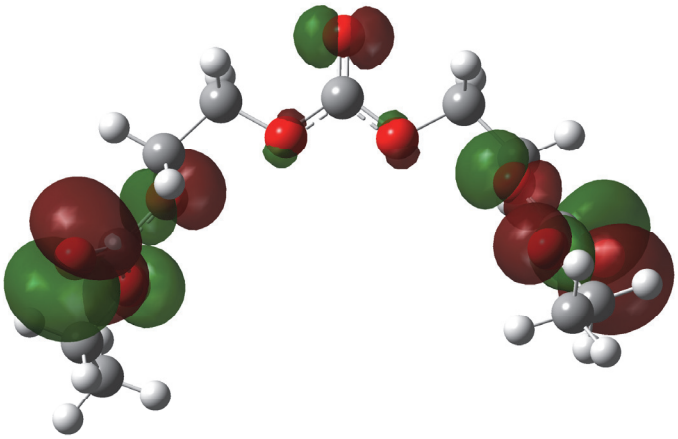


Figure S22. Optimized structure and HOMO of $C_{11}H_{18}O_9$ obtained by DFT calculations using an IEFPCM (acetonitrile) solvation model.

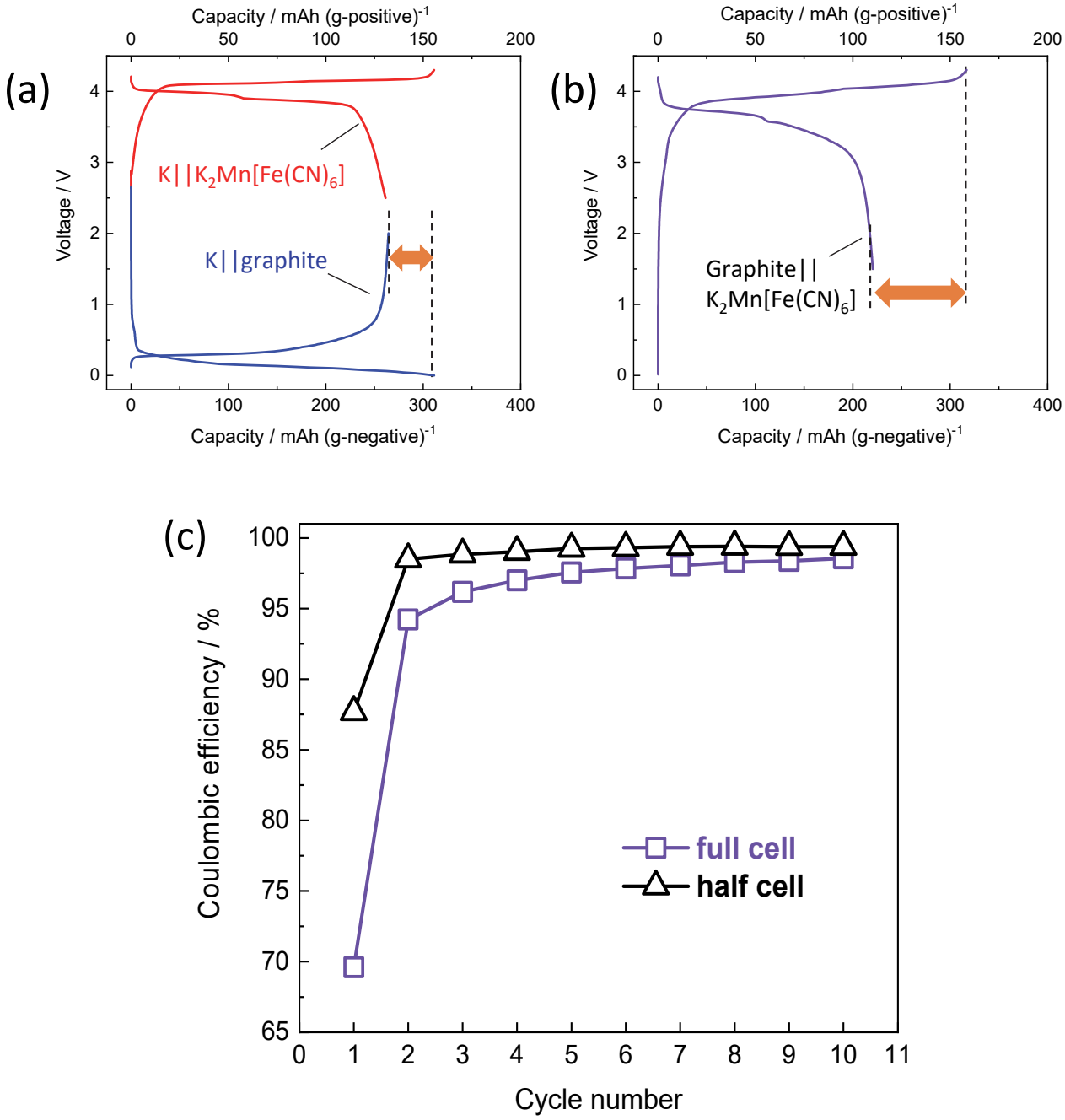


Figure S23 Charge/discharge curves of (a) half cells: AC||$K_2Mn[Fe(CN)_6]$ in the three-electrode cells and K||graphite in coin cells and (b) a graphite||$K_2Mn[Fe(CN)_6]$ full cell. (c) Coulombic efficiency of the electrodes : full cell of graphite||$K_2Mn[Fe(CN)_6]$ (purple) and K metal cell of K||graphite (black).

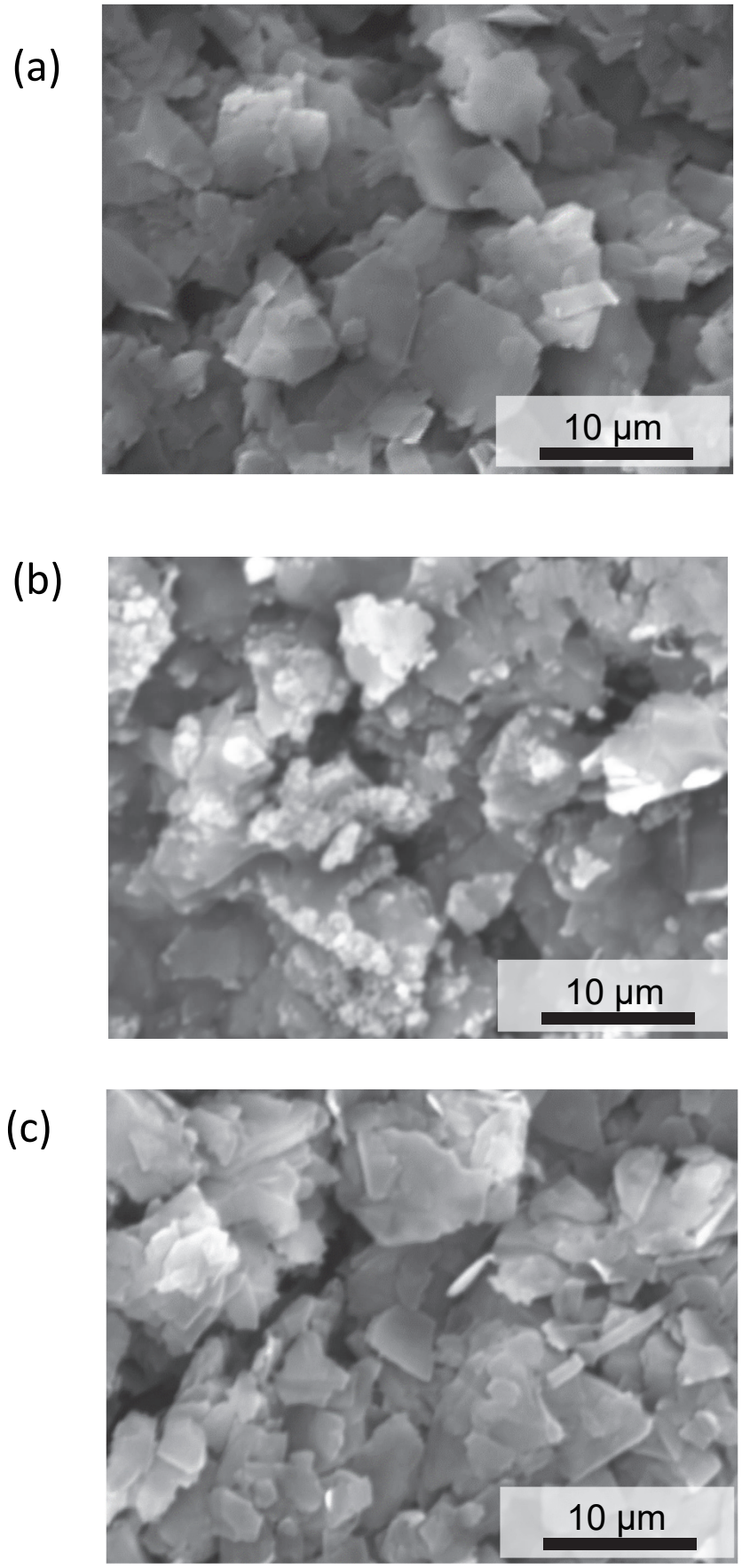


Figure S24. SEM images of graphite electrodes: (a) pristine, (b) tested in full cell and (c) tested in K metal cell for 10 cycles.

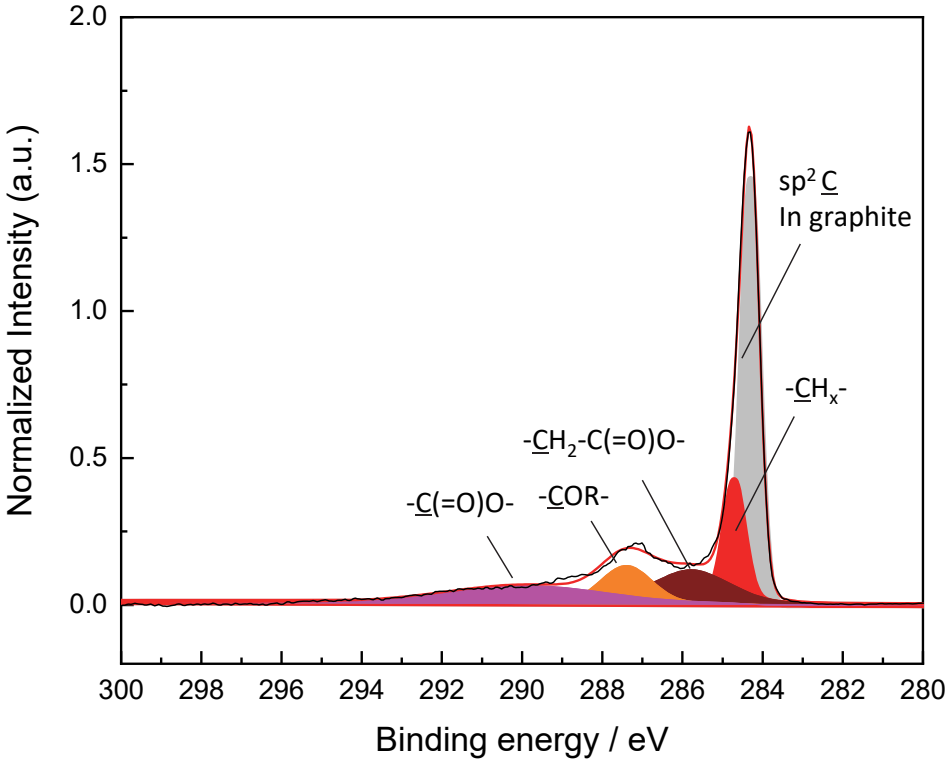


Figure S25 HAXPES spectra of the pristine graphite electrode: C 1s spectrum.

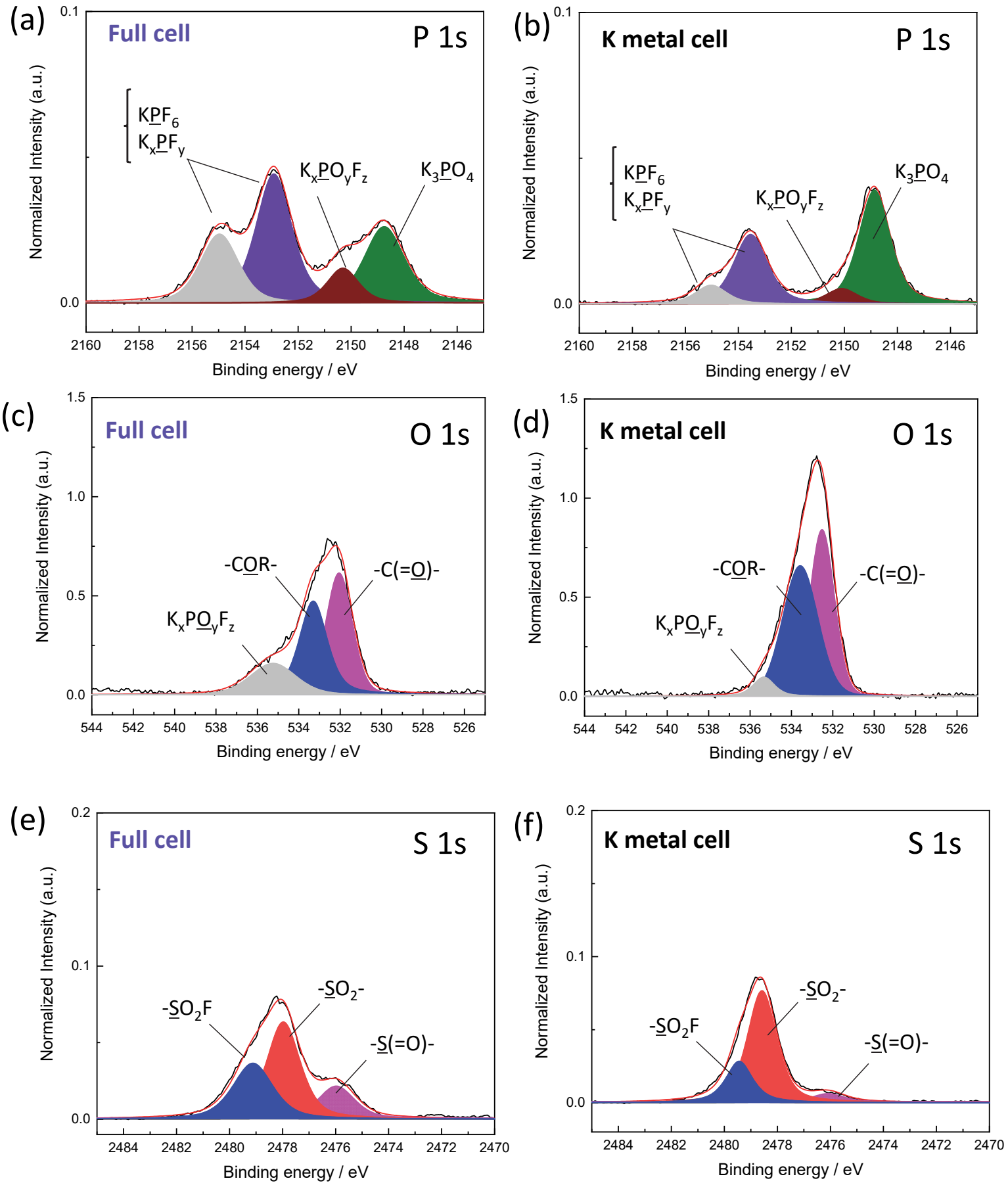


Figure S26 HAXPES spectra of the graphite electrode after 10 cycles: P 1s in (a) full and (b) half-cells, O 1s in (c) full and (d) half cells, F 1s in (e) full and (f) half-cells.

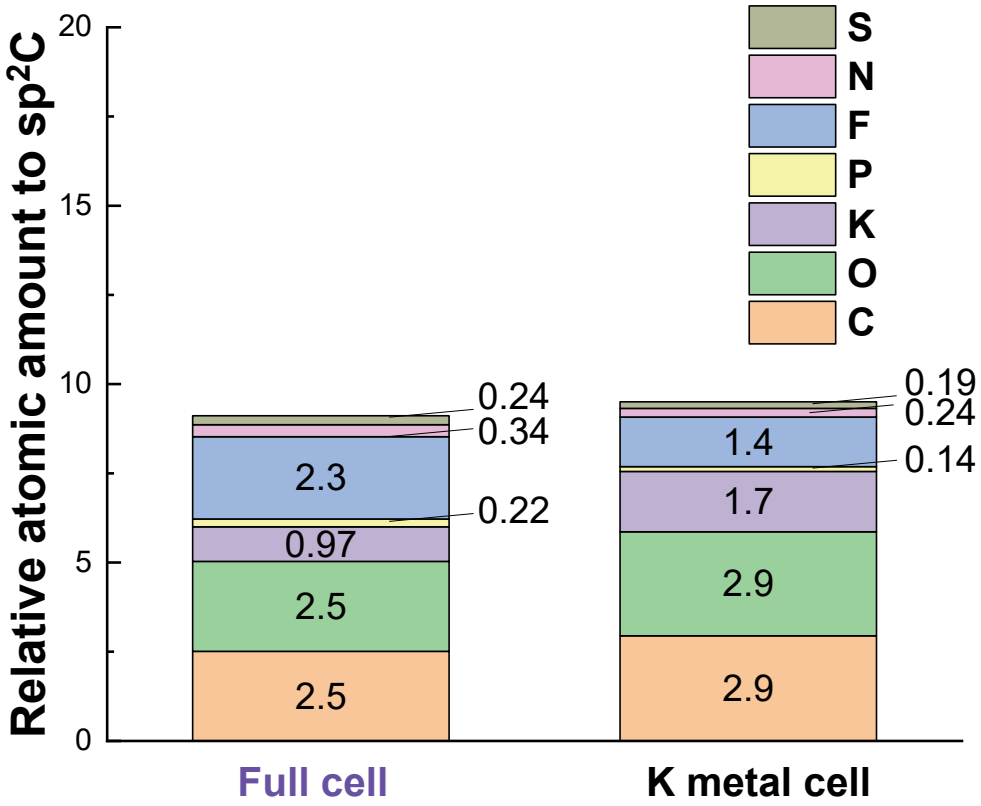


Figure S27 Atomic fractions relative to sp^2 carbon calculated from the HAXPES data using relative sensitivity factors.