

## Supporting Information

### Insight into the capacity fading of layered lithium-rich oxide and its suppression via film-forming electrolyte additive

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#### Theoretical calculations

Density functional theory (DFT) calculations were performed using the Gaussian 09 package <sup>1</sup>. The equilibrium structures were optimized at the B3LYP/6-311++G(d) level <sup>2,3</sup>. To investigate the effects of solvents, the equilibrium state structures are optimized by using the polarized continuum model (PCM), with a dielectric constant of 20.5 (acetone). To confirm that each optimized structure corresponded to a stationary one, frequency calculations were performed at the same level. Atomic charge distributions were obtained by the natural bond orbital (NBO) theory.

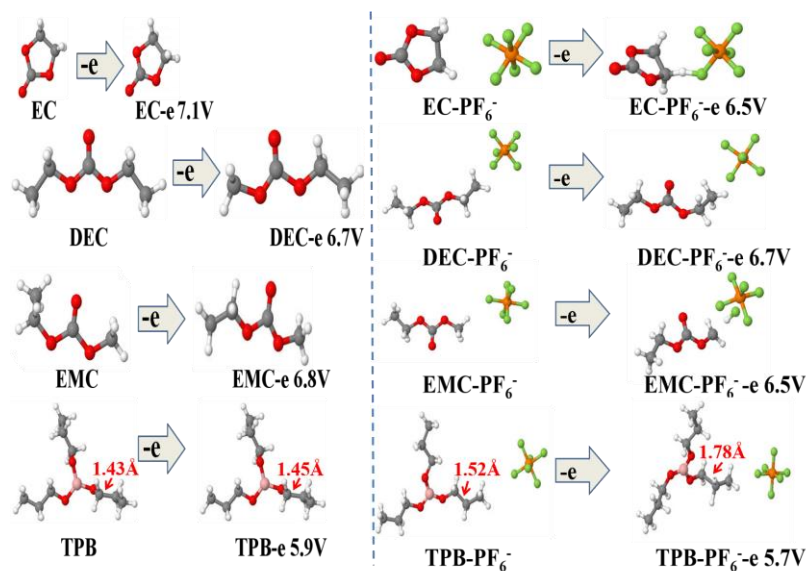
The oxidation activity of TPB and STD electrolyte was investigated via DFT calculation, as

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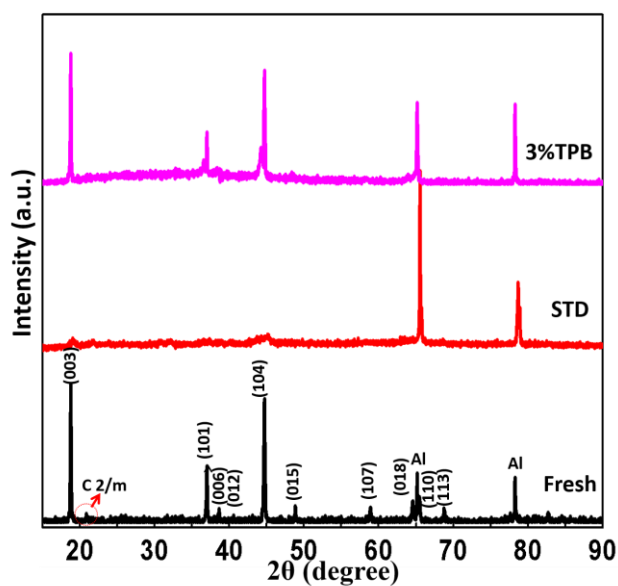
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shown in Fig. S1. A film-forming electrolyte additive should have higher oxidation activity than the STD electrolyte, and its decomposition products should help to build a passivating layer on the electrode surface to prevent the subsequent oxidative reaction of STD electrolyte. In our previous works, we demonstrated that the existence of lithium salt anion lowers the oxidation activity of electrolytes<sup>4</sup>. It can be seen from Fig.S1 that even taking the influence of  $\text{PF}_6^-$  into account, the calculated oxidation potential of TPB is still lower than EC, DEC and EMC, which means that TPB would oxidize preferentially to STD electrolyte during the initial cycling. When TPB- $\text{PF}_6^-$  losing one electron (oxidation reaction), the length of C-C bond that is close to B-O bond increases from 1.52 Å to 1.78 Å. This suggests that a C-C bond breakage reaction of TPB after oxidation may be expected, generating  $(\text{C}_3\text{H}_7\text{O})_2(\text{CH}_3\text{O})\text{B}$  cation and  $\text{C}_2\text{H}_4$  radical. The  $(\text{C}_3\text{H}_7\text{O})_2(\text{CH}_3\text{O})\text{B}$  cation and  $\text{C}_2\text{H}_4$  radical may further react with the interfacial negatively charged O and radicals of LLO, respectively, forming borate and oligomer deposited on the LLO surface.



**Fig. S1** Optimized structures (in Å) and calculated oxidation potential (in V vs.  $\text{Li}/\text{Li}^+$ ) of EC, DEC, EMC and TPB solvent molecular and anion-solvent clusters before and after oxidation.



**Fig. S2.** XRD patterns of fresh LLO and LLO in the STD and 3%TPB-containing electrolytes after 250 cycles at 0.5C rate.

**Table S1** Comparison of cycling performance of LLO in this work with other reported literatures.

LLO	Electrolyte additive	Discharge current density mA g <sup>-1</sup>	Cutoff voltage V	Initial discharge capacity mA g <sup>-1</sup>	Capacity retention % (cycles)
Li <sub>1.17</sub> Ni <sub>0.17</sub> Mn <sub>0.5</sub> Co <sub>1.17</sub> O <sub>2</sub>	Tris(trimethylsilyl) phosphite <sup>5</sup>	100	2.0-4.6	225	77.1 (100)
Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	Trimethyl phosphite <sup>6</sup>	100	2.5-4.8	230	81.3 (100)
Li <sub>1.2</sub> Mn <sub>0.56</sub> Ni <sub>0.16</sub> Co <sub>0.08</sub> O <sub>2</sub>	(Trimethylsilyl)methanesulfonate <sup>7</sup>	125	2.0-4.6	230	77.0 (100)
Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	Tripropyl borate (This work)	125	2.0-4.8	227	88.0 (100)
					78.0 (250)

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