

Electronic Supplementary Information

Mechanistic Insights into the Thermodynamics and Kinetics Underlying the Reductive Decomposition of Fluoroethylene and Difluoroethylene Carbonates for SEI Formation in LIBs

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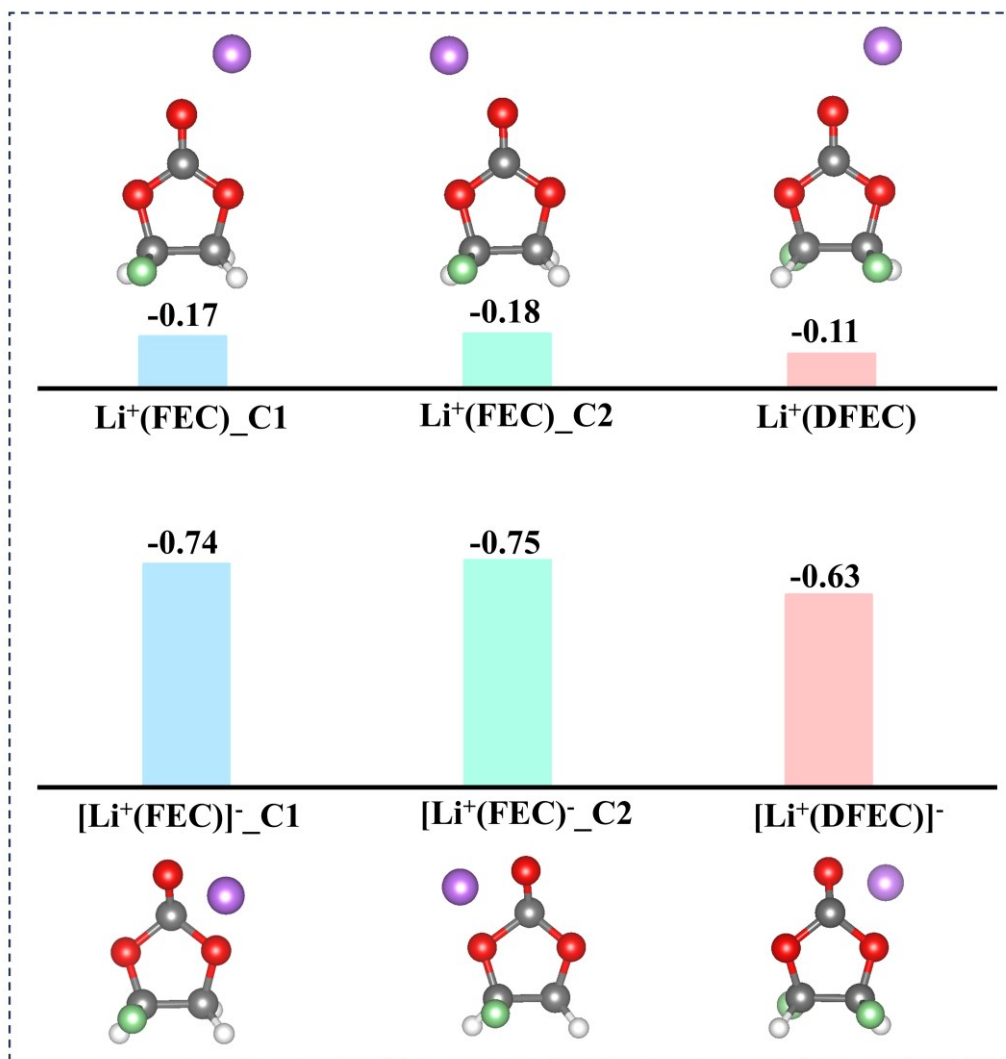


Fig. S1 Binding energies (in eV) of $\text{Li}^+(\text{FEC})$ and $\text{Li}^+(\text{DFEC})$ complexes before and after electron addition.
 Gray, red, green, white and purple spheres denote C, O, F, H and Li, respectively.

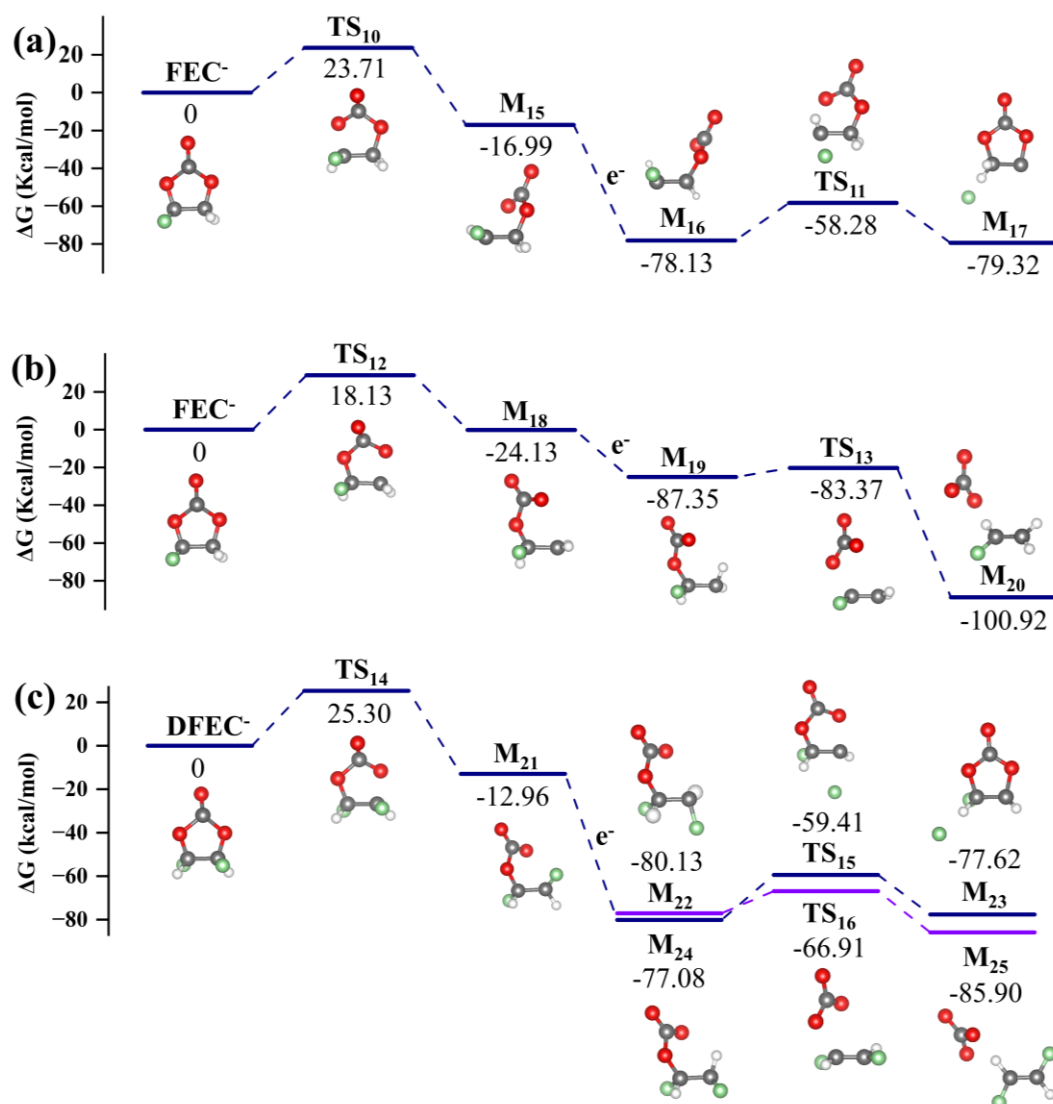


Fig. S2 Considered the two-electron reduction pathways and decomposition products of (a), (b) FEC^- and (c) DFEC^- . Gray, red, green, white and purple spheres denote C, O, F, H and Li, respectively.

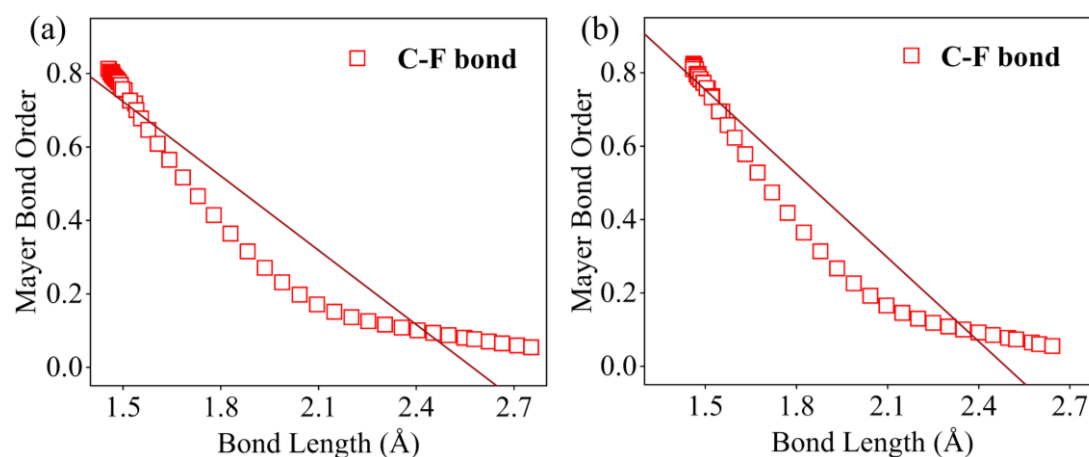


Fig. S3 Correlation between Mayer bond order (MBO) and C-F bond lengths. (a) From M_4 to M_5 in the $[\text{Li}^+(\text{FEC})]^-$ C2 reduction pathways along the IRC, and (b) M_{13} to M_{14} in $[\text{Li}^+(\text{DFEC})]^-$ reduction pathways along the IRC.

Table S1 Analysis of the number and values of imaginary frequencies (IF, in cm^{-1}) for all transition states (TSs).

Structure	IF	
	Number	Value (cm^{-1})
TS ₁	1	-1192.81
TS ₂	1	-335.03
TS ₃	1	-198.96
TS ₄	1	-141.33
TS ₅	1	-1252.90
TS ₆	1	-413.75
TS ₇	1	-228.24
TS ₈	1	-115.39
TS ₉	1	-165.56
TS ₁₀	1	-1218.99
TS ₁₁	1	-427.53
TS ₁₂	1	-1218.99
TS ₁₃	1	-254.84
TS ₁₄	1	-1275.63
TS ₁₅	1	-477.60
TS ₁₆	1	-276.20

Table S2 Comparison of key parameters in the $[\text{Li}^+(\text{DFEC})]^-$ and $[\text{Li}^+(\text{DFEC})]^-$ reaction pathways.

Comparison Parameter	$[\text{Li}^+(\text{DFEC})]^-$	$[\text{Li}^+(\text{DFEC})]^-$	
		single-defluorination	double-defluorination
LiF formation quantity (mol)	LiF	LiF	2LiF
ΔG^\ddagger value (in kcal/mol)	1.82	3.35	10.49
ΔG^\ddagger difference ratios	1 (vs $[\text{Li}^+(\text{DFEC})]^-$)	1.84 (vs $[\text{Li}^+(\text{DFEC})]^-$)	5.76 (vs $[\text{Li}^+(\text{DFEC})]^-$) 3.13 (vs $[\text{Li}^+(\text{DFEC})]^-$ single-defluorination)