

## Supplementary Material: Enhancing cycle life of Nickel-rich $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ via a Highly Fluorinated Electrolyte Additive – Pentafluoropyridine

### MAIN TEXT

HOMO and LUMO energies of EC, DEC, and PFP with and without solvation with  $\text{Li}^+$ , oxidation potential of EC, DEC, and PFP with and without solvation with  $\text{Li}^+$ , dQ/dV curves of Si/C anode with different electrolytes, initial charge/discharge curves NCM90 with different electrolytes, Coulombic efficiency of NCM90||Li cells with different electrolytes, cycling performance of NCM90||Li cells at cut-off voltage 4.4 V and 4.5 V, dQ/dV curves of NCM90 electrodes with different electrolytes, Cycle performance and rate capability of P-NCM92||Li cells with different electrolytes, XPS (P 2p spectra) of NCM90 electrodes after 3 formation cycles, Li||Cu cells cycling data, cycling performance of NCM90||Li cell with high loading.



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30 **Supplementary Table 1. HOMO and LUMO energies of EC, DEC and PFP**

<b>Solvent/Additive</b>	<b>EC</b>	<b>DEC</b>	<b>PFP</b>
HOMO (eV)			
Without solvation with Li	-8.43	-8.09	-7.70
LUMO (eV)			
Without solvation with Li	-0.09	-0.12	-0.06
HOMO(eV)			
Solvation with Li	-9.17	-8.89	-7.96
LUMO(eV)			
Solvation with Li	-0.66	-0.59	-1.91

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32 **Supplementary Table 2. Theoretically calculated oxidation potentials of EC, DEC**33 **and PFP**

<b>Solvent/Additive</b>	<b>EC</b>	<b>DEC</b>	<b>PFP</b>
Potential (V vs. Li/Li <sup>+</sup> )			
Without solvation with Li	6.64	6.42	5.93
Potential (V vs. Li/Li <sup>+</sup> )			
Solvation with Li	7.17	6.97	6.10

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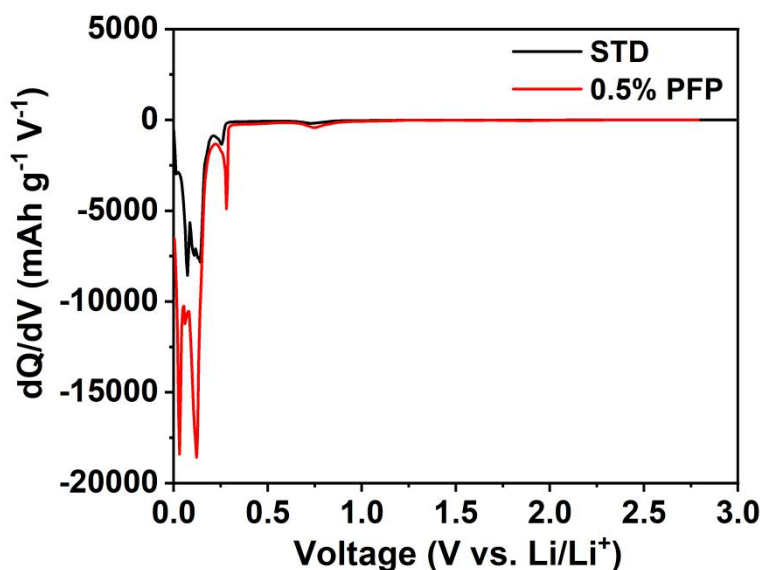
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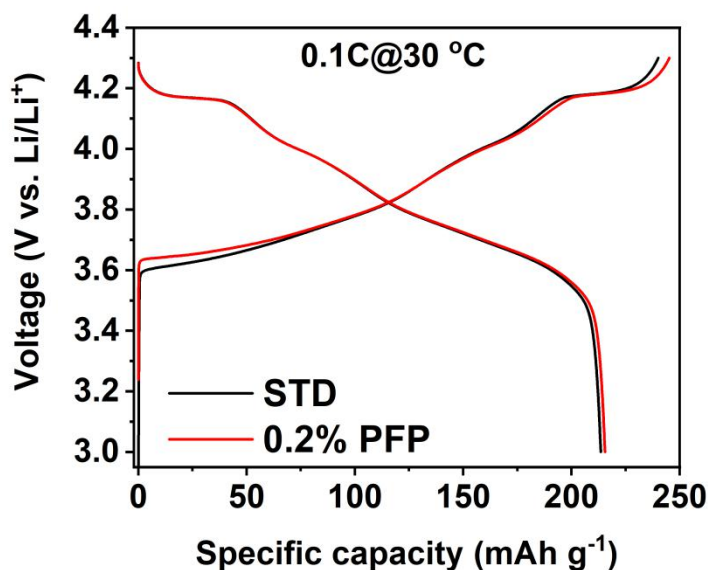
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44 **Supplementary Figure 1.** The initial dQ/dV curves of Si/C electrode with STD and  
 45 PFP-containing electrolytes at 0.1C (1C = 800 mA g<sup>-1</sup>). Si/C anode electrodes were  
 46 prepared by casting a slurry of Si/C material, acetylene black and alginate binder with a  
 47 mass ratio of 8:1:1 utilizing deionized water as solvent, on a Cu foil current collector  
 48 with active material loading of ca. 0.5 mg cm<sup>-2</sup>.

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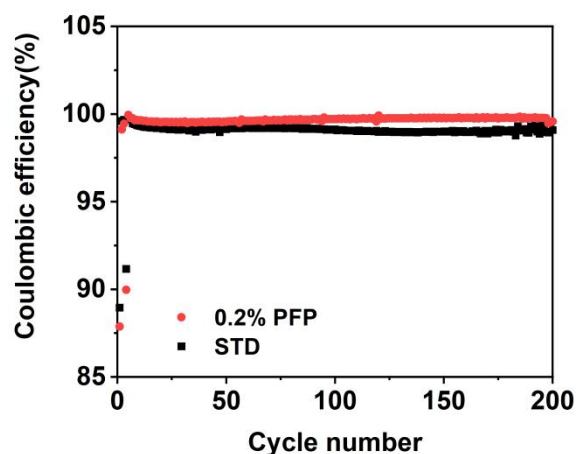


50 **Supplementary Figure 2.** Initial charge/discharge curves of NCM90 electrodes with  
 51 STD and 0.2% PFP-containing electrolytes in the voltage range of 3.0~4.3 V at 30 °C.

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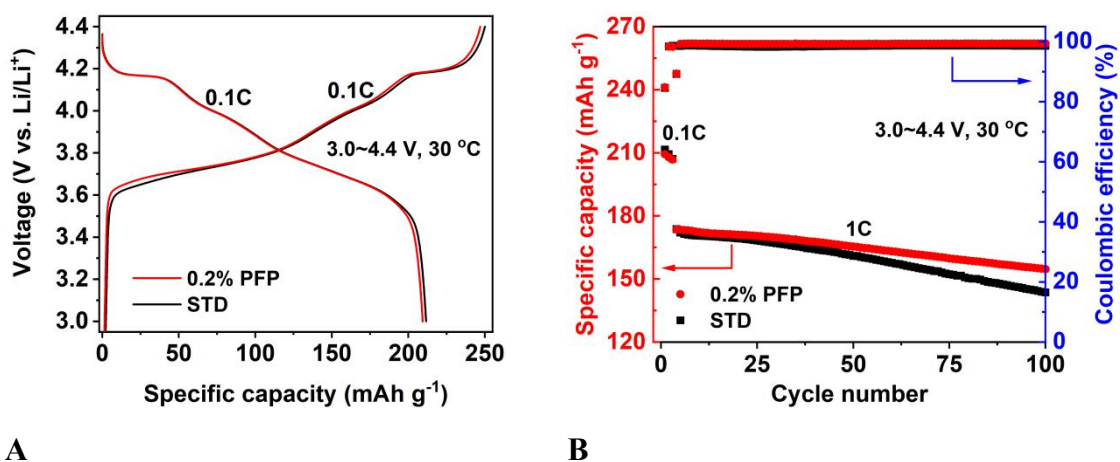
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55 **Supplementary Figure 3.** Coulombic efficiency of NCM90||Li cells with STD and  
 56 0.2% PFP containing electrolytes in the voltage range of 3.0~4.3 V at 30 °C.

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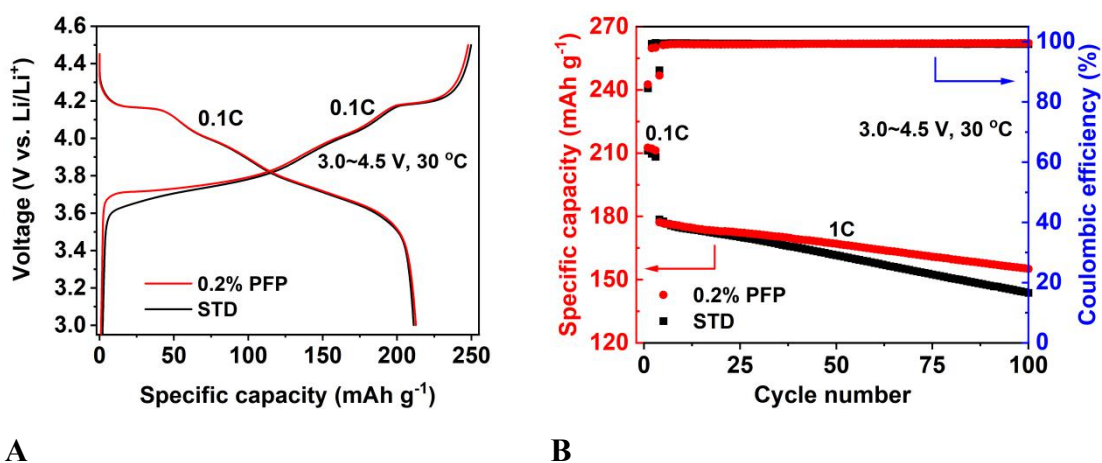
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60 **Supplementary Figure 4.** A: Initial charge/discharge curves at 0.1C; B: Cycling  
 61 performance of NCM90||Li cells with STD and 0.2% PFP-containing electrolytes at  
 62 charge cut-off 4.4 V at 30 °C. The NCM90 electrode is consisted of 90% active  
 63 materials, 5% acetylene black as conductive agent, and 5% poly (vinylidene fluoride)  
 64 as binder.

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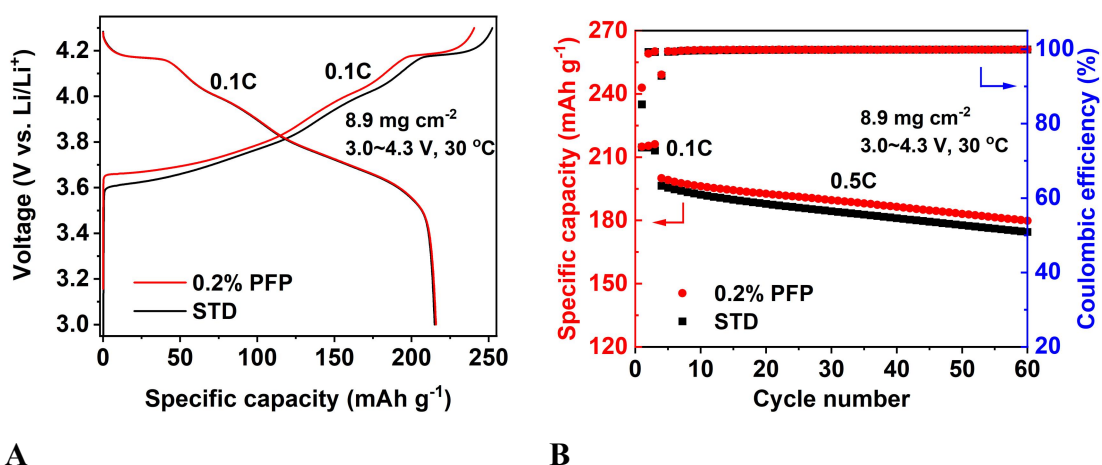
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71 **Supplementary Figure 5.** A: Initial charge/discharge curves at 0.1C; B: Cycling  
 72 performance of NCM90||Li cells with STD and 0.2% PFP-containing electrolytes at  
 73 charge cut-off 4.5 V at 30 °C. The NCM90 electrode is consisted of 90% active  
 74 materials, 5% acetylene black as conductive agent, and 5% poly (vinylidene fluoride)  
 75 as binder.

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79 **Supplementary Figure 6.** A: Initial charge/discharge curves at 0.1C; B: Cycling  
 80 performance of NCM90 with high active material loading (8.9 mg cm<sup>-2</sup>) in the voltage  
 81 range of 3.0~4.3 V at 30 oC.

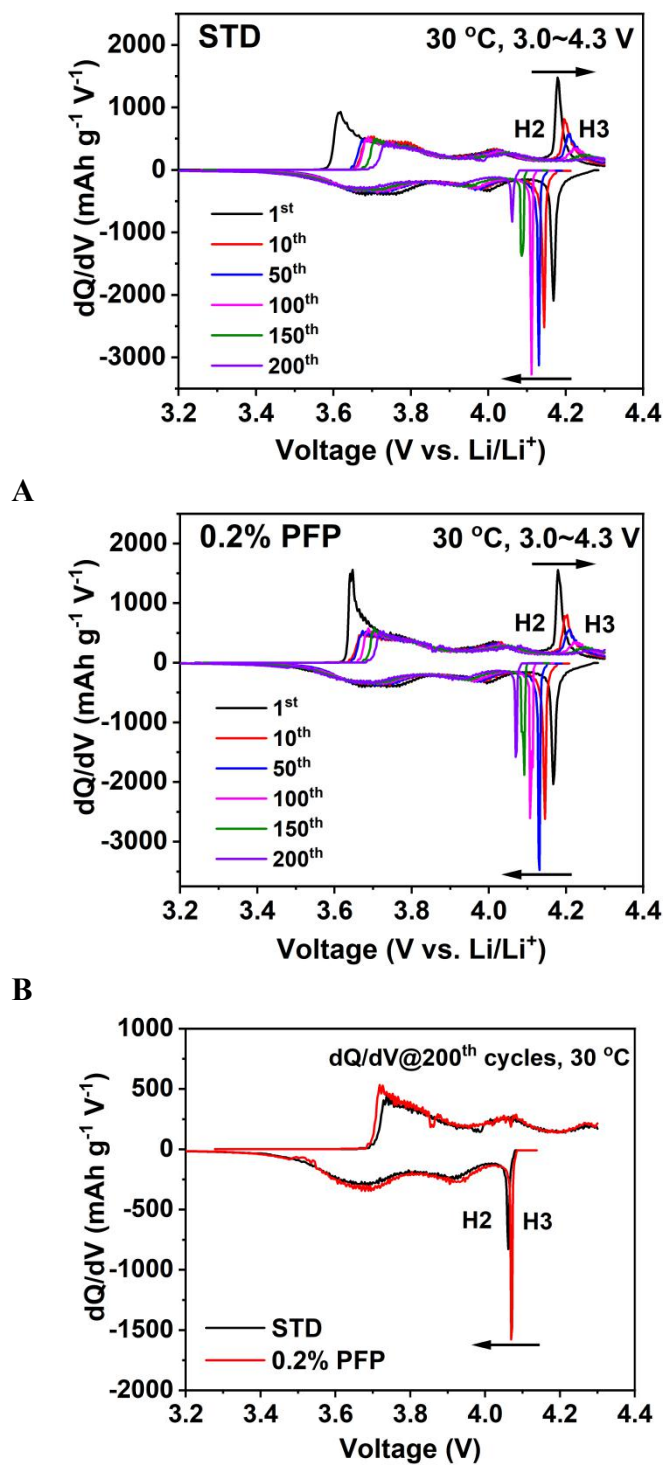
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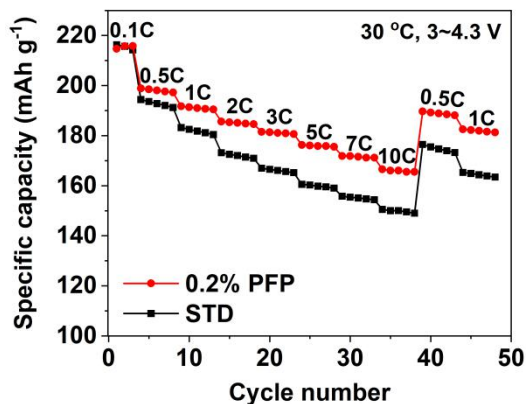
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87 **Supplementary Figure 7.** A, B: The dQ/dV curves of NCM90||Li cells at 30 °C in the  
 88 voltage range of 3.0~4.3 V with (A) STD and (B) 0.2% PFP-containing electrolyte  
 89 during 200 cycles; C: Comparison of dQ/dV for NCM90||Li cells with and without PFP

90 additive at 30 °C at 200 cycles.

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92 **Supplementary Figure 8.** Rate performance of P-NCM92||Li cells with STD and 0.2%  
93 PFP-containing electrolytes in the voltage range of 3.0~4.3 V at 30 °C, respectively.  
94 The P-NCM92 electrode is consisted of 80% active materials, 10% acetylene black as  
95 conductive agent, and 10% poly (vinylidene fluoride) as binder.

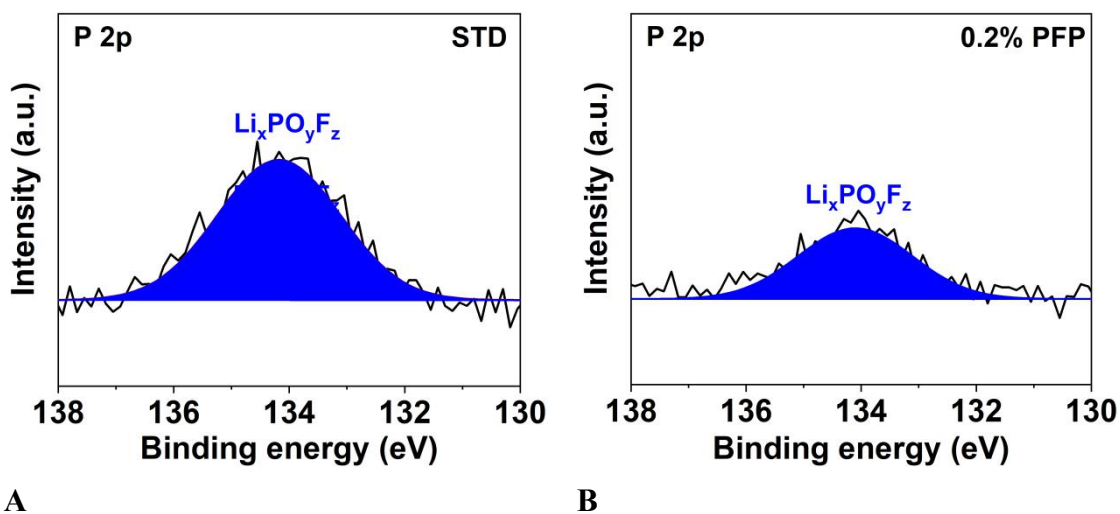
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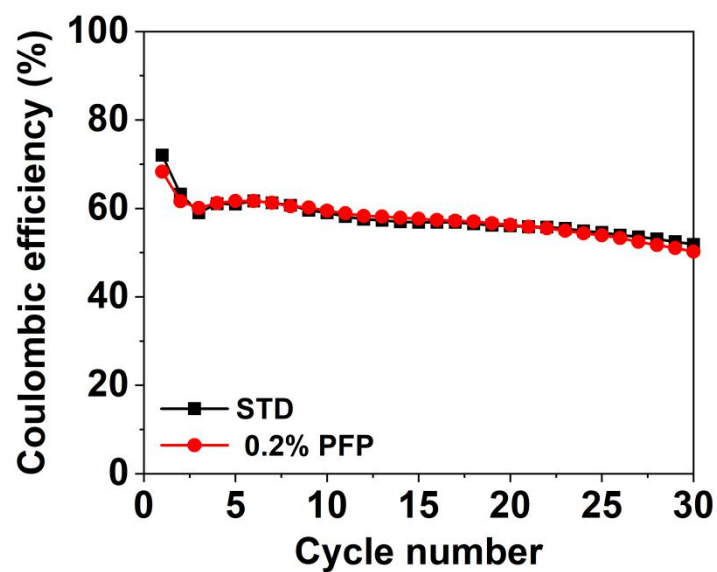
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101 **Supplementary Figure 9.** A, B: XPS of NCM90 electrodes after 3 formation cycles at  
102 0.1C with (A) STD and (B) 0.2% PFP- containing electrolytes. (A, B) P 2p spectra.

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104 **Supplementary Figure 10.** Coulombic efficiency of Li||Cu cells at 1 mA cm<sup>-2</sup> with  
105 STD and 0.2% PFP-containing electrolytes. The Li||Cu cells were assembled by using  
106 Cu foil (19.0 mm in diameter, 10 um in thickness) as working electrode and Li metal  
107 (15.8 mm in diameter, 2 mm in thickness) as counter and reference electrode. At each  
108 cycle, lithium was deposited on Cu foil at 1 mA cm<sup>-2</sup> and then stripped from Cu foil  
109 until the cell potential reached 1.0 V (vs. Li/Li<sup>+</sup>).

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