

Electronic Supplementary Information

Intrinsic effects of electrolytes on lithium metal deposition and dissolution investigated through a separator-free cell

Tomoki Takahashi,[†] Di Wang,[†] Jinkwang Hwang* and Kazuhiko Matsumoto*

Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

[†]Equal contribution

*Corresponding author:

KM (matsumoto.kazuhiko.4c@kyoto-u.ac.jp)

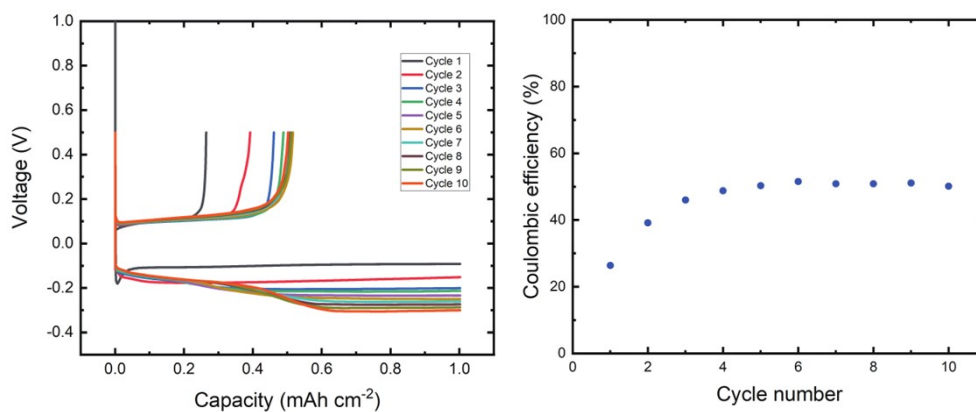
JH (hwang.jinkwang.5c@kyoto-u.ac.jp)

Table S1 List of the electrolytes used in this study.

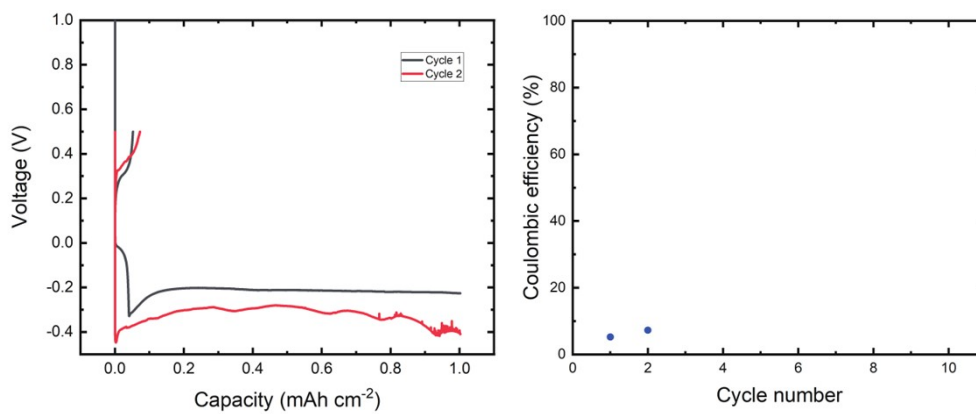
Salt	Concentration	Solvent	Additive
Li[PF ₆]	1 M	SL	
Li[PF ₆]	1 M	TMP	
Li[PF ₆]	1 M	TEP	
Li[PF ₆]	1 M	DMC	
Li[PF ₆]	1 M	PC	
Li[PF ₆]	1 M	EC:DMC	
Li[PF ₆]	1 M	EC:DMC	3 wt% FEC
Li[PF ₆]	1 M	AN	
Li[PF ₆]	1 M	DMSO	
Li[PF ₆]	1 M	G2	
Li[PF ₆]	1 M	DME	
Li[FSA]	1 M	SL	
Li[FSA]	1 M	TMP	
Li[FSA]	1 M	TEP	
Li[FSA]	1 M	DMC	
Li[FSA]	1 M	PC	
Li[FSA]	1 M	PC	3 wt% FEC
Li[FSA]	4 M	PC	
Li[FSA]	4 M	PC	3 wt% FEC
Li[FSA]	1 M	EC:DMC	
Li[FSA]	1 M	EC:DMC	3 wt% FEC
Li[FSA]	4 M	EC:DMC	
Li[FSA]	4 M	EC:DMC	3 wt% FEC
Li[FSA]	1 M	AN	
Li[FSA]	1 M	DMSO	
Li[FSA]	1 M	G2	
Li[FSA]	1 M	DME	
Li[FSA]	1 M	DME	3 wt% LiNO ₃
Li[FSA]	4 M	DME	
Li[FSA]	20 mol%	[C ₃ C ₁ pyrr][FSA]	
Li[FSA]	40 mol%	[C ₃ C ₁ pyrr][FSA]	
Li[FSA]	20 mol%	[C ₂ C ₁ im][FSA]	
Li[FSA]	40 mol%	[C ₂ C ₁ im][FSA]	
Li[TFSA]	1 M	SL	
Li[TFSA]	1 M	TMP	
Li[TFSA]	1 M	TEP	

Li[TFSA]	1 M	DMC	
Li[TFSA]	1 M	PC	
Li[TFSA]	1 M	EC:DMC	
Li[TFSA]	1 M	EC:DMC	3 wt% FEC
Li[TFSA]	1 M	AN	
Li[TFSA]	1 M	DMSO	
Li[TFSA]	1 M	G2	
Li[TFSA]	1 M	DME	
Li[TFSA]	1 M	DME	3 wt% LiNO ₃
Li[TFSA]	Saturated	DME	
Li[TFSA]	20 mol%	[C ₃ C ₁ pyrr][TFSA]	
Li[TFSA]	20 mol%	[C ₂ C ₁ im][TFSA]	

(a) 1 M Li[PF₆]-SL



(b) 1 M Li[PF₆]-TMP



(c) 1 M Li[PF₆]-PC

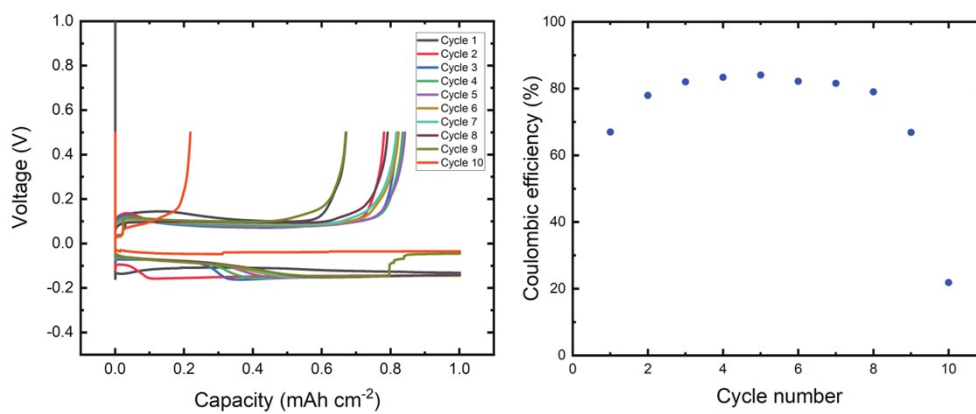
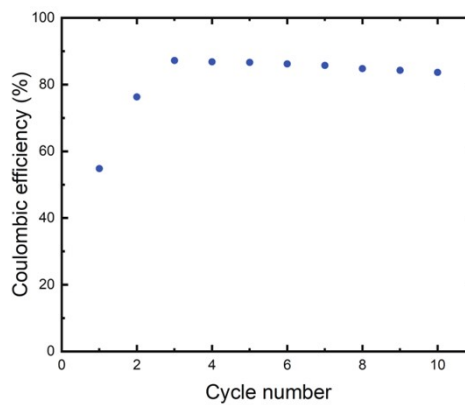
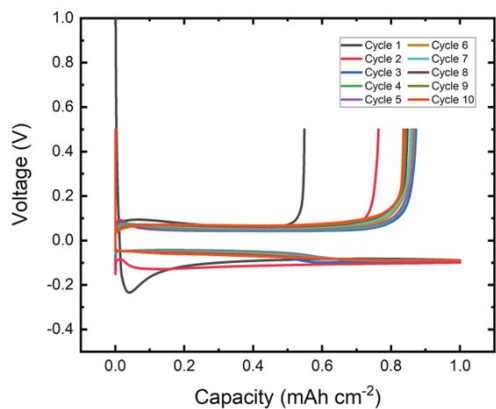
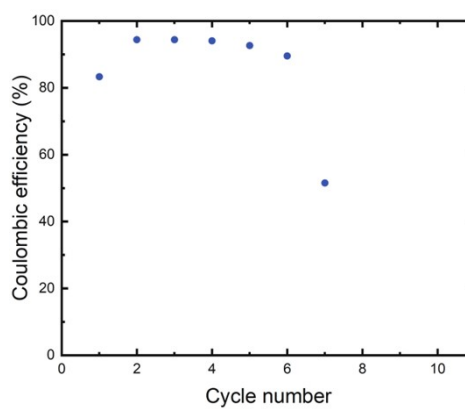
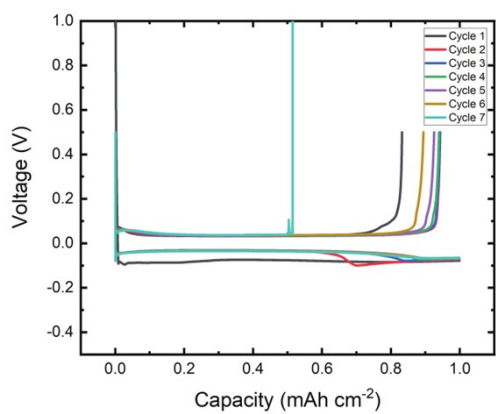


Fig. S1 Summary of the Li metal deposition/dissolution tests in the Li[PF₆]-based electrolytes. (left) voltage profiles and (right) CE.

(d) 1 M Li[PF₆]-EC:DMC



(e) 1 M Li[PF₆]-EC:DMC 3 wt% FEC



(f) 1 M Li[PF₆]-DMSO

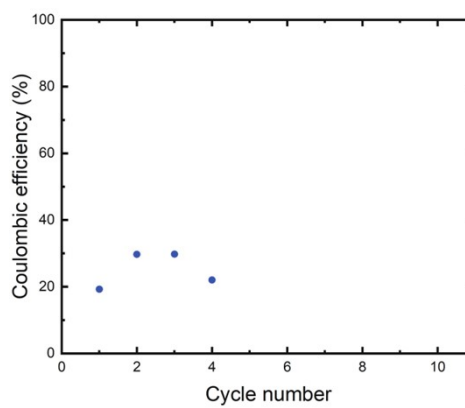
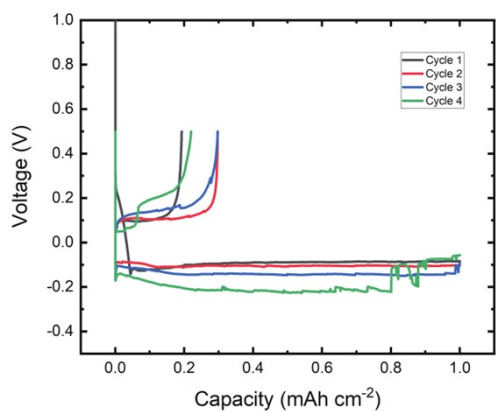
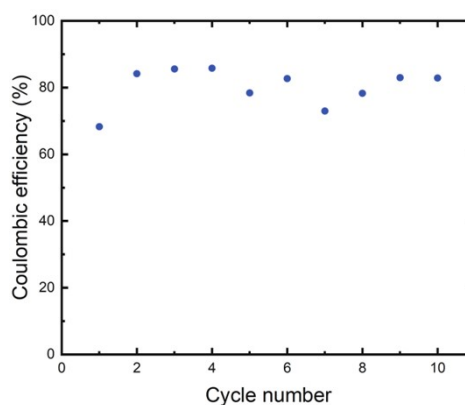
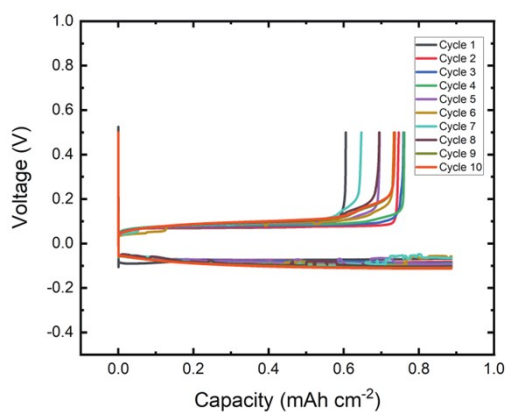
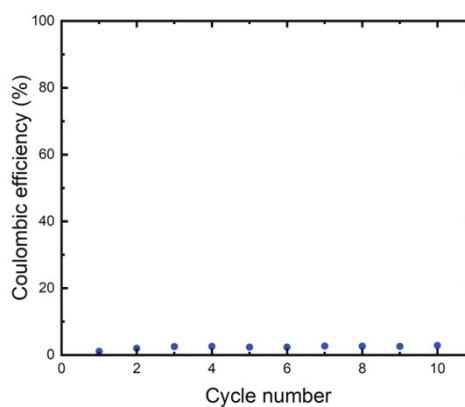
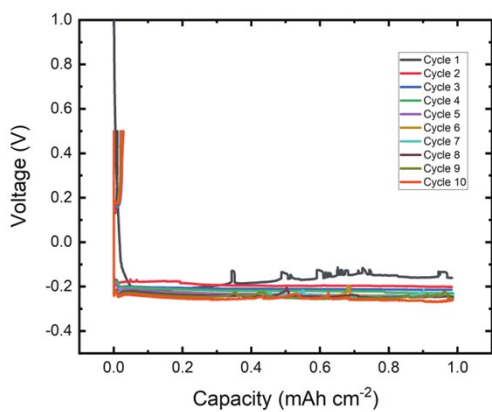


Fig. S1 (cont.)

(a) 1 M Li[FSA]-SL



(b) 1 M Li[FSA]-DMC



(c) 1 M Li[FSA]-PC

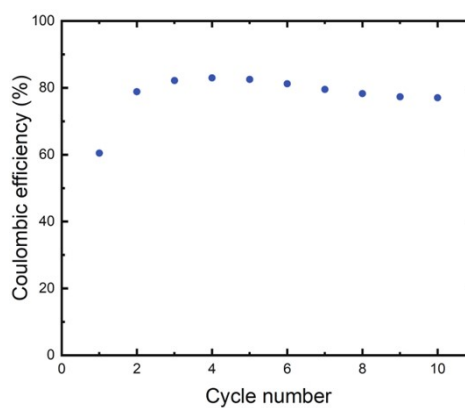
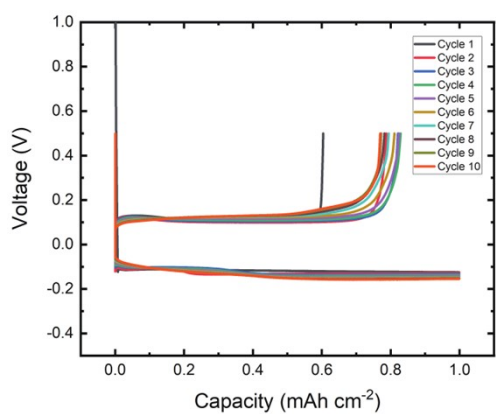
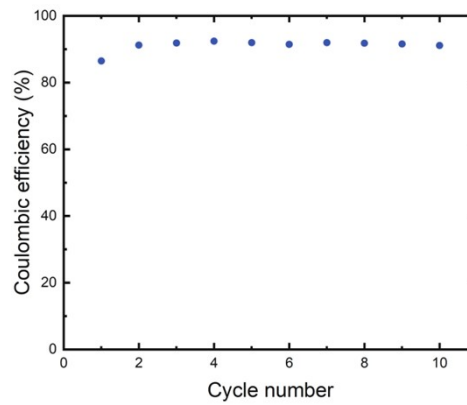
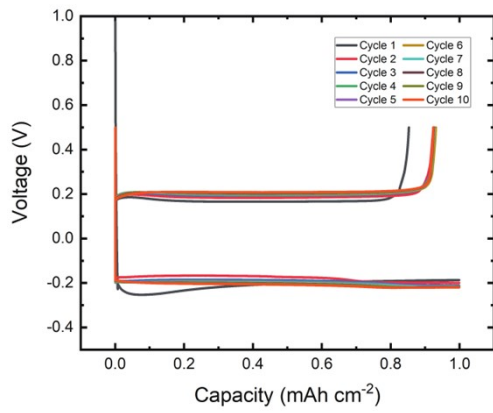
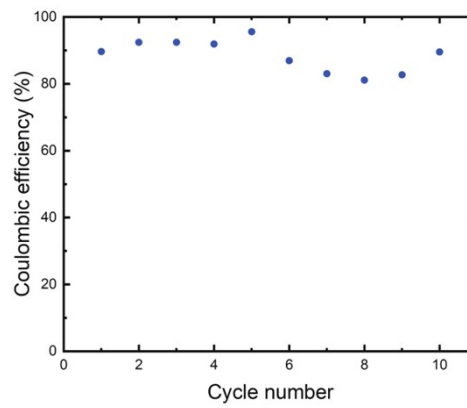
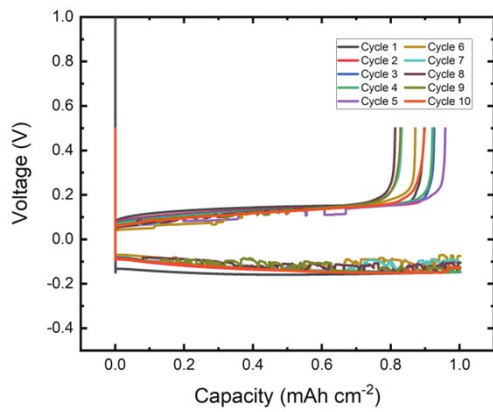


Fig. S2 Summary of the Li metal deposition/dissolution tests in the Li[FSA]-based electrolytes. (left) voltage profiles and (right) CE.

(d) 1 M Li[FSA]-PC 3 wt% FEC



(e) 4 M Li[FSA]-PC



(f) 4 M Li[FSA]-PC 3 wt% FEC

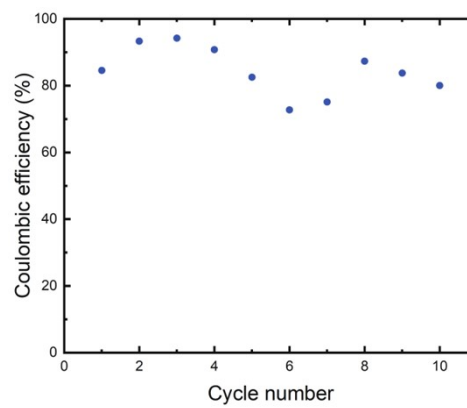
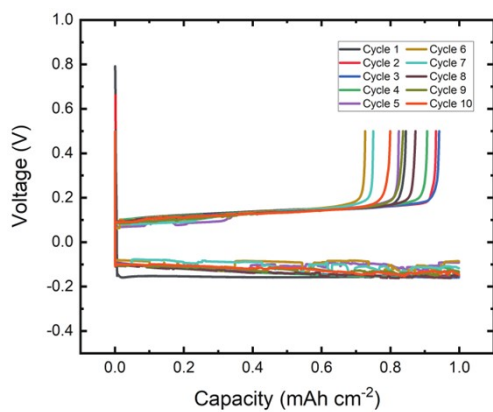
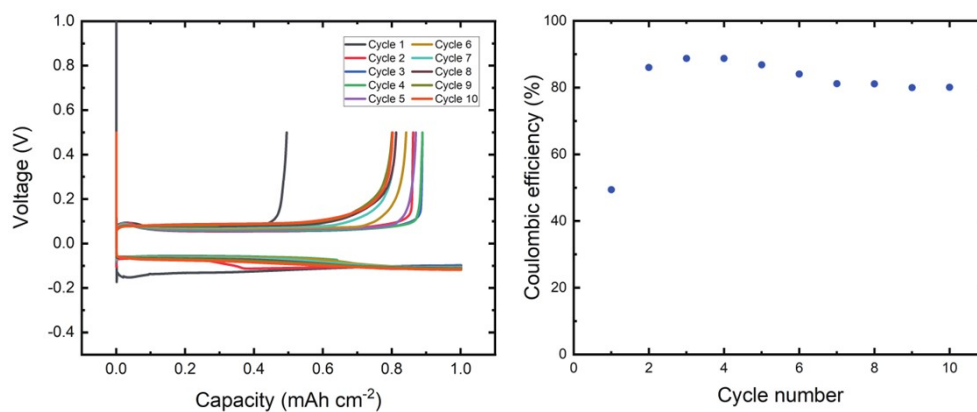
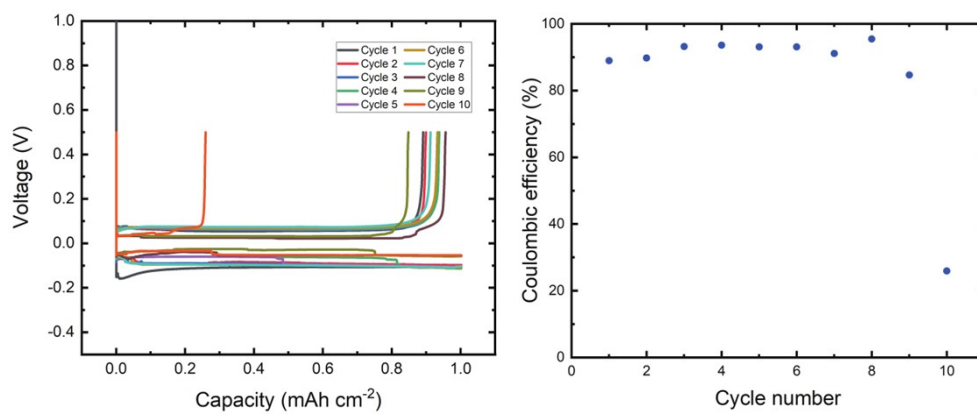


Fig. S2 (cont.)

(g) 1 M Li[FSA]-EC:DMC



(h) 1 M Li[FSA]-EC:DMC 3 wt% FEC



(i) 4 M Li[FSA]-EC:DMC

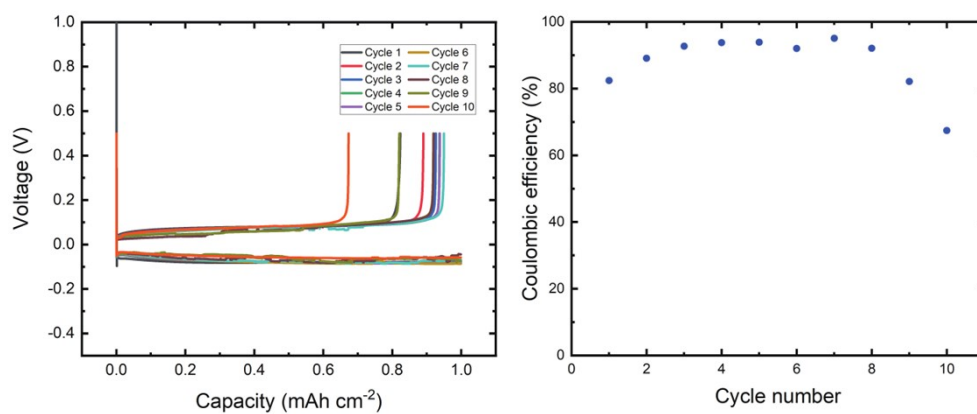
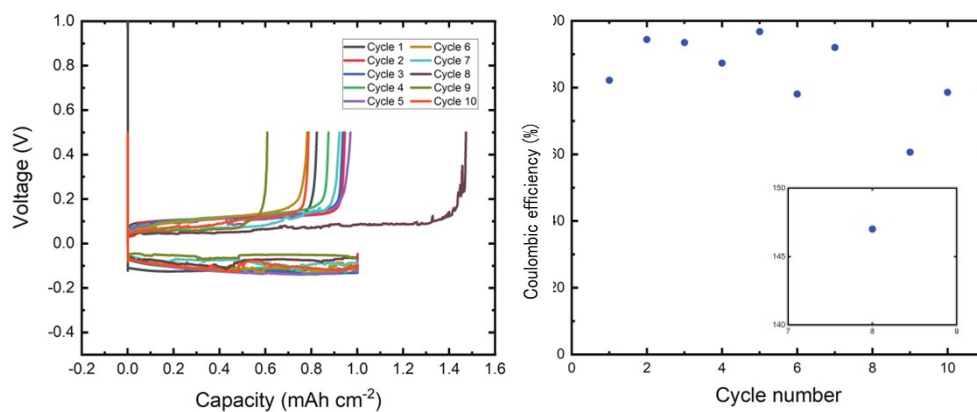
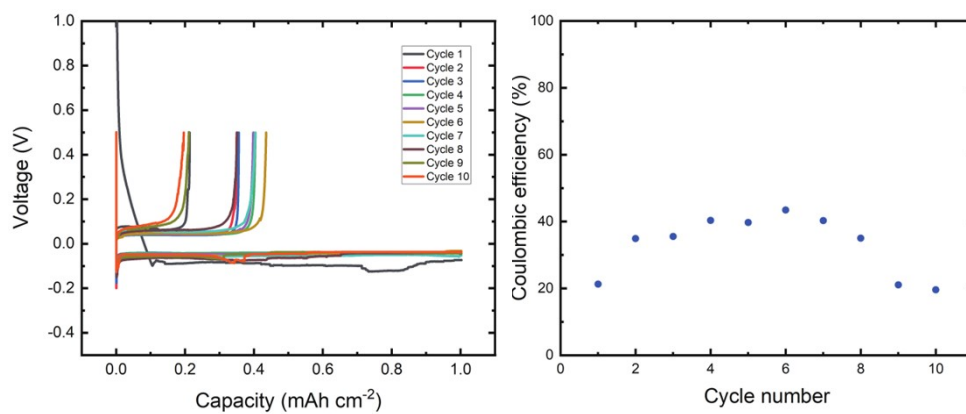


Fig. S2 (cont.)

(j) 4 M Li[FSA]-EC:DMC 3 wt% FEC



(k) 1 M Li[FSA]-DMSO



(l) 1 M Li[FSA]-DME

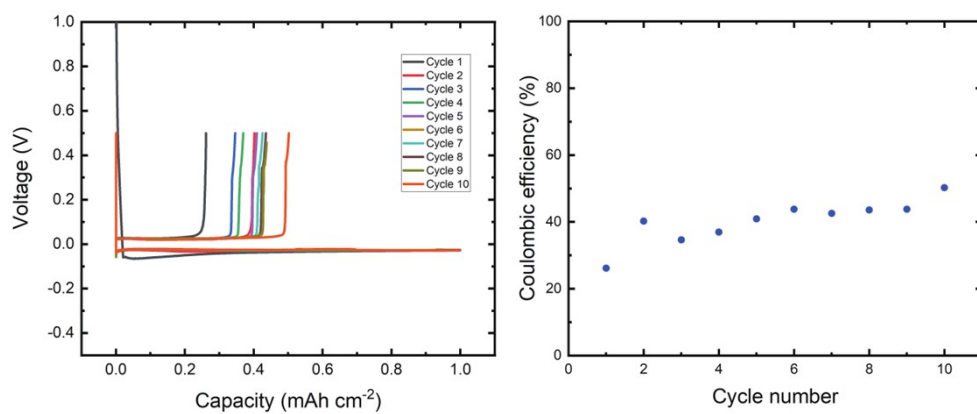
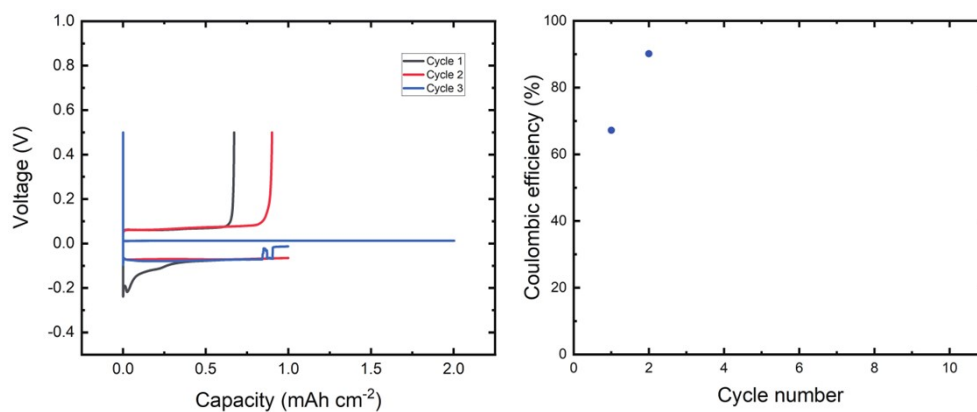
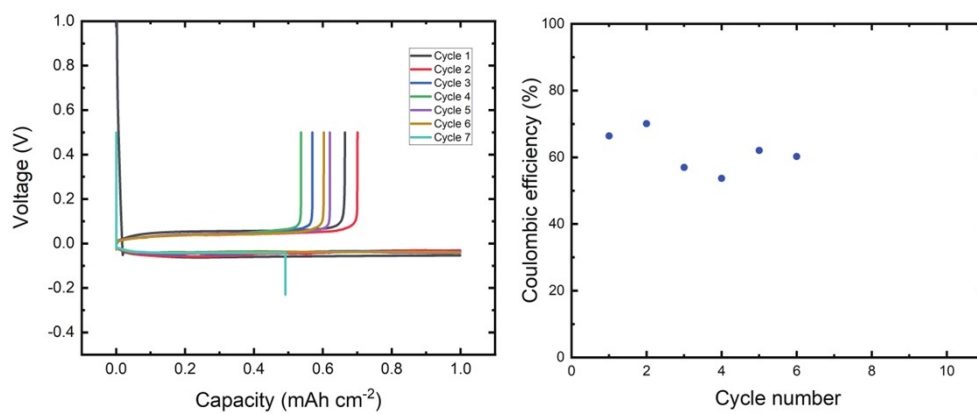


Fig. S2 (cont.)

(m) 1 M Li[FSA]-DME 3 wt% LiNO₃



(n) 4 M Li[FSA]-DME



(o) 20 mol% Li[FSA]-[C₃C₁pyrr][FSA]

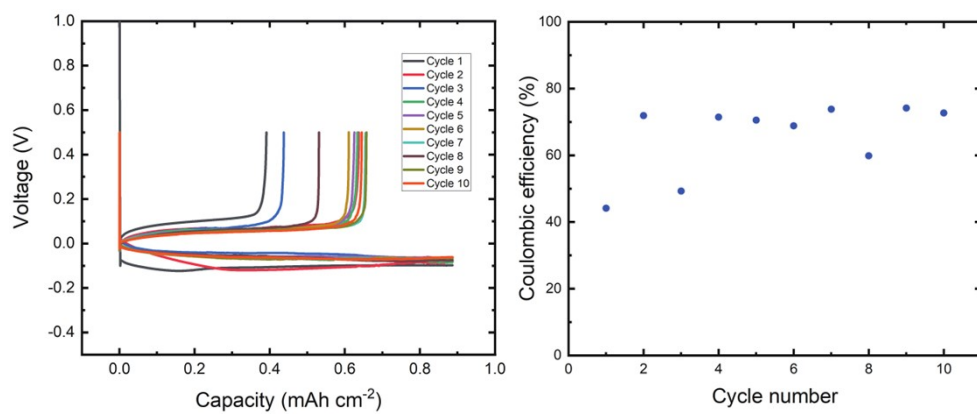
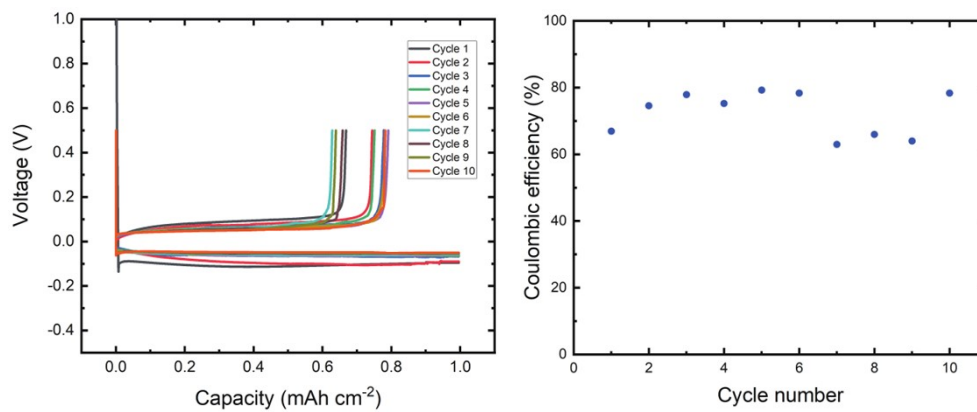
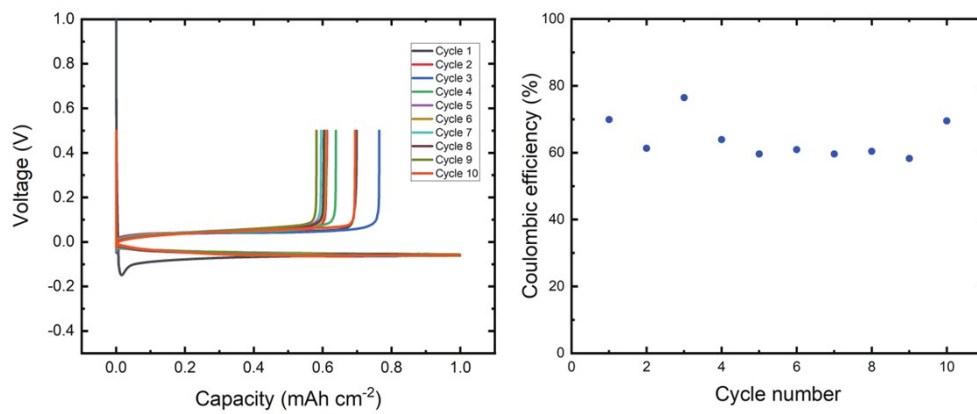


Fig. S2 (cont.)

(p) 40 mol% Li[FSA]-[C₃C₁pyrr][FSA]



(q) 20 mol% Li[FSA]-[C₂C₁im][FSA]



(r) 40 mol% Li[FSA]-[C₂C₁im][FSA]

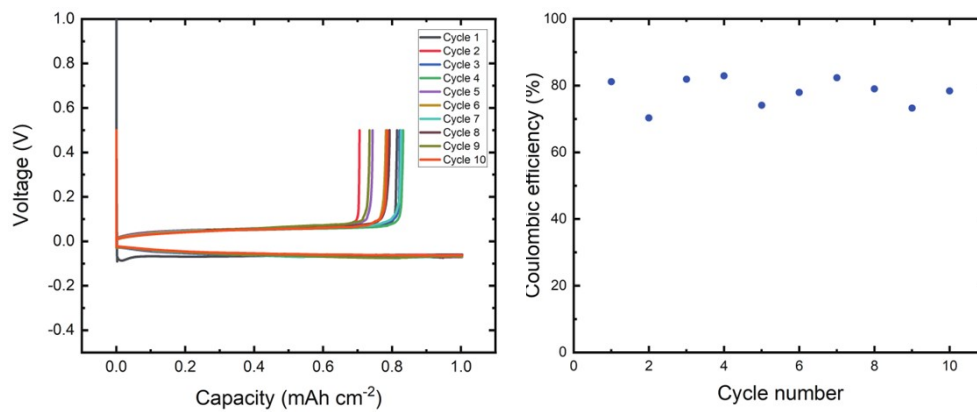
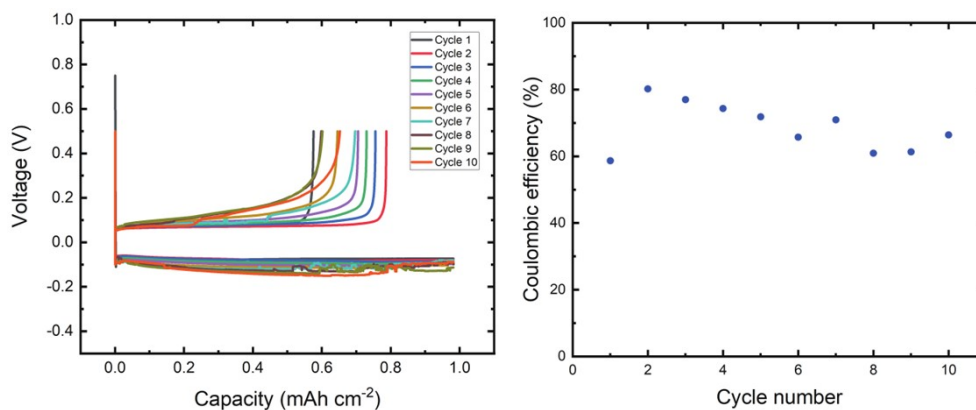
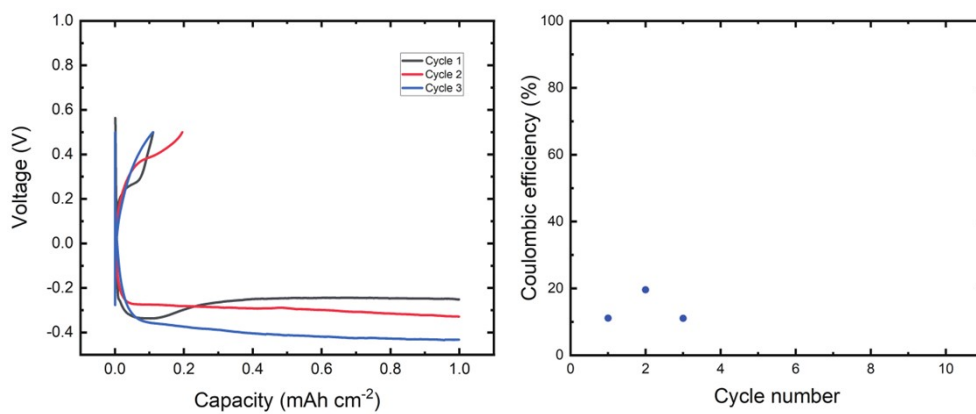


Fig. S2 (cont.)

(a) 1 M Li[TFSA]-SL



(b) 1 M Li[TFSA]-TEP



(c) 1 M Li[TFSA]-DMC

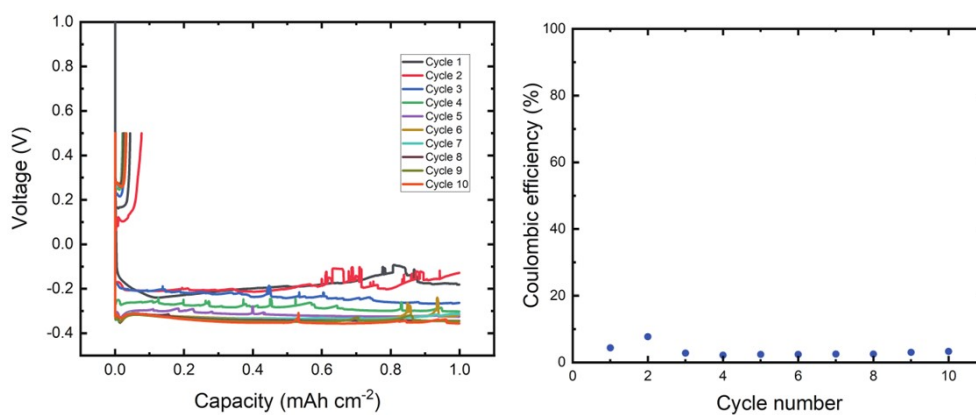
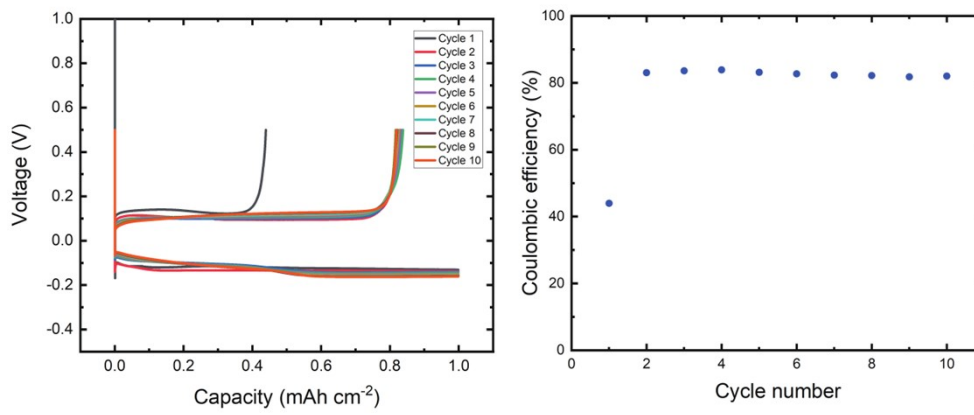
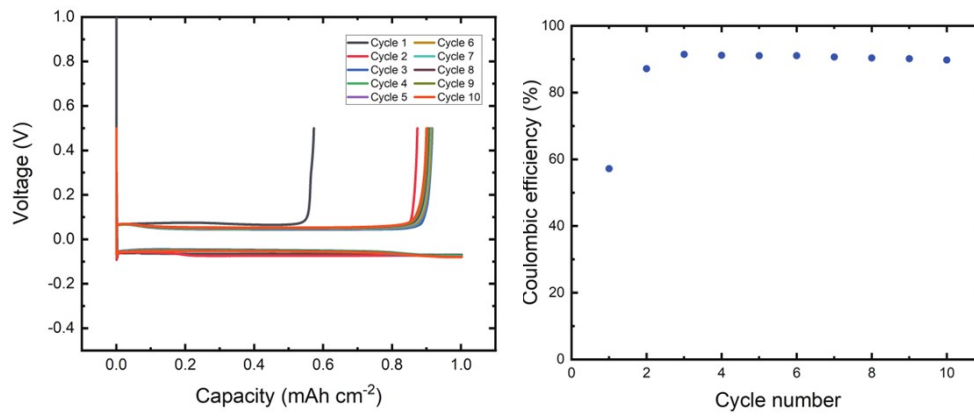


Fig. S3 Summary of the Li metal deposition/dissolution tests in the Li[TFSA]-based electrolytes. (left) voltage profiles and (right) CE.

(d) 1 M Li[TFSA]-PC



(e) 1 M Li[TFSA]-EC:DMC



(f) 1 M Li[TFSA]-EC:DMC 3 wt% FEC

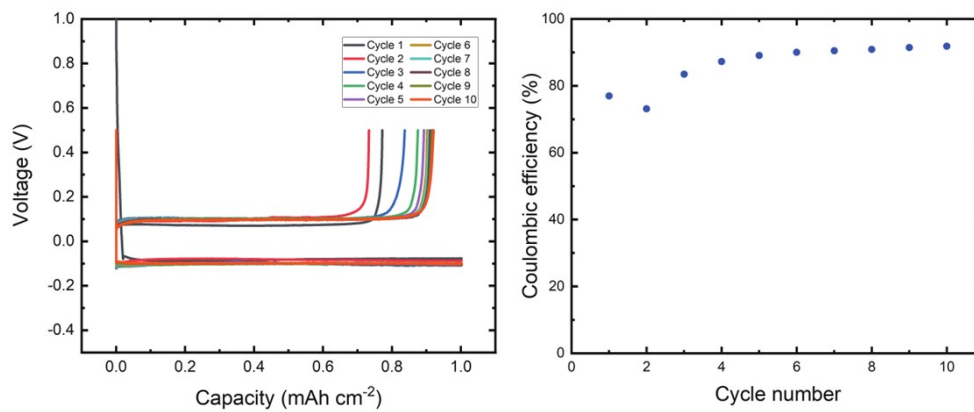
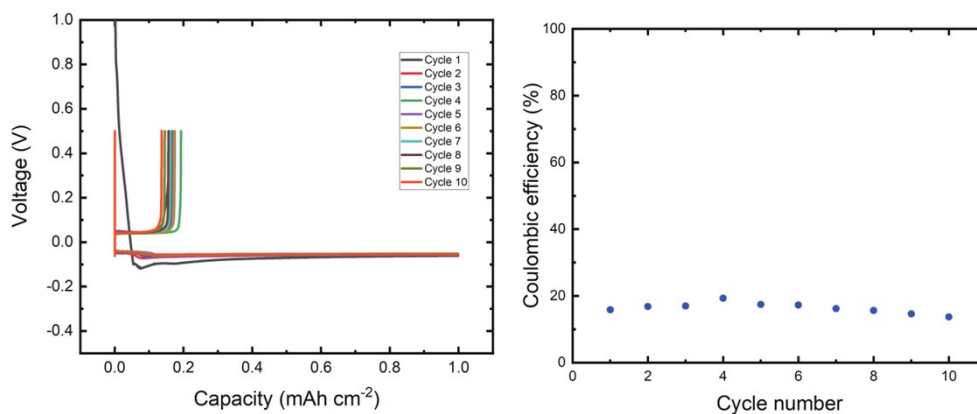
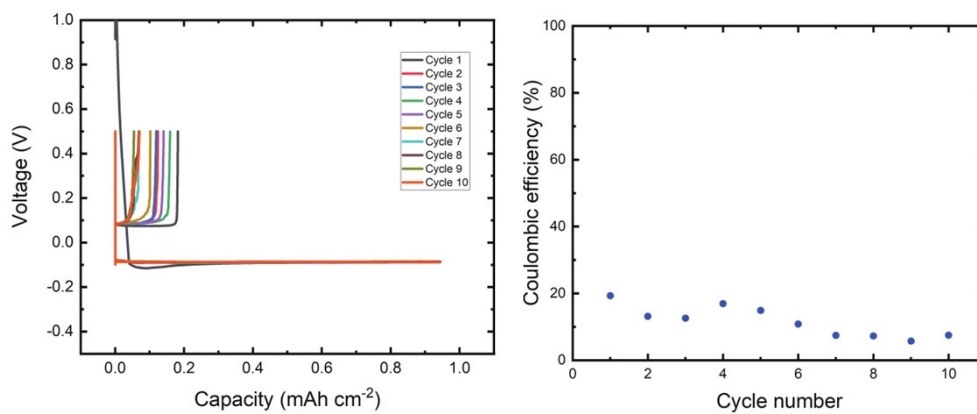


Fig.S3 (cont.)

(g) 1 M Li[TFSA]-G2



(h) 1 M Li[TFSA]-DME



(i) 1 M Li[TFSA]-DME 3 wt% LiNO₃

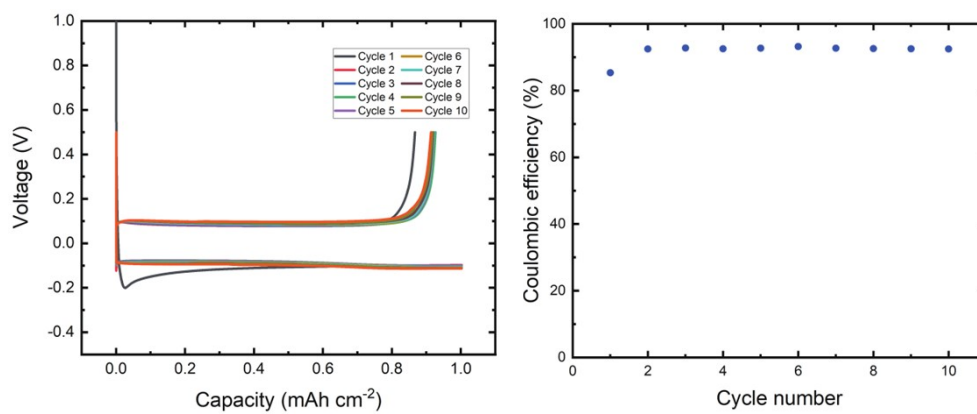
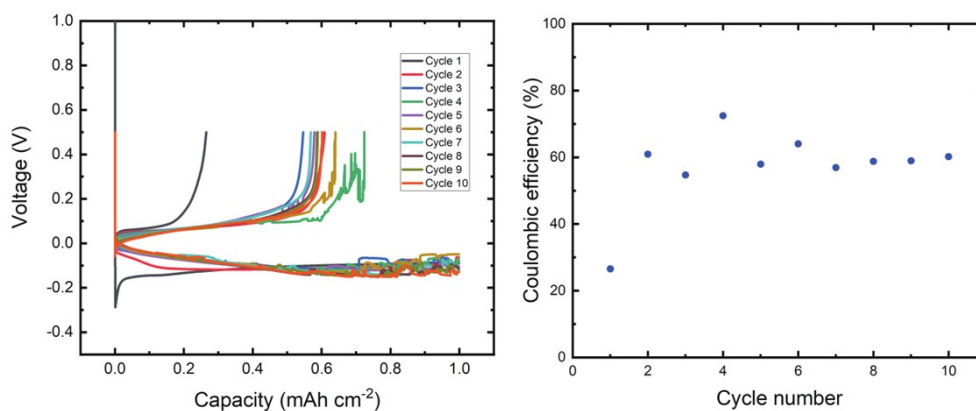
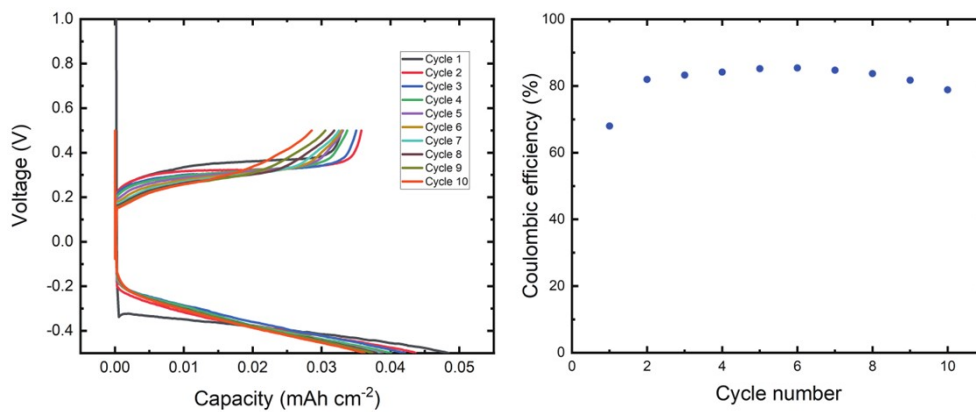


Fig. S3 (cont.)

(j) Saturated Li[TFSA]-DME



(k) 20 mol% Li[TFSA]-[C₃C₁pyrr][TFSA]



(l) 20 mol% Li[TFSA]-[C₂C₁im][TFSA]

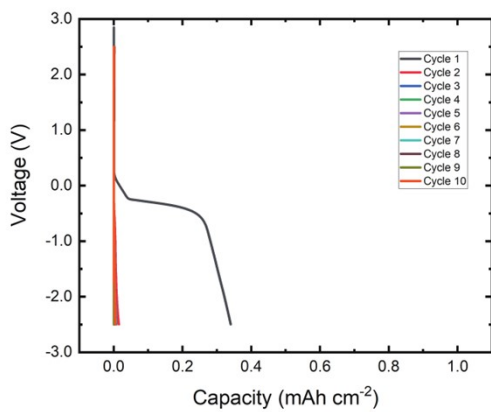


Fig. S3 (cont.)

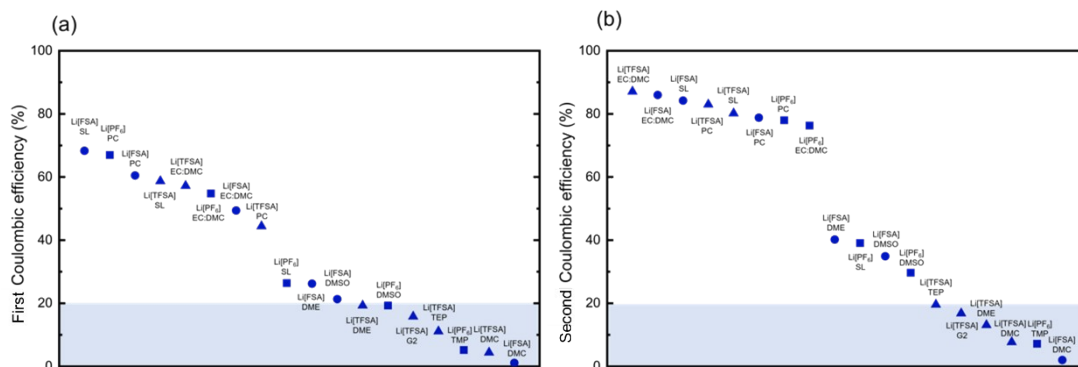


Fig. S4 CE of lithium deposition/dissolution test for 1 M electrolytes without additives in the separator-free cell (Li/Cu). (a) the first and (b) the second cycles. The colored areas indicate CE less than 20%. Square, circle, and triangle symbols indicate Li[PF₆]-, Li[FSA]- based electrolytes, triangle symbols indicate Li[TFSA] based electrolyte, Blue color indicates the concentration of 1 M electrolytes and red color does the high concentrations of 4 M, 40 mol%, or saturated electrolytes. Filled and unfilled symbols denote the absence and presence of additives, respectively.

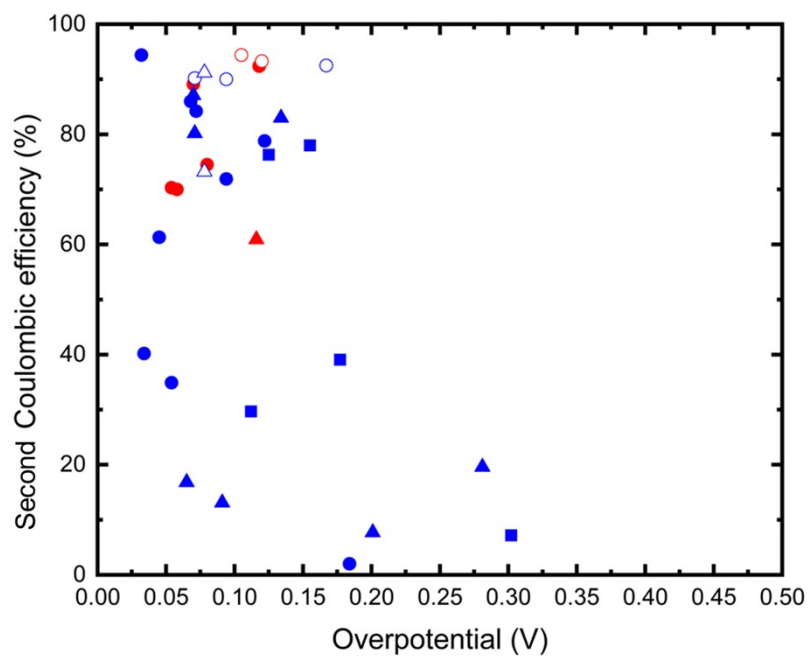


Fig. S4 Correlation plots of overpotential at 0.2 mA h cm⁻² and CE in the second cycle.

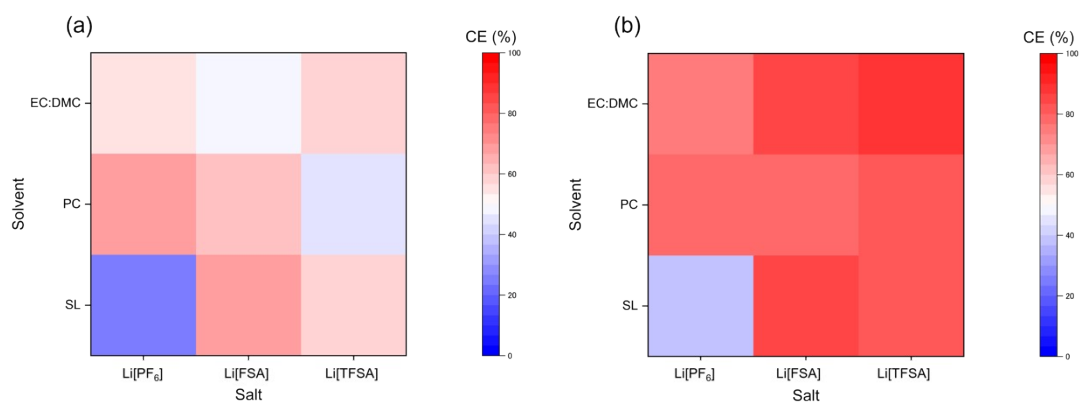


Fig. S5 Heatmaps of the CE for electrolytes using Li[PF₆], Li[FSA], Li[TFSA] as salts and SL, PC, EC:DMC as solvents in the first (a) and second (b) cycle.