

Electronic Supplementary Information

5V-Class High-Voltage Batteries with Over-Lithiated Oxide and a Multi-Functional Additive

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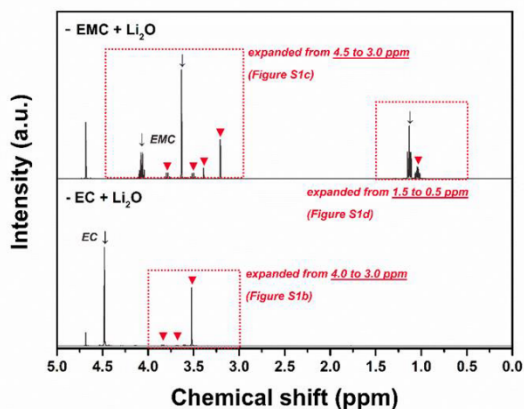
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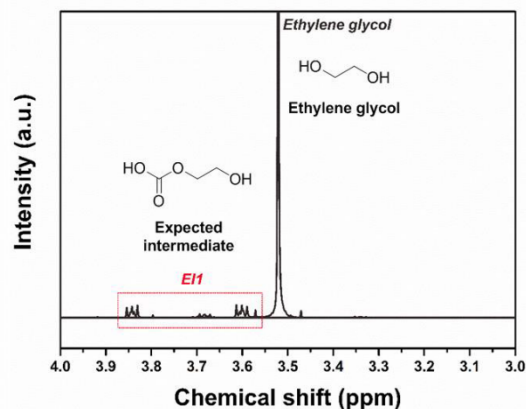
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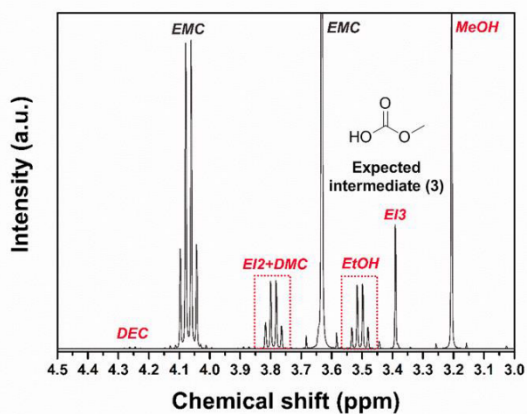
(a) $^1\text{H-NMR}$ for EC and EMC with Li_2O



(b) $^1\text{H-NMR}$ for EC with Li_2O (4.0 to 3.0 ppm)



(c) $^1\text{H-NMR}$ for EMC with Li_2O (4.5 to 3.0 ppm)



(d) $^1\text{H-NMR}$ for EMC with Li_2O (1.5 to 0.5 ppm)

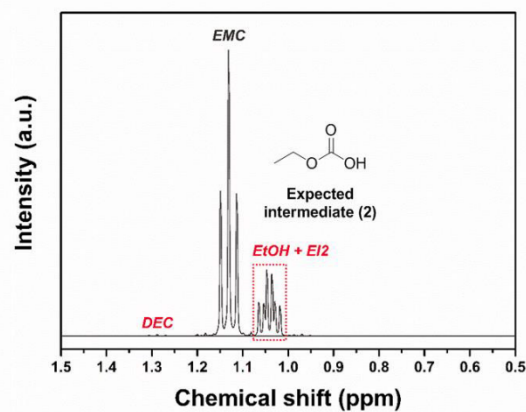
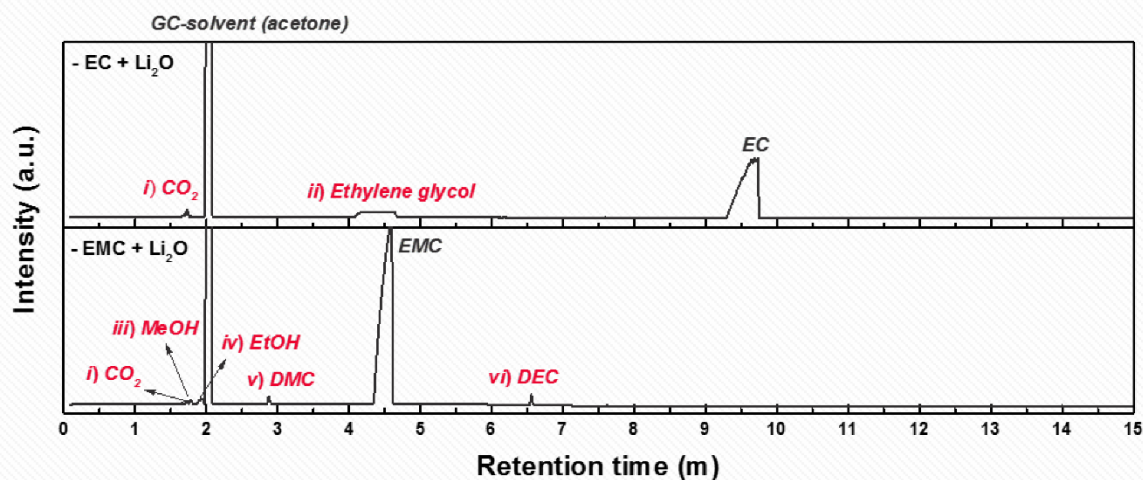


Fig. S1 (a) $^1\text{H-NMR}$ analysis results for supernatants of carbonate-based solvents (EC and EMC) with Li_2O , (b) expanded $^1\text{H-NMR}$ spectrum for EC supernatant (4.0 to 3.0 ppm), (c) expanded $^1\text{H-NMR}$ spectrum for EMC supernatant (4.5 to 3.0 ppm), (d) expanded $^1\text{H-NMR}$ spectrum for EMC supernatant (1.5 to 0.5 ppm)

(a) Gas chromatography results



(b) Mass analysis results

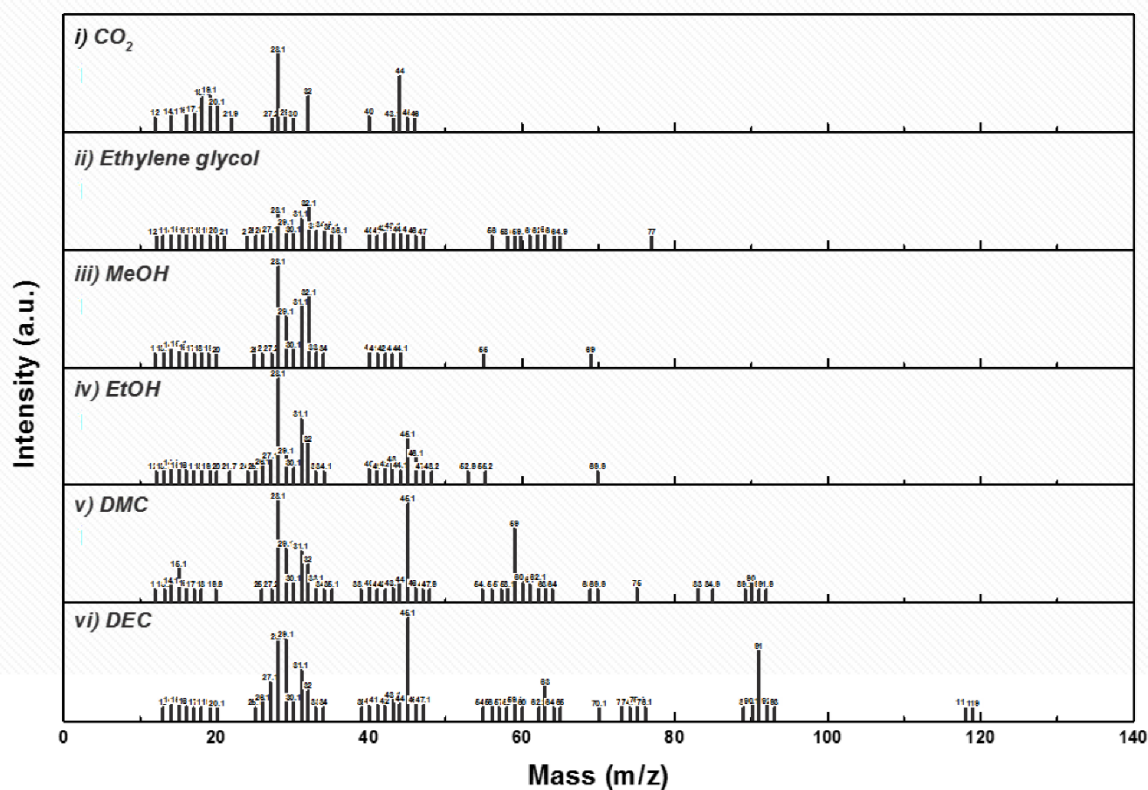
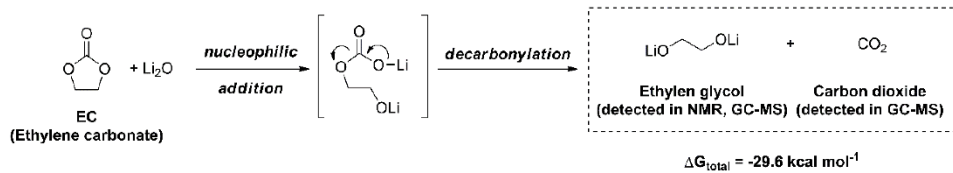


Fig. S2 (a) GC analysis results for supernatants of carbonate-based solvents (EC and EMC) with Li₂O, (b) Mass patterns for individual components formed by carbonate-based solvents decomposition

(a) Decomposition reaction of cyclic carbonate



(b) Decomposition reaction of acyclic carbonate

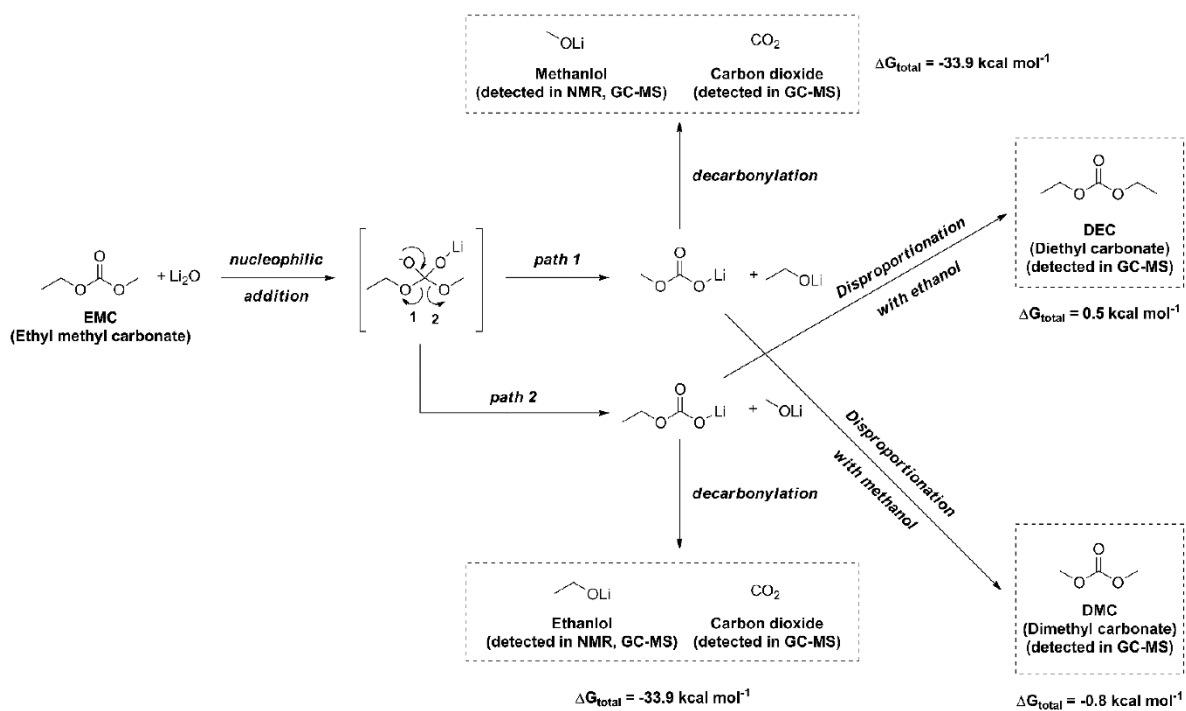
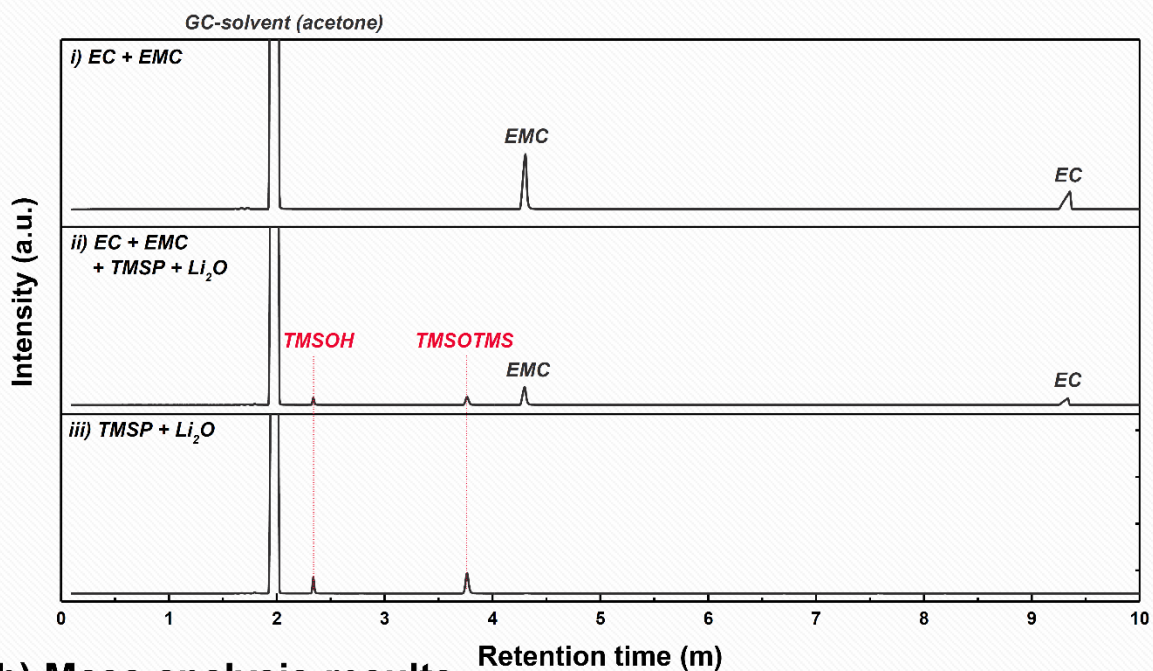


Fig. S3 Suggested mechanism for chemical decomposition of solvents by Li₂O: (a) EC, (b) EMC

(a) Gas chromatography results



(b) Mass analysis results

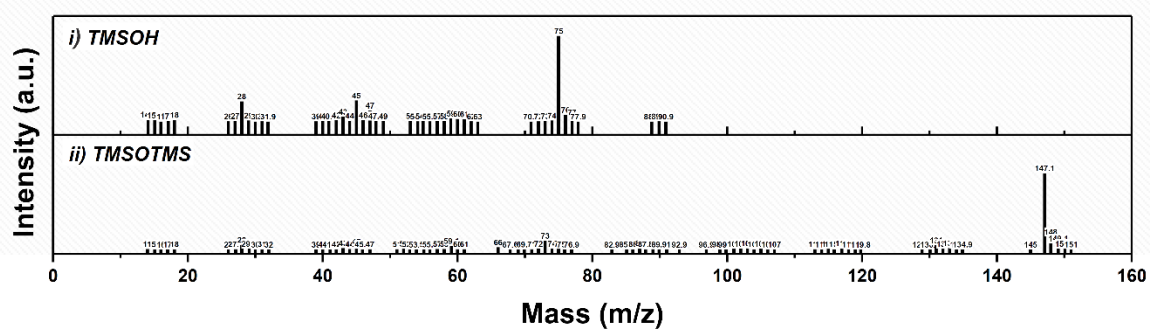


Fig. S4 (a) GC analysis results of i) EC + EMC, ii) EC + EMC + TMSP + Li₂O, and iii) TMSP + Li₂O, (b) Mass pattern of i) TMSOH, and ii) TMSOTMS

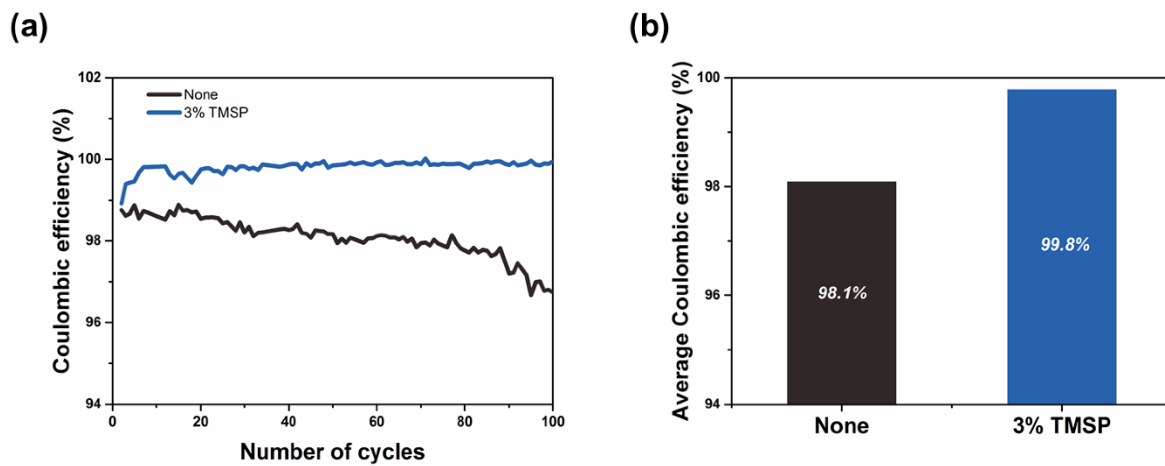


Fig. S5 (a) Coulombic efficiency of the cell, (b) average Coulombic efficiency of the cell (black: standard electrolyte and blue: 3% TMSP-controlled electrolyte)

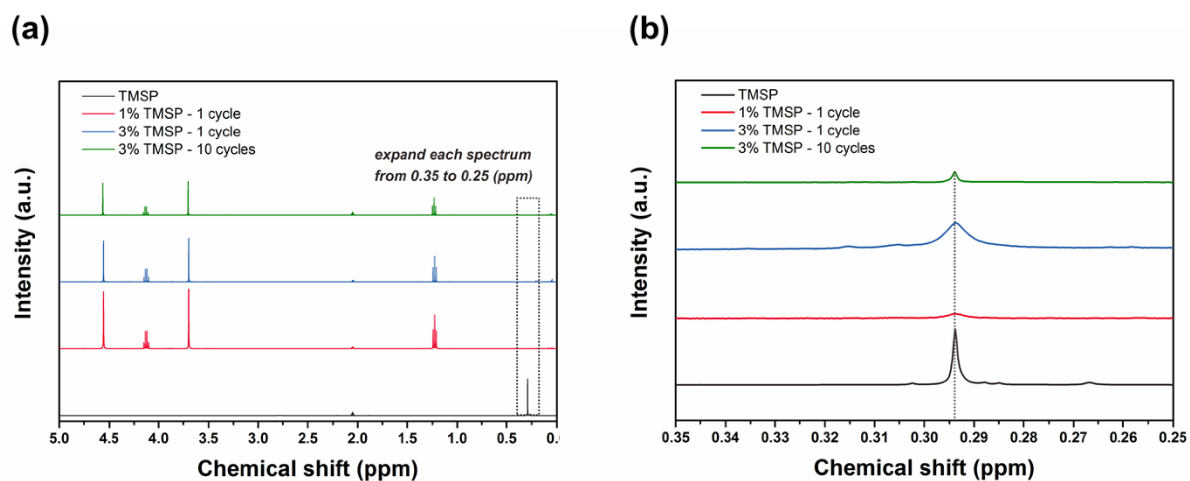


Fig. S6 (a) $^1\text{H-NMR}$ analyses of supernatants from cycled cell, (b) expanded $^1\text{H-NMR}$ spectra from 0.35 to 0.25 (ppm) (black: reference TMSP, red: from the cell cycled with 1% TMSP-controlled electrolyte after 1 cycle, blue: from the cell cycled with 3% TMSP-controlled electrolyte after 1 cycle, green: from the cell cycled with 3% TMSP-controlled electrolyte after 10 cycles)

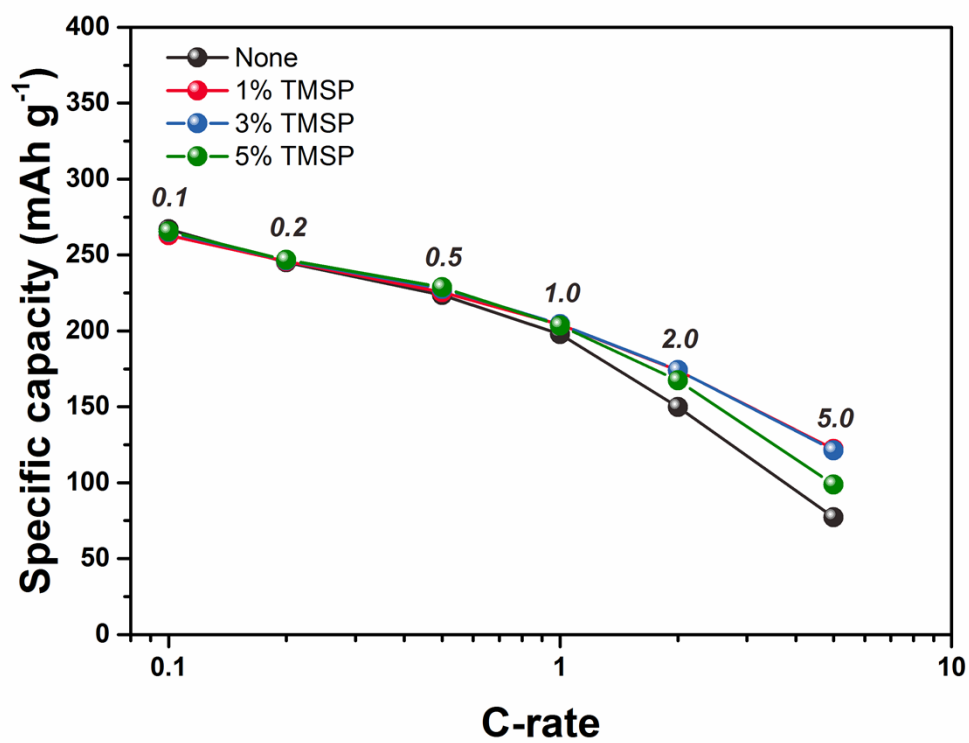
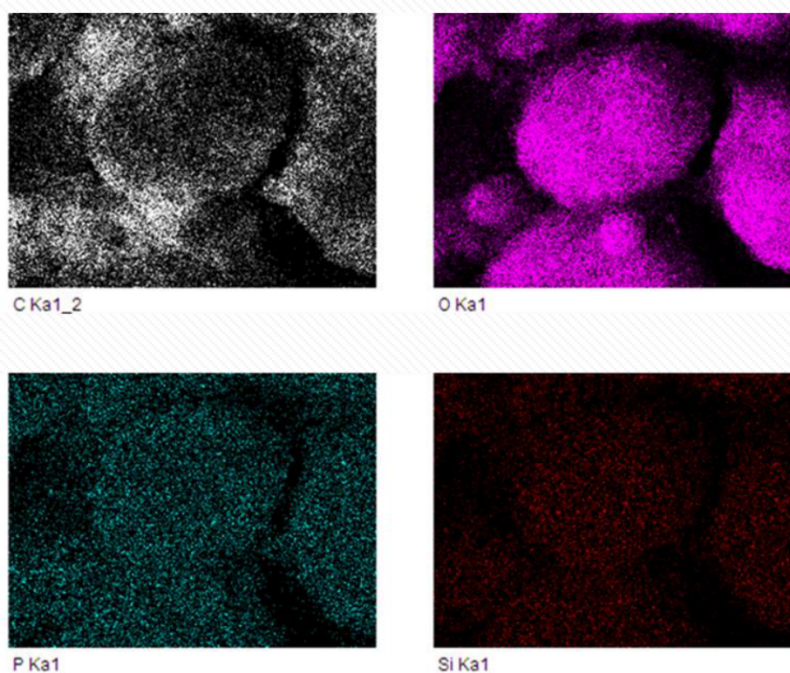


Fig. S7 Rate capability of the cell with a variation of TMSP contents (black: standard electrolyte, red: 1% TMSP controlled electrolyte, blue: 3% TMSP-controlled electrolyte, green: 5% TMSP-controlled electrolyte)

(a) After 1 cycle (TMSP)



(b) After 100 cycles (TMSP)

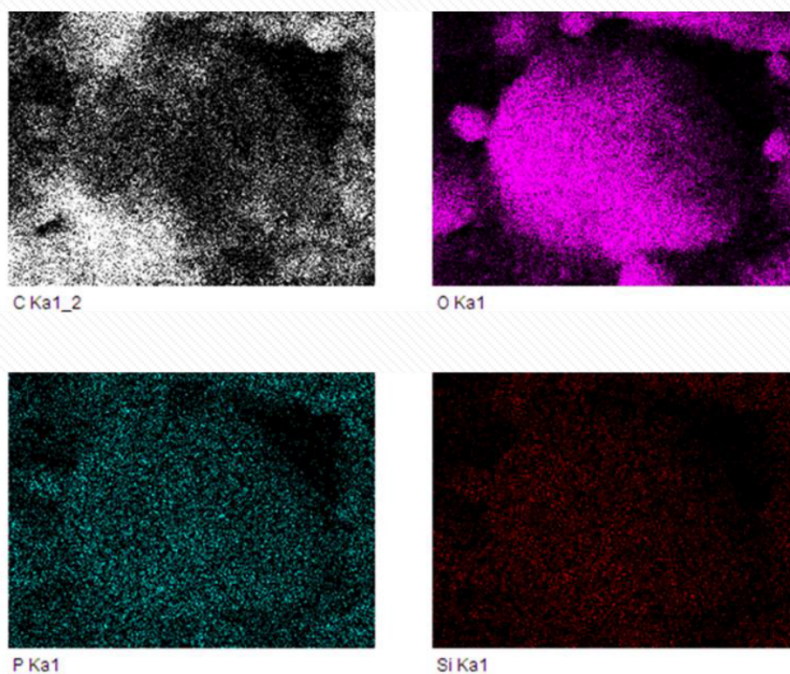
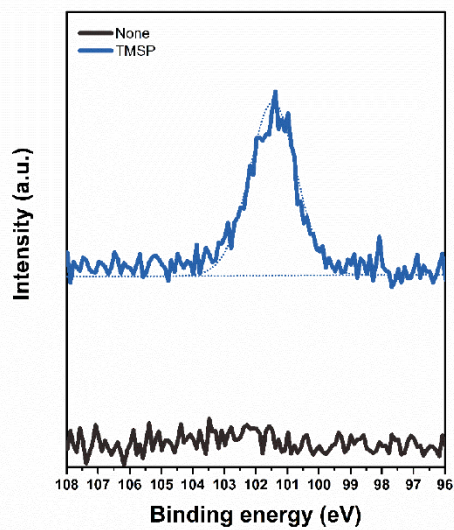


Fig. S8 EDS analysis for cycled electrode with 3% TMSP (a) after 1 cycle, (b) after 100 cycles (black: carbon, purple: oxygen, green: phosphorus, red: silicon)

(a) Si2p analysis after 1 cycle



(b) Si2p analysis after 100 cycles

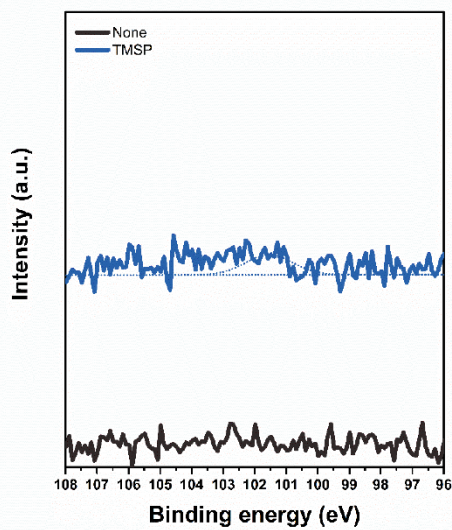


Fig. S9 Si2p spectroscopic results (characterized by XPS) for cycled electrodes (a) after 1 cycle, (b) after 100 cycles (black: cycled with standard electrolyte, blue: cycled with TMSP-controlled electrolyte)