Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Self-extinguishing electrolyte using fluorinated alkyl phosphate for lithium batteries

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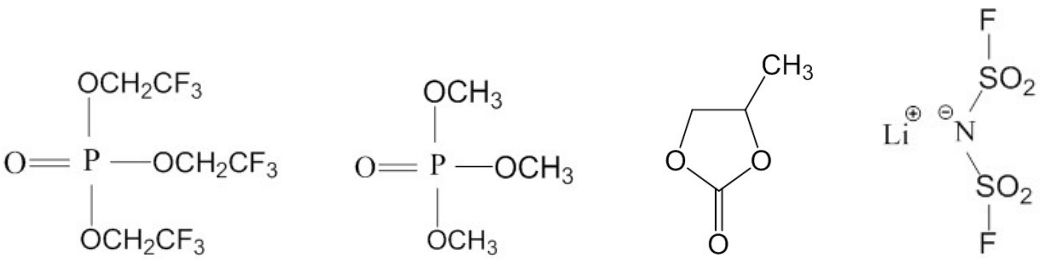
1. Materials



(TFEP) (TMP) (PC) (LiFSA)

Figure S1. Chemical structures of solvents and supporting salt.

2. Experimental

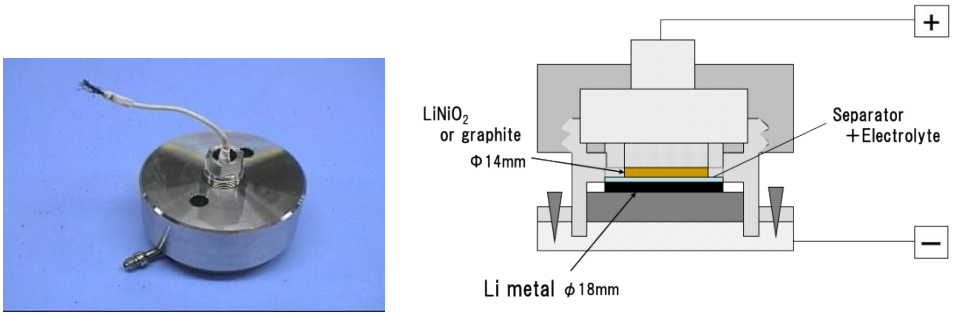


Figure S2. Photograph and schematic illustration of coin cell.

3. Results

3.1 Raman results

The Raman profile due to the stretching vibration of P=O in TFEP, located near 1300 cm^{-1}, was curve-fitted by three components A, B, and C with peaks at 1286, 1309, and 1328 cm^{-1} (Fig. S3 and Table I). The results showed the existence of three components, A, B, and C. The DFT calculation was made to assign the three components. Although the calculated and experimental data did not match perfectly (Fig.S4), the signal at 1328 cm^{-1} (component C) was assigned to the bending vibration of the OCH_2CF_3 units. Therefore, the peak at 1328 cm^{-1} was unchanged for LiFSA concentrations up to 3.3 M ([TFEP]/[LiFSA]=2). The component A was estimated to be the stretching of P=O group in free TFEP. The component B reflected stretching of P=O group in solvated TFEP, but unfortunately involved information for the deformation of P-O-CH_2CF_3 of solvated and free TFEP molecules. Thus the Raman results gave no distinct information about Li-ion solvation.

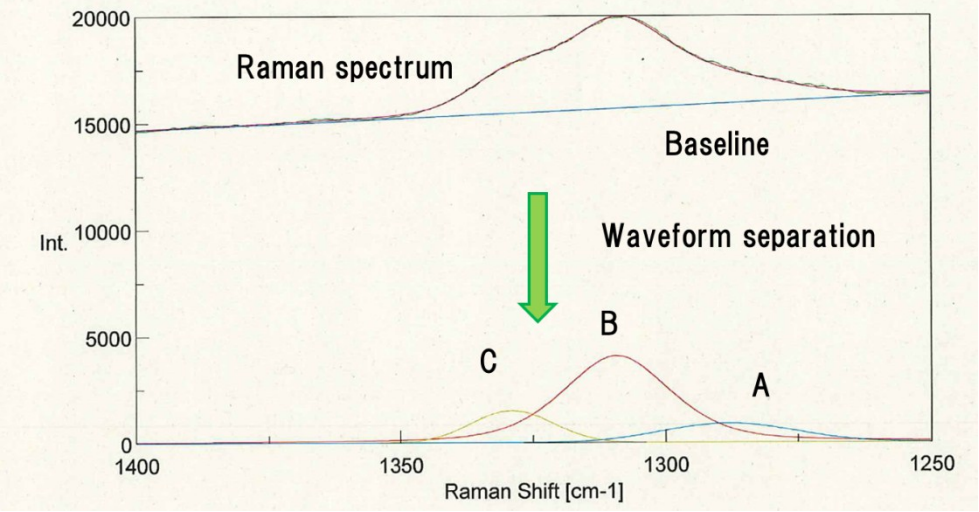


Figure S3. Waveform separation of Raman spectra for the [TFEP]/[LiFSA]=2 electrolyte.

Table SI: Waveform separation of Raman spectra for the TFEP electrolytes with various concentrations of LiFSA.

Sample	Peak intensity (counts) / Ratio (%)		
LiFSA : TFEP	Component A	Component B	Component C
0 : 1	1320 / 16	5263 / 64	1670 / 20
1 : 8	1049 / 15	4634 / 65	1499 / 21
1 : 4	889 / 14	4055 / 63	1509 / 23
1 : 2	624 / 12	3584 / 69	1008 / 19

The experimental spectra were curve-fitted as three components (A, B, and C) with peaks at 1286, 1309, and 1328 cm^{-1}.

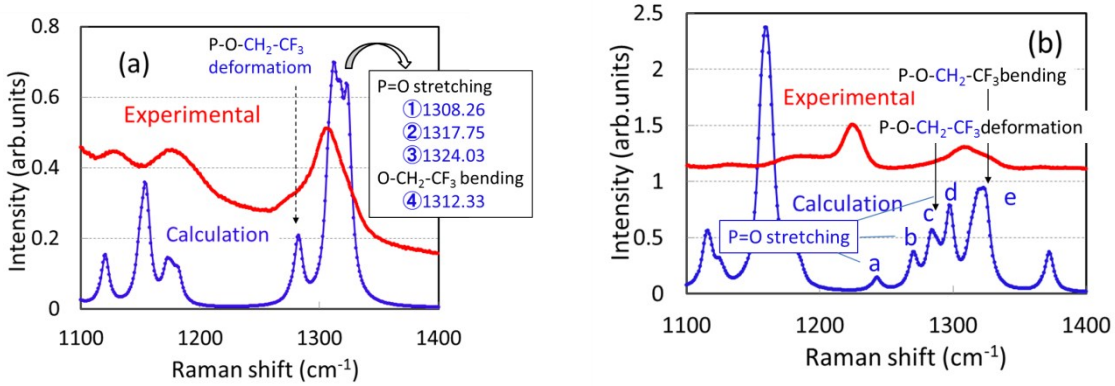
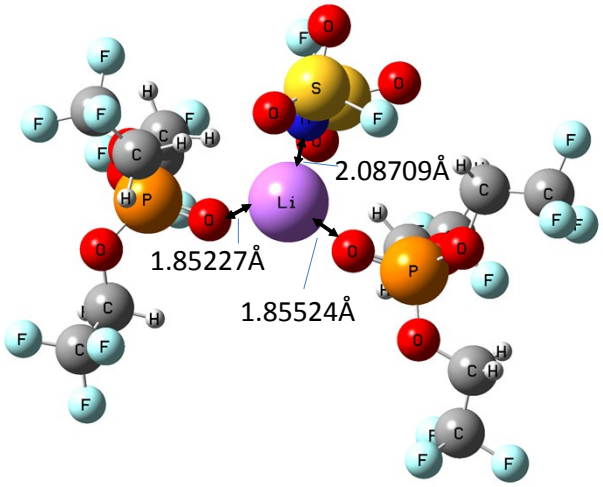
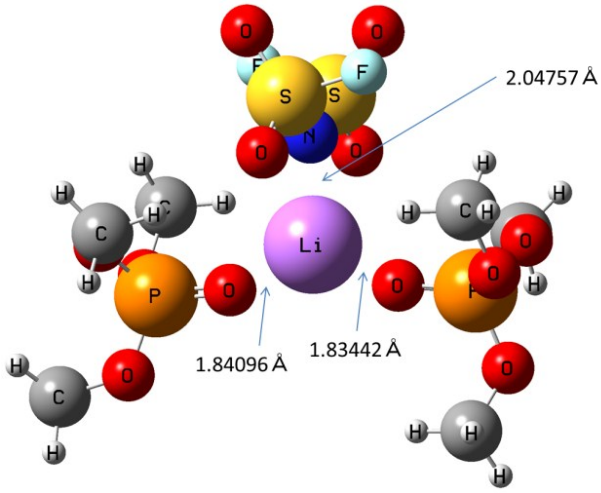


Figure S4: Comparison of the experimental and calculated Raman spectra for TFEP (left) and the [TFEP]/[LiFSA]=2 electrolyte (right).

3.2 Representative geometry of a Li ion with FSA anion and two solvent molecules.



(a) [TFEP]/[LiFSA] = 2



(b) [TMP]/[LiFSA] = 2

Figure S5: Structure of Li ion solvated by one LiFSA and two solvent molecules.

3.3 Potential window of the [TFEP]/[LiFSA]=2 electrolyte

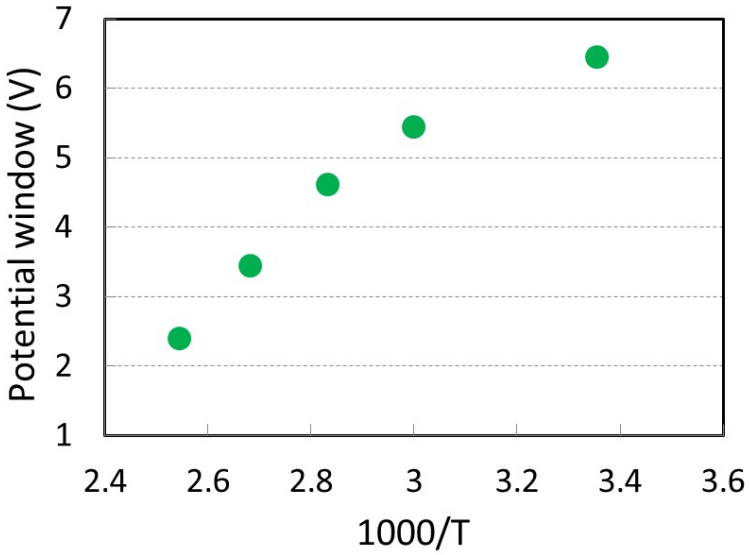


Figure S6. Potential window of the [TFEP]/[LiFSA]=2 electrolyte between 25 and 120 °C.

3.4 Cell performance

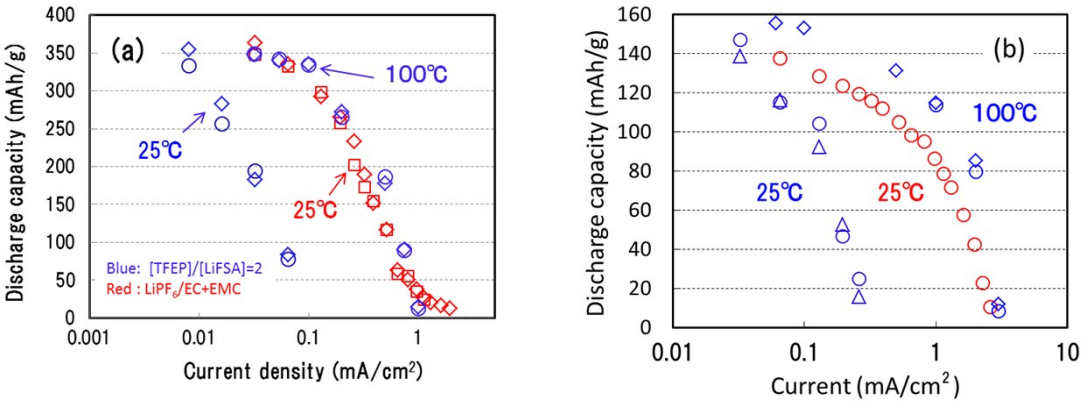


Figure S7. Discharge rate performance of (a) graphite/Li and (b) $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/Li half cells at 25 °C and 100 °C. The electrolytes were the [TFEP]/[LiFSA]=2 electrolyte (blue), and 1mol/L $LiPF_6$/EC+EMC (red).

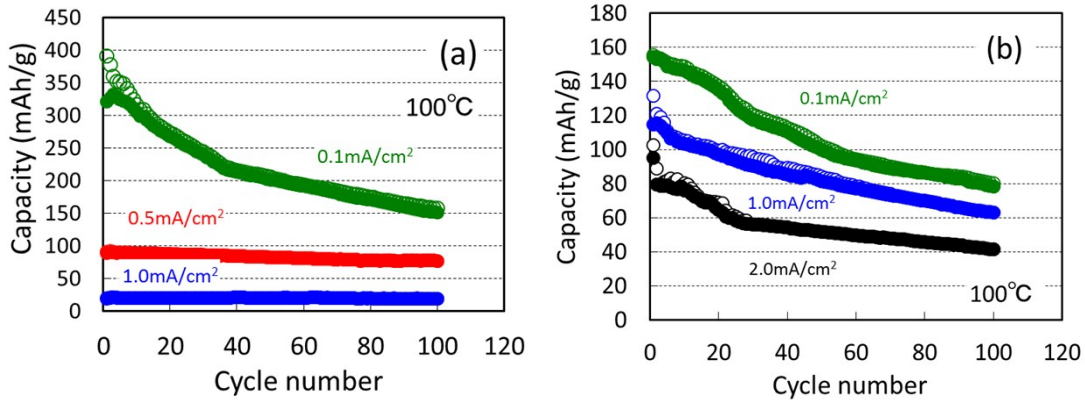


Figure S8. Cycle performance of (a) graphite/Li and (b) $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/Li half cells using the electrolytes were the [TFEP]/[LiFSA]=2 electrolyte at 100 °C.

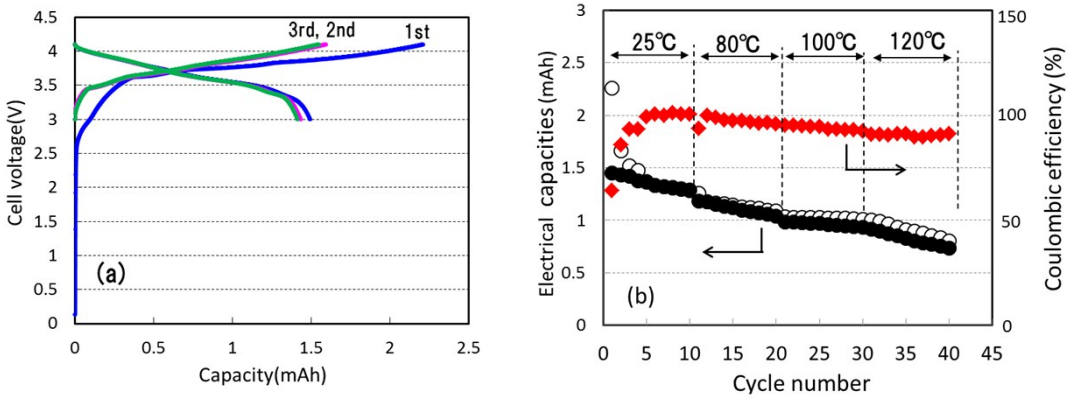


Figure S9. (a) Charge and discharge curves of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/graphite full cell with the [TFEP]/[LiFSA]=2 electrolyte at 25 °C, and (b) cycle performance between 25 and 120 °C; (○) charge capacity, (●) discharge capacity , and (◆) coulombic efficiency.