Supplementary Material: Enhancing cycle life of Nickel-rich $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ via a Highly Fluorinated Electrolyte Additive – Pentafluoropyridine

MAIN TEXT

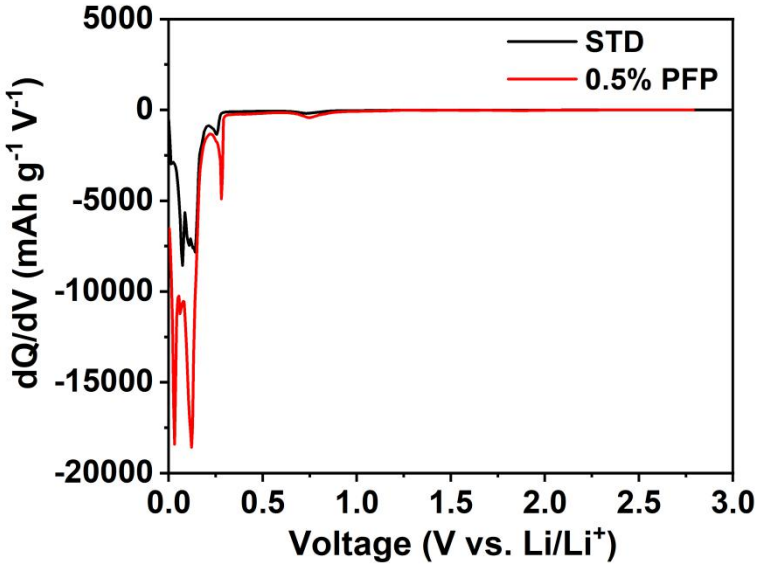
HOMO and LUMO energies of EC, DEC, and PFP with and without solvation with Li^+, oxidation potential of EC, DEC, and PFP with and without solvation with Li^+, dQ/dV curves of Si/C anode with different electrolytes, initial charge/discharge curves NCM90 with different electrolytes, Coulombic efficiency 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.

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

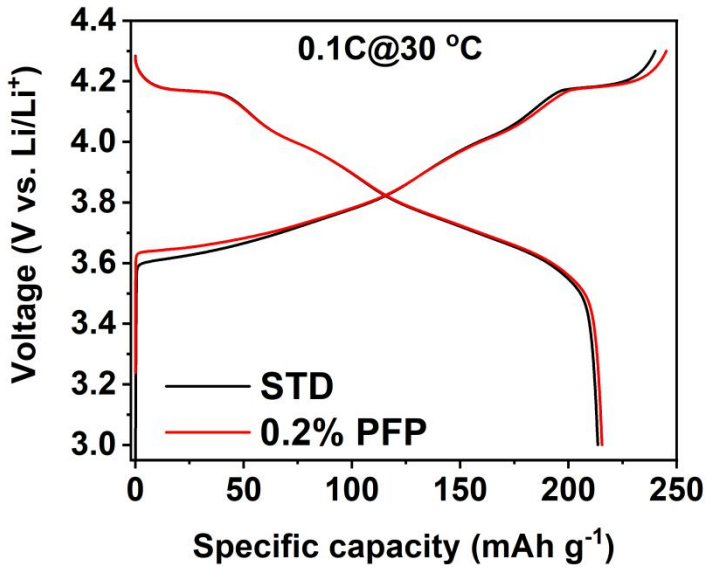
Solvent/Additive	EC	DEC	PFP
HOMO (eV) Without solvation with Li	-8.43	-8.09	-7.70
LUMO (eV) Without solvation with Li	-0.09	-0.12	-0.06
HOMO(eV) Solvation with Li	-9.17	-8.89	-7.96
LUMO(eV) Solvation with Li	-0.66	-0.59	-1.91

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

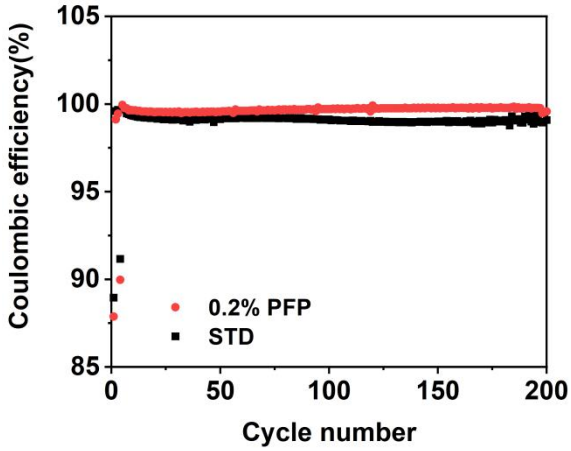
Solvent/Additive	EC	DEC	PFP
Potential (V vs. Li/Li^+) Without solvation with Li	6.64	6.42	5.93
Potential (V vs. Li/Li^+) Solvation with Li	7.17	6.97	6.10



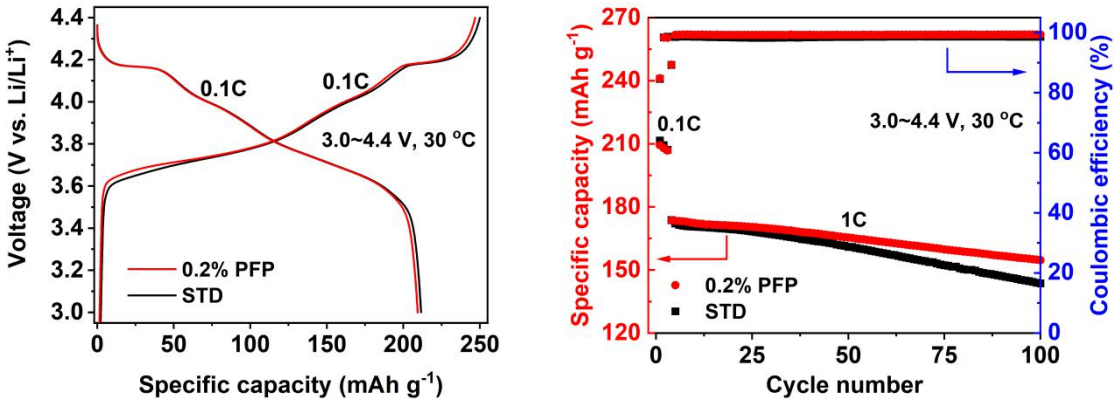
Supplementary Figure 1. The initial dQ/dV curves of Si/C electrode with STD and PFP-containing electrolytes at 0.1C (1C = 800 mA g^{-1}). Si/C anode electrodes were prepared by casting a slurry of Si/C material, acetylene black and alginate binder with a mass ratio of 8:1:1 utilizing deionized water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



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

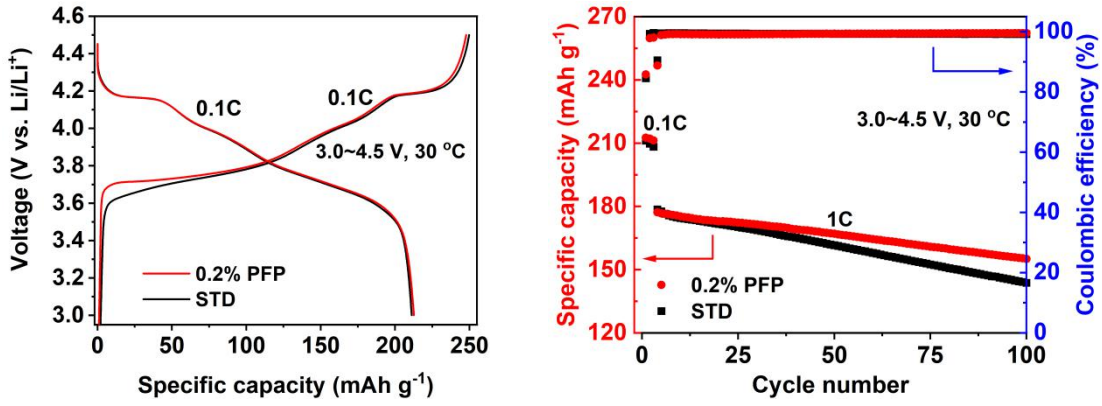


Supplementary Figure 3. Coulombic efficiency of NCM90||Li cells with STD and 0.2% PFP containing electrolytes in the voltage range of 3.0~4.3 V at 30 °C.



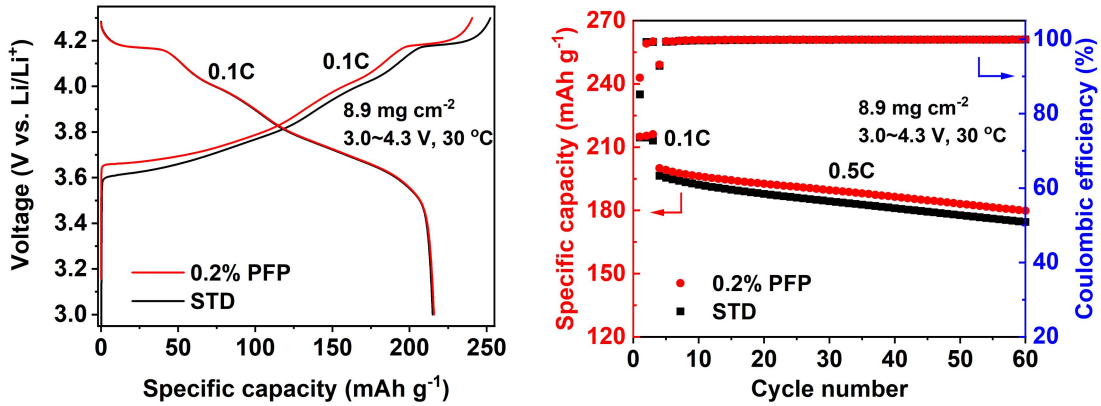
A **B**

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



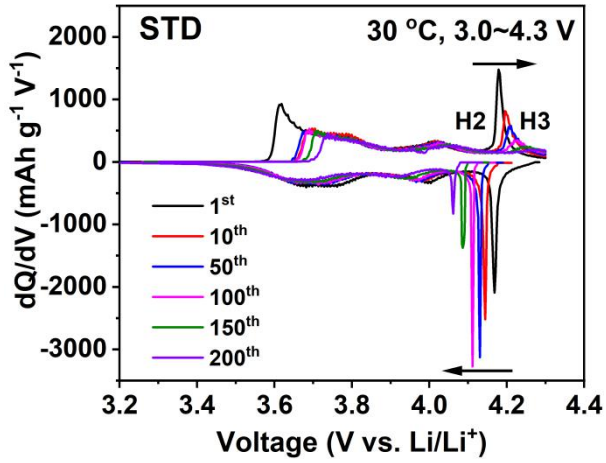
A B

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

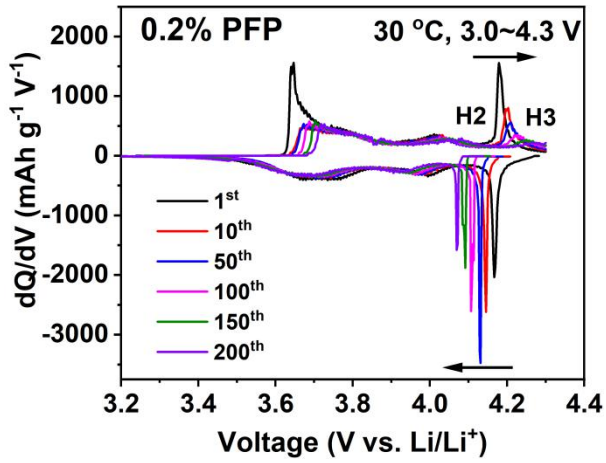


A B

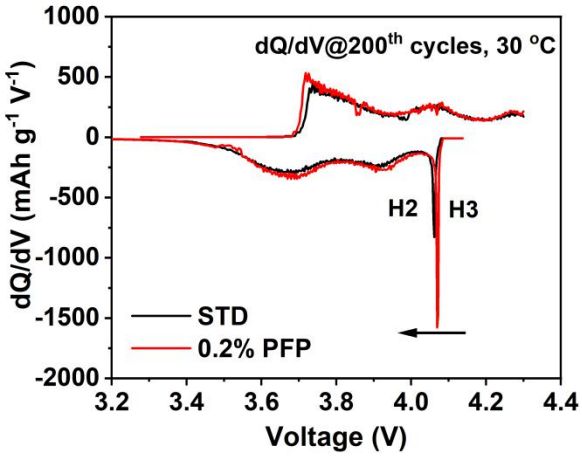
Supplementary Figure 6. A: Initial charge/discharge curves at 0.1C; B: Cycling performance of NCM90 with high active material loading (8.9 mg cm-2) in the voltage range of 3.0~4.3 V at 30 oC.



A



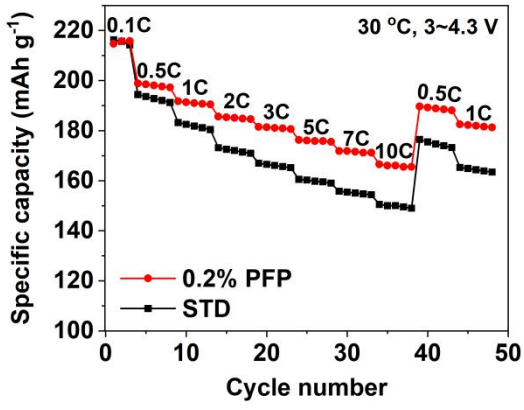
B



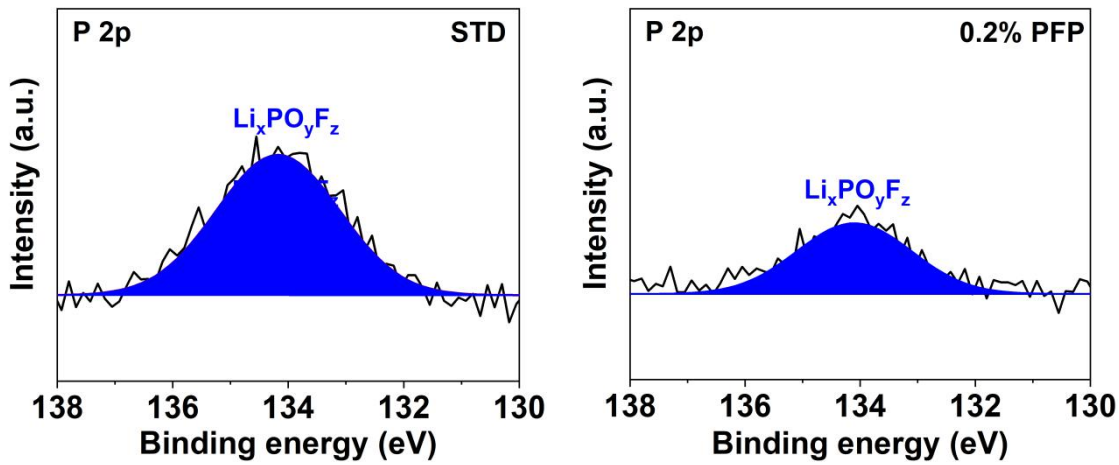
C

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

additive at 30 ºC at 200 cycles.

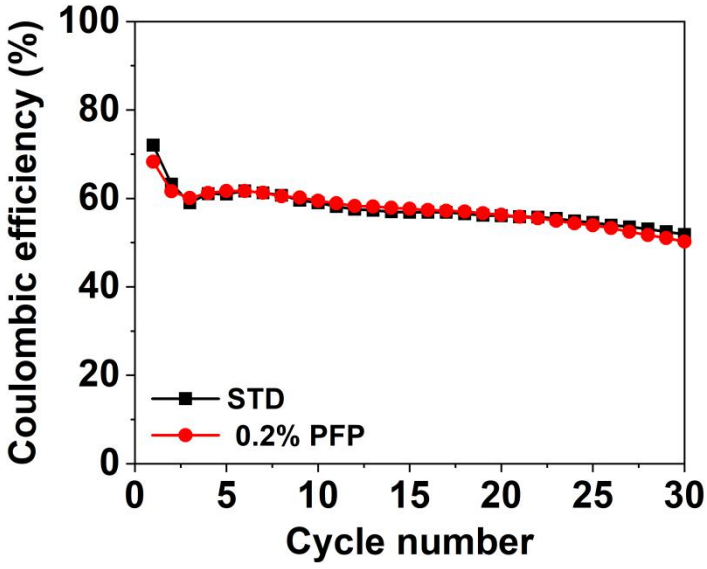


Supplementary Figure 8. Rate performance of P-NCM92||Li cells with STD and 0.2% PFP-containing electrolytes in the voltage range of 3.0~4.3 V at 30 ºC, respectively. The P-NCM92 electrode is consisted of 80% active materials, 10% acetylene black as conductive agent, and 10% poly (vinylidene fluoride)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



A **B**

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



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