Supporting Information

Enabling Electrochemical Compatibility of Non-flammable Phosphate

Electrolytes for Lithium-ion Batteries by Tuning Their Molar Ratios of

Salt to Solvent

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1. Experimental Procedures

1.1 Chemicals

TMP, TEP, TPP, TBP, TAP and fluoroethylene carbonate (FEC) were purchased from Aladdin and LiFSI was purchased from Chemspec Co. Ltd., Shanghai, China. Molecule sieves were used to remove water in the solvents. The graphite was obtained from Shanshan Tech Co. Ltd.

1.2 Experimental details

The electrolytes were prepared by adding LiFSI into phosphate solvents with different molar ratio of salt to solvent in argon-filled glove box. 5% FEC by volume as a film-forming was added into all the electrolytes. The graphite electrodes were prepared by mixing 85% graphite, 6% super P, 4.5% sodium carboxymethyl cellulose (dissolved in water) and 4.5% styrene butadiene rubber (mixed with water). Then, the slurry was coated on the Cu foil and dried under vacuum at 100 °C for 10 hours. The Li/graphite half cell was assembled in argon-filled glove box with CR2032 coin cells.

1.3 Characterizations method

The electrochemical performance was tested by multichannel battery tester (Neware CT-4008). The Raman spectra was recorded with the DXR2 Raman microscope (Thermo Scientific) using a 532 nm excitation laser. Density Functional Theory (DFT) calculations were carried out using Gaussian (G09) program. The B3LYP/6-311G++G(d, p) basis set was used to optimize the geometry and calculate energy level of the five phosphate molecules. Moreover, in order to get the precise structure, frequency analysis was employed.

2. Results and Discussion



Fig. S1. Structural formula of the five phosphate solvents.



Fig. S2. Solvation structure of (a) 1:2 LiFSI-TEP, (b) 1:2 LiFSI-TPP and (c) 1:2 LiFSI-TBP electrolytes.

 Table S1 Properties of five electrolytes at MR of 1:2

| Solvent | ρ (g L ⁻¹) | Msol (g mol⁻¹) | Msol+93.5 (g mol ⁻¹) |
|---------|------------------------|----------------|----------------------------------|
| TMP | 1441 | 140 | 233.5 |
| TEP | 1234 | 182 | 275.5 |
| ТРР | 1192 | 224 | 317.5 |
| ТВР | 1130 | 266 | 359.5 |
| ТАР | 1082 | 308 | 401.5 |

. Table S2 Molar concentration of electrolytes at MR of 1:2.

| LiFSI: Solv= 1: 2 | Molar Concentration/ mol L ⁻ |
|-------------------|---|
| ТМР | 3.07 |
| TEP | 2.24 |
| ТРР | 1.88 |
| ТВР | 1.57 |
| ТАР | 1.35 |
| | |

Table S3 Initial reversible capacities and ICEs for the electrolytes at MR of 1:2

| Solvent | Reversible Capacities | ICE | |
|---------|-------------------------|-------|--|
| TMP | 356 mAh g ⁻¹ | 85.8% | |
| TEP | 333 mAh g ⁻¹ | 85.7% | |
| ТРР | 352 mAh g ⁻¹ | 84.9% | |
| ТВР | 302 mAh g ⁻¹ | 83.5% | |
| ТАР | 350 mAh g ⁻¹ | 89.5% | |

3. References

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