

## Electronic Supplementary Information

### Liquid electrolyte chemistries for solid electrolyte interphase construction on silicon and lithium-metal anodes

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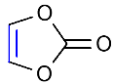
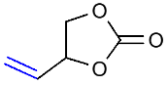
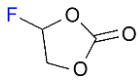
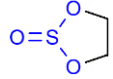
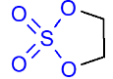


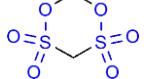
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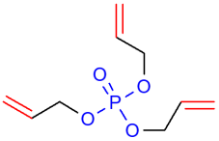
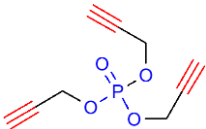
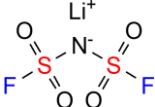
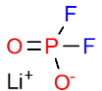
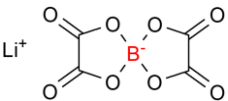
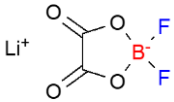
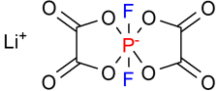
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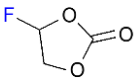
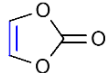

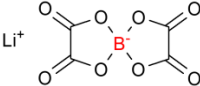
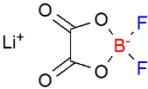
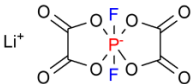
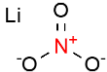
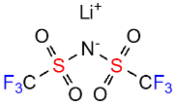
<sup>\*</sup>Corresponding author. Email: nschoi@kaist.ac.kr

**Table S1.** Commercialized SEI forming electrolyte additives for lithium-ion batteries

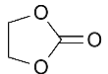
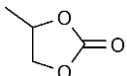
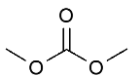
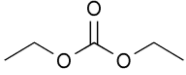
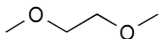

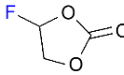
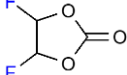
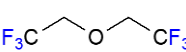
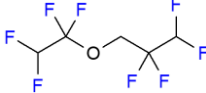
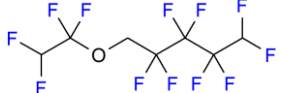
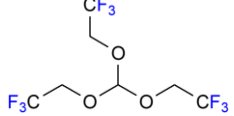
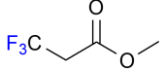
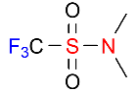
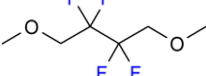
Additive compound	Patent	Company	Priority
 Vinylene carbonate (VC)	FR2719161B1 <sup>1</sup>	SAFT	1994
 Vinylethylene carbonate (VEC)	JP4489207B2 <sup>2</sup>	Mitsui Chemicals	1998
 Fluoroethylene carbonate (FEC)	US6506524B1 <sup>3</sup>	NRCC	1996
 Ethylene sulfite (ES)	JP3546566B2 <sup>4</sup>	Sony	1995
 Ethylene sulfate (DTD)	JP3760540B2 <sup>5</sup>	Mitsubishi Chemical	1996
 1,3-Propane sultone (PS)	JP3978881B2 <sup>6</sup>	Ube Industries	1997
 1,3-Propene 1,3-sultone (PES)	JP4190162B2 <sup>7</sup>	Mitsui Chemicals	2001
 Methylene methanedisulfonate (MMDS)	JP4033074B2 <sup>8</sup>	NEC	2002

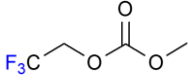
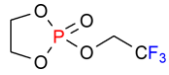
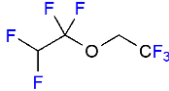
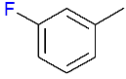
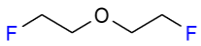
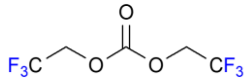
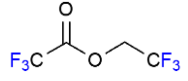
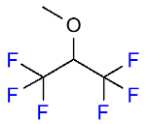
 <p>Triallyl phosphate (TALP)</p>	US6919141B2 <sup>9</sup>	Wilson Greatbatch	2003
 <p>Tripropargyl phosphate (TPGP)</p>	US6919141B2 <sup>9</sup>	Wilson Greatbatch	2003
 <p>Lithium bis(fluorosulfonyl)imide (LiFSI)</p>	EP0699349B1 <sup>10</sup>	CNRS, Hydro-Québec	1994
 <p>Lithium difluorophosphate (LiDFP)</p>	JP3439085B2 <sup>11</sup>	Sanyo Electric	1997
 <p>Lithium bis(oxalato) borate (LiBOB)</p>	DE19829030C1 <sup>12</sup>	Chemetall	1998
 <p>Lithium difluoro(oxalato)borate (LiFOB)</p>	JP3722685B2 <sup>13</sup>	Central Glass	2000
 <p>Lithium difluorobis(oxalato)phosphate (LiDFBOP)</p>	JP3722685B2 <sup>13</sup>	Central Glass	2000

**Table S2.** Properties of electrolyte additives used in lithium batteries containing silicon and lithium metal as anodes

Name	Chemical structure	Density (g mL <sup>-1</sup> )	Molecular weight (g mol <sup>-1</sup> )	Melting point (°C)	Boiling point (°C)
FEC		1.50	106.05	18–23	210–212
VC		1.35	86.05	19–22	162
LiDFP		N/A	107.91	>300	decomposes
LiBOB		N/A	193.79	>300	decomposes
LiFOB		N/A	143.77	265–271	decomposes
LiDFBOP		N/A	251.95	255	decomposes
LiNO <sub>3</sub>		2.38	68.95	255	decomposes
LiFSI		1.05	187.06	126	decomposes

**Table S3.** Properties of nonfluorinated and fluorinated solvents used in lithium batteries containing silicon and lithium metal as anodes

	Name	Chemical structure	Density (g mL <sup>-1</sup> )	Molecular weight (g mol <sup>-1</sup> )	Boiling point (°C)
Nonfluorinated solvents	EC		1.321	88.06	243–244
	PC		1.204	102.09	240–242
	DMC		1.069	90.08	90
	DEC		0.975	118.13	126–128
	DME		0.867	90.12	84–85
	DOL		1.07	74.08	74–76
Fluorinated solvents	FEC		1.50	106.05	210–212
	DFEC		1.52	124.04	233.8
	BTFE		1.404	180.06	62–64
	TTE		1.54	232.07	92
	TFOFE (OTE)		1.66	332.09	133
	TFEO		1.457	310.12	144–146
	MTFP		1.29	142.08	96
	DMTMSA		1.443	177.16	116.9
	FDMB		1.21	190.14	154

TFEMC		1.34	158.08	90
TFEP		1.52	206.06	160
TFETFE		1.49	200.06	56
mFT		0.991	110.13	115
BFE		0.98	110.10	128
DFDEC		1.51	226.07	118
TFE		1.464	196.05	55
HFPM		1.38	182.07	50

**Section S1.** On lithium dendrite suppression ability<sup>14</sup>

During lithium plating, lithium dendrites need to penetrate the passivation layer along grain boundaries. Based on Griffith's energy-based analysis, interfacial energy ( $E_{\text{interface}}$ ) increases because of the construction of a new interface at Li/SEI, while strain energy ( $E_{\text{strain}}$ ) is released upon the growth of lithium dendrites. Therefore, the total energy ( $E_{\text{total}}$ ) for lithium dendrite growth (Eq. S1) can be expressed as the sum of  $E_{\text{interface}}$  and  $E_{\text{strain}}$ :

$$E_{\text{total}} = E_{\text{interface}} + E_{\text{strain}}. \quad (\text{S1})$$

$E_{\text{interface}}$  can be expressed as follows:

$$E_{\text{interface}} = 2\gamma LB, \quad (\text{S2})$$

where  $\gamma$  is the interfacial energy required to create a new Li/SEI interface per unit area,  $L$  is the interface length, and  $B$  is the interface thickness.

$E_{\text{strain}}$  can be expressed as follows:

$$E_{\text{strain}} = \frac{\sigma^2}{2E}V - \frac{\sigma^2}{2E}B\pi L^2, \quad (\text{S3})$$

where  $\sigma$  is the stress at the tip of the crack or grain boundary,  $E$  is the bulk modulus, and  $V$  is the volume.

Therefore, Eq. S1 can be rewritten as

$$E_{\text{total}} = 2\gamma LB + \frac{\sigma^2}{2E}V - \frac{\sigma^2}{2E}B\pi L^2. \quad (\text{S4})$$

$E_{\text{total}}$  increases with the increasing length of lithium dendrites, reaching a maximum at a critical dendrite length ( $L_c$ ) and subsequently decreasing. Therefore,  $L_c$  is the value at which the derivative of  $E_{\text{total}}$  with respect to  $L$  becomes zero:

$$\frac{dE_{total}}{dL} = 2\gamma B - \frac{\sigma^2}{E} B\pi L = 0. \quad (S5)$$

The above equation implies

$$L_c = \frac{2\gamma E}{\pi\sigma^2}. \quad (S6)$$

The lithium dendrite suppression abilities listed in Table 1 are expressed as the products of  $\gamma$  and  $E$  and are therefore positively correlated with  $L_c$ , which indicates a delay of lithium dendrite growth according to SEI properties.

### Supplementary references

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