## Supporting Information for

# Negative redox potential shift in fire-retardant electrolytes and consequences for high-energy hybrid batteries

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# 1. Materials and Methods

## <u>Materials</u>

Lithium metal foils purchased from Gelon. Trimethyl phosphate (TMP, 99%, Acros), triethyl phosphate (TEP, ReagentPlus,  $\geq$ 99.8%), triphenyl phosphate (TPhP, 99+%, Acros), tributyl phosphate (TBP,  $\geq$ 99%, Sigma-Aldrich), trimethylphosphine oxide (TMPOx, Alfa Aesar) and trimethyl thiophosphate (TMThP, Alfa-Aesar) were dried in vacuum before use. 2,2,6,6-Tetramethylpiperidine 1-oxyl free radical (TEMPO, >98.0%, TCl), ferrocene (Fc, Sigma-Aldrich), LiPF<sub>6</sub> (battery grade  $\geq$ 99.99% trace metals basis, Sigma-Aldrich), LiTFSI (battery grade, Sigma-Aldrich), NaPF<sub>6</sub> (battery grade, Sigma-Aldrich) and all phosphorous-based chemicals are degassed under vacuum prior use in an argon filled glovebox. All electrolyte solutions were purchased from Solvionic and were used as received: EC/DEC 1:1 (v:v) 1 M LiPF<sub>6</sub>; PC 1 M LiPF<sub>6</sub>; EC/DEC 1 M LiPF<sub>6</sub>; EC/DEC 1 M LiPF<sub>6</sub>; EC/DEC 1 M MaPF<sub>6</sub>. 1-Butanol (99%, extra pure, Acros), MWCNT NC7000 (Nanocyl, Ltd.), copper wire (0.64 mm diameter, Puratronic, 99.999% metal basis, oxygen free,  $\approx$  2.87 g/m, Alfa Aesar), NMP (ACS Reagent, Acros), were used as received. Ag, Ni and Pt pseudo-RE disc electrodes (diameter 2mm), and Pt wire counter-electrodes, styrene-butadiene rubber (SBR) and carboxymethyl cellulose (CMC) are purchased from MTI Corp.

## <u>Methods</u>

# *Cyclic voltammetry of the Li<sup>+</sup>/Li<sup>0</sup> redox process.*

This experiment was carried in a glovebox under argon. A beaker cell was loaded with the electrolyte solution, TMP 1 M LiPF<sub>6</sub>. The first electrochemical test involved the following set of electrodes: a Ni disc as WE, a lithium chip stuck on a copper support as CE, Ag/AgCl in presence of NBu<sub>4</sub>Cl (0.004 M) as pseudo-RE electrode. Using this setup, a linear scan voltammetry was performed at 1 mV.s<sup>-1</sup> (cathodic polarization) between -2.30V and -3.60 V.

Next the calibration (anodic polarization) was carried out using ferrocene (2 mg/mL) added to the same electrolyte medium as reference electrochemical system, in combination with and a Pt disc WE, a Pt wire CE and same Ag/AgCl RE. The voltage window was scanned between 0.00 V and 0.80 V at 50 mV.s<sup>-1</sup>.

The same two experiments were then carried out with PC 1 M LiPF<sub>6</sub> commercial electrolyte, only the voltage window for the cathodic polarization was adjusted to be -2.3 V to -3.3 V.

# Cyclic voltammetry to study the Li-salt concentration effect

The same setup presented beforehand to study the Li<sup>+</sup>/Li<sup>0</sup> redox process was used to evidence the voltage upshift effect via the variation of the Li<sup>+</sup> salt concentration in TMP. The electrolytes used here are based on LiTFSI, varying the concentrations thereof (0.5 M; 1 M; 2 M; 3 M) dissolved in TMP.

## Synthesis of PTMA-10%C

The synthesis was carried out as reported elsewhere.<sup>1</sup> This material has been used for all PTMA-based electrodes.

# PTMA electrodes used for studies of phosphate concentration effect

600 mg Of PTMA-10%C composite were mixed with 250 mg of SC45 and thoroughly grinded. To this mixture, 50 mg of SBR (dissolved in water, 5 wt.%) and 100 mg of CMC (dissolved in water at a concentration of 2 - 4 wt.%) were added and thoroughly stirred. The obtained slurry was coated on carbon coated aluminum foil followed by drying in air at 50 °C. Disks of 0.5 in diameter (loading around 5 mg/cm<sup>2</sup>) were subsequently

punched and pressed at 6 tons/cm<sup>2</sup>. Prior the cell assembly, the electrodes were dried at 55 °C in vacuum for 12 h.

The electrodes were tested in half-cell configuration using Li-metal foil as reference and counter electrode. CR2032 coin-cells were used. One sheet of Celgard separator was placed in between the working electrode and lithium disk. The cells were activated by soaking the electrodes and the separator with the electrolyte solution. The electrolyte solution was prepared by mixing EC/DEC 1 M LiPF<sub>6</sub> commercial electrolyte, adding either TEP or TMP, and LiPF<sub>6</sub> to adjust the final lithium salt concentration to be equal to 1 M. The cells were assembled in an argon-filled glove box.

# PTMA-based hybrid electrodes preparation

Same procedure as described beforehand for all-PTMA slurry preparation and coin-cell assembly was applied for hybrid electrodes with the following compositions (weight ratios): PTMA-10%C / LFP / SC45 / CMC / SBR 40:20:25:10:5. These cells were tested in cyclic voltammetry experiments using either EC/DEC/TMP 25:25:50 (v:v:v) 1 M LiPF<sub>6</sub> or EC/DEC 50:50 (v/v) 1 M LiPF<sub>6</sub>. (scan rate =  $0.2 \text{ mV.s}^{-1}$ )

# Cell design of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-PTMA dual-ions batteries

LTO anode. Slurry preparation from LTO, SC45 and PVDF (80:10:10 w/w/w) through ball-milling of the constituents (400 rpm, 45 min). The slurry was spread on carbon coated Al foil by means of the doctor blade method. The wet film thicknesses were adjusted to 500  $\mu$ m (loadings around 3.0 mg/cm<sup>2</sup>). The coated foil was then cut into discs (diameter, 0.5 in, coating mass around 8.0 mg each).

PTMA cathode. Self-standing electrodes were produced using a vacuum filtration process over a PVDF 0.2 μm filter. The filtration device is a Millipore set-up. Pristine MWCNTs (6.25 mg) were dispersed in butanol (200 mL) using bath sonication for 30 min. This first suspension was filtered on the PVDF filter. A suspension of PTMA/10%C (25 mg) and pristine MWCNTs (6.25 mg) was then prepared in BuOH (400 mL, bath sonicated for 30 min) and filtered over the first layer formed on PVDF (3.40 cm diameter). Electrodes were first dried in ambient air at room temperature for 2 hours, then at 60°C under vacuum for 24 hours. The resulting buckypaper was then cut into discs (diameter, 0.5 in, mass around 7.5 mg each).

Cell assembly. The electrodes were assembled in a CR2025 case, using Celgard separator, in a glovebox under argon, using either EC/DEC 1 M LiPF<sub>6</sub>, or TMP 1 M LiPF<sub>6</sub> as electrolyte.

Electrochemical testing. Galvanostatic cycling was carried out at C-rate equal to C/5 with respect to the LTO electrode capacity.

## Electrolyte stability window

The electrolyte anodic stability was obtained in a CR2032 coin cell assembled in an Ar filled glovebox, using Li as WE and pseudo-RE, carbon-coated Al foil as CE and Celgard as separator. The electrolyte was either TMP 1 M LiPF<sub>6</sub> or either EC/DEC 1 M LiPF<sub>6</sub> and cyclic voltammetry experiments were carried out at 1 mV.s<sup>-1</sup>.

## Voltage shifts with other phosphorus-based derivatives

These experiments are relying on the same procedure designed to study the phosphate concentration effect. The electrolytes used here have the following composition: EC / DEC / Pi 25:25:50 (v/v/v) 1 M LiPF<sub>6</sub>, where Pi is one of the following compounds, TBP, TMPOx, TMThP.

## Na based systems

This experiment was carried in a glovebox under argon. A beaker cell was loaded with the electrolyte solution, TMP 1M NaPF<sub>6</sub>. The first test involved the following set of electrodes: a Ni disc as WE, a sodium chip stuck on a copper support as CE, Ag/AgCl in presence of NBu<sub>4</sub>Cl (0.004 M) as pseudo-RE electrode. Ferrocene (2 mg/mL) was added to the electrolyte medium as reference electrochemical system (RES). An anodic polarization was carried out and ferrocene redox response was recorded at 50 mV.s<sup>-1</sup> both versus the Na<sup>+</sup>/Na CE and the Ag/AgCl pseudo-RE.

## Instrumentation

Cyclic voltammetry. All experiments have been carried out under an argon atmosphere (<0.1 ppm H<sub>2</sub>O, <0.1 ppm O<sub>2</sub>) in a glovebox from Innovative Technology, Inc., using a PARTSTAT 3000 potentiostat from Princeton Applied Research.

## 2. Electrochemical Data.

#### Figure S1.



In this set of experiments, we highlight the effect of phosphates on the redox potential of the Na<sup>+</sup>/Na<sup>0</sup> couple, which is found to be significantly affected in a similar manner as for the Li<sup>+</sup>/Li<sup>0</sup> redox couple. To this end we compare the voltage difference obtained between a Na<sup>+</sup>/Na<sup>0</sup> electrode and the redox response of the reference electrochemical system Fc<sup>+</sup>/Fc. The redox shift measured in these conditions was found to be of ca. 210 mV.

Figure S2.



Redox potential shift with other phosphates. All data are obtained at a concentration of 3.68 M phosphate in the ternary EC/DEC/Phosphate system, all at 1 M Lithium salt.

**Table S1.** Composition and molar ratio of the ternary systems presented in Fig. 2.

TMP/Li	vol% TMP	vol% FC		Li molar	TMP/Li	EC/Li	DEC/Li	TMP/(EC+DEC)	Solvent to Li
molar ratio	V01/0_11VII	V01/0_EC	VOI/0/ DEC	Limolai	molar ratio	molar ratio	molar ratio	molar ratio	molar ratio
0	0	50	50	1	0.0	7.5	4.1	0.0	11.6
0.85	10	45	45	1	0.9	6.7	3.7	0.1	11.3
2.14	25	37.5	37.5	1	2.1	5.6	3.1	0.2	10.9
3.16	37.5	31.25	31.25	1	3.2	4.7	2.6	0.4	10.4
4.27	50	25	25	1	4.3	3.7	2.1	0.7	10.1
5.13	60	20	20	1	5.1	3.0	1.7	1.1	9.8
6.41	75	12.5	12.5	1	6.4	1.9	1.0	2.2	9.3
8.55	100	0	0	1	8.6	0	0		8.6

TEP/Li molar ratio	vol%_TEP	vol%_EC	vol%/DEC	Li molar	TEP/Li molar ratio	EC/Li molar ratio	DEC/Li molar ratio	TEP/(EC+DEC) molar ratio	Solvent to Li molar ratio
0	0	50	50	1	0	7.5	4.1	0.0	11.6
0.59	10	45	45	1	0.59	6.7	3.7	0.1	11.0
1.47	25	37.5	37.5	1	1.47	5.6	3.1	0.2	10.2
2.17	37	31.25	31.25	1	2.17	4.7	2.6	0.3	9.4
2.94	50	25	25	1	2.94	3.7	2.1	0.5	8.8
3.52	60	20	20	1	3.52	3.0	1.7	0.8	8.2
4.41	75	12.5	12.5	1	4.41	1.9	1.0	1.5	7.3
5.87	100	0	0	1	5.87	0	0		5.9

#### Figure S3.



Tempo redox response recorded in TMP based electrolytes against a Li/Li<sup>+</sup> electrode. The concentration of the lithium salt is varying from 0.5 M to 3 M. This set of CV experiments evidences the influence of Li salt concentration on Li<sup>+</sup>/Li redox potential in TMP based electrolytes. According to Nernst equation, the effect on the measured voltage difference between the Tempo redox couple and the Li<sup>+</sup>/Li<sup>0</sup> should affect both electrodes symmetrically: (i) Due to the increase of the counter-anion concentration (TFSI<sup>-</sup>), Tempo should be shifted towards lower values by a factor of 59 mV per concentration decade;<sup>2</sup> (ii) the Li electrode should be affected the same way, 59 mV per decade, due to the increase of the Li<sup>+</sup> concentration of the system;<sup>3</sup> (iii) these two effects should be cancelling out each other on the resulting voltage. Yet a much important difference (about 410 mV) is observed between the lowest and highest electrolyte concentration (respectively 0.5 and 3 M), which is due to deviations from Nernst equation. The deviation from Nernst should be related to the high concentration regime of the measurements and is ascribed to the change of the activities of Li(TMP)<sub>n</sub><sup>+</sup> complex and free solvent.

	TMP-to-Li
Li/Molarity	molar ratio
0.5	17.1
1	8.6
2	4.3
3	2.9



Dual-ion graphite-Li cells cycled with 1M LiPF<sub>6</sub> in EC-DEC and TMP electrolytes. The higher polarization in the phosphate electrolyte is also the result of high solvation strength by phosphates resulting in poorer desolvation kinetics of the lithium cations.

#### 3. NMR experiments

A series of electrolyte solutions were prepared in an argon atmosphere glovebox by dissolving 1 mol dm<sup>-1</sup> LiPF<sub>6</sub> or LiTFSI in a mixture of EC\DEC\TMP or EC\DMC\TMP (1:1:*x*, v:v:v %), respectively. Percentage of TMP ranges from 0 (EC\DEC\TMP or EC\DMC\TMP 1:1:0 v:v:v) to 100 (EC\DEC\TMP or EC\DMC\TPM 0:0:1 v:v:v), passing by 10%, 25%, 37.5%, 50%, 60% and 75% (as reported in the Table S1). Toluene (Sigma-Aldrich, anhydrous, aliquots of 25  $\mu$ L to each NMR tube) was added as internal standard for DOSY NMR analyses. Moreover, in DOSY NMR analyses some of these solutions have been compared with the corresponding unsalted electrolyte mixtures.

Neat samples of these solutions were analyzed by NMR spectroscopy using standard 5 mm thin-walled tubes with coaxial NMR inserts (0.15 mL of C<sub>6</sub>D<sub>6</sub> (Eurisotop) therein) placed inside the NMR tubes. All <sup>1</sup>H, <sup>7</sup>Li, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded at room temperature (296 K) on a Bruker Avance 500 spectrometer operating at 500.13 MHz, 194.37 MHz, 125.76 MHz and 202.46 MHz, respectively. Experiments were run using a BBO{1H,X} probehead equipped with a z-gradient coil, allowing a maximum gradient strength of 0.5 T/m. The <sup>1</sup>H and <sup>13</sup>C resonances were referenced to  $C_6D_6$  (7.16 ppm for <sup>1</sup>H and 128.06 ppm for <sup>13</sup>C NMR spectra). <sup>31</sup>P and <sup>7</sup>Li NMR spectra were calibrated using external references: a 85% H<sub>3</sub>PO<sub>3</sub> solution in H<sub>2</sub>O ( $\delta$ = 0.00 ppm) for <sup>31</sup>P NMR spectra and 1.0 M <sup>7</sup>LiCl solution in D<sub>2</sub>O for <sup>7</sup>Li NMR experiments. Standard zg programs were employed for 1D NMR experiments. A Waltz-16 decoupling scheme with a pulse of 80 µsec was used for <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR analyses. <sup>1</sup>H DOSY measurements were performed using the standard Bruker ledbpgp2s pulse program with 16 t1 increments on 32 K data points. Acquisition times were fixed to 4.2 s, 2.0 s and 0.65 s for <sup>1</sup>H, <sup>7</sup>Li and <sup>31</sup>P, respectively, and relaxation delays (D1) ranged from 2 s (<sup>7</sup>Li and <sup>31</sup>P) to 30 s (<sup>1</sup>H). Diffusion times (D20) of 0.5 s (<sup>1</sup>H) and 1.0 s (<sup>7</sup>Li and <sup>31</sup>P) and rectangular gradient pulse durations (P30) of 0.8 ms, 2 ms and 3.0 ms were applied for <sup>1</sup>H, <sup>7</sup>Li and <sup>31</sup>P, respectively. Gradient recovery delays between 0.15 (<sup>1</sup>H) and 0.5 ms (<sup>7</sup>Li and <sup>31</sup>P) followed the application of each gradient pulse. Data were accumulated by linearly varying the diffusion encoding gradients over a range from 2 to 95 % for 16 gradient increment values. Individual rows of the guasi-2D diffusion databases were phased and baseline corrected. Processing of NMR data were performed using Topspin software (by Bruker supplier), and the actual diffusion coefficients used for diffusion analysis were measured by  $T_1/T_2$  relaxation module.

<sup>1</sup>H, <sup>7</sup>Li and <sup>31</sup>P NMR chemical shift analysis



**Figure S5.** <sup>13</sup>C{<sup>1</sup>H} NMR spectra. Left: (a) EC + DEC, (b) EC + DEC + LiPF<sub>6</sub>, (c) EC + DMC + LiPF<sub>6</sub> + (10%) TMP, (d) EC + DEC + LiPF<sub>6</sub> + (25%) TMP, (e) EC + DEC + LiPF<sub>6</sub> + (37.5%) TMP, (f) EC + DEC + LiPF<sub>6</sub> + (50%) TMP, (g) EC + DEC + LiPF<sub>6</sub> + (60%) TMP, (h) EC + DEC + LiPF<sub>6</sub> + (75%) TMP. Right: (i) EC + DMC, (j) EC + DMC + LiTFSI, (k) EC + DMC + LiTFSI + (10%) TMP, (l) EC + DMC + LiTFSI + (25%) TMP, (m) EC + DMC + LiTFSI + (37.5%) TMP, (n) EC + DMC + LiTFSI + (50%) TMP, (o) EC + DMC + LiTFSI + (60%) TMP, (p) EC + DMC + LiTFSI + (75%) TMP. The spectra are restricted to the 160.0 ppm  $\div$  155.0 ppm zone. Note that, on the spectra on the right, NMR chemical shifts of "free" DMC/EC in (i) and the "supposed" to be "free DMC/EC species" in (n-p) don't line up well probably because of a different viscosity of the solutions.



**Figure S6.** <sup>7</sup>Li NMR spectra. Left: (a) EC + DEC + LiPF<sub>6</sub>, (b) EC + DMC + LiPF<sub>6</sub> + (10%) TMP, (c) EC + DEC + LiPF<sub>6</sub> + (25%) TMP, (d) EC + DEC + LiPF<sub>6</sub> + (37.5%) TMP, (e) EC + DEC + LiPF<sub>6</sub> + (50%) TMP, (f) EC + DEC + LiPF<sub>6</sub> + (60%) TMP, (g) EC + DEC + LiPF<sub>6</sub> + (75%) TMP, (h) LiPF<sub>6</sub> + TMP. Right: (i) EC + DMC + LiTFSI, (j) EC + DMC + LiTFSI + (10%) TMP, (k) EC + DMC + LiTFSI + (25%) TMP, (l) EC + DMC + LiTFSI + (37.5%) TMP, (m) EC + DMC + LiTFSI + (50%) TMP, (n) EC + DMC + LiTFSI + (60%) TMP, (o) EC + DMC + LiTFSI + (75%) TMP (p) LiTFSI + TMP.



**Figure S7.** <sup>31</sup>P{<sup>1</sup>H} NMR spectra. Left (a) EC + DMC + LiPF<sub>6</sub> + (10%) TMP, (b) EC + DEC + LiPF<sub>6</sub> + (25%) TMP, (c) EC + DEC + LiPF<sub>6</sub> + (37.5%) TMP, (d) EC + DEC + LiPF<sub>6</sub> + (50%) TMP, (e) EC + DEC + LiPF<sub>6</sub> + (60%) TMP, (f) EC + DEC + LiPF<sub>6</sub> + (75%) TMP, (g) LiPF<sub>6</sub> + TMP, (h) TMP. Right: (i) EC + DMC + LiTFSI + (10%) TMP, (j) EC + DMC + LiTFSI + (25%) TMP, (k) EC + DMC + LiTFSI + (37.5%) TMP, (l) EC + DMC + LiTFSI + (50%) TMP, (m) EC + DMC + LiTFSI + (60%) TMP, (n) EC + DMC + LiTFSI + (75%) TMP, (o) LiTFSI + TMP, (p) TMP.

# <sup>1</sup>*H*, <sup>7</sup>*Li* and <sup>31</sup>*P* DOSY and diffusion coefficient (Diff.) analysis

Solutions	Composition <sup>(a)</sup>	<sup>1</sup> H <sub>Tol</sub> Diff. <sup>(b)</sup>	<sup>1</sup> H <sub>DEC(CH2)</sub> Diff. <sup>(b)</sup>	<sup>1</sup> H <sub>EC</sub> Diff. <sup>(b)</sup>	<sup>1</sup> H <sub>TMP</sub> Diff. <sup>(b)</sup>	<sup>31</sup> P <sub>TMP</sub> Diff. <sup>(b)</sup>	<sup>7</sup> Li Diff. <sup>(b)</sup>
A : EC + DEC	1:1	11.01	9.14	9.62	n/a	n/a	n/a
$B : EC + DEC + LiPF_6$	7.5:4.1:1	5.96	7.21	3.75	n/a	n/a	1.73
C : : (25%) TMP + EC + DEC	1:1.5:1,5	10.26	8.32	8.96	7.46	1.27	n/a
D : (25%) TMP + EC + DEC + LiPF <sub>6</sub>	2.1:5.6:3.1: 1	6.28	7.81	4.57	3.43	0.28	1.81
E : (50%) TMP + EC + DEC	1.5:1:1	10.02	8.20	8.78	7.24	1.21	n/a
F : (50%) TMP + EC + DEC + LiPF <sub>6</sub>	4.2:3.7:2.1:1	6.33	8.81	5.34	4.05	0.42	2.15
G : (75%) TMP + EC + DEC	6:1:1	9.24	7.78	8.22	6.74	1.11	n/a
H : (75%) TMP + EC + DEC + LiPF <sub>6</sub>	6.4:1.9:1:1	4.72	8.71	4.02	4.94	0.34	1.60
I : TMP	1	9.18	n/a	n/a	8.38	1.17	n/a
_J : (100%) TMP + LiPF <sub>6</sub>	8.5:1	5.10	n/a	n/a	5.49	0.43	1.48

**Table S2.** Experimental diffusion coefficient  $(10^{-10} \text{ m}^2 \text{ s}^{-1})$  data.

(a): Determined by considering the molar ratios in a 1 M LiPF<sub>6</sub> (or unsalted) solution prepared from a mixture of TMP+EC+DEC (v:v:v%, where v = volume) (see Table S1); (b): <sup>1</sup>H Diffusion Coefficients have been extrapolated from <sup>1</sup>H DOSY measures and reported in units of  $10^{-10}$  m<sup>2</sup>/s.



**Figure S8.** <sup>1</sup>H DOSY NMR spectra of A-J solutions. (A): EC + DMC, (B): EC + DMC + LiPF<sub>6</sub>, (C): EC + DEC + (25%) TMP, (D): EC + DEC + LiPF<sub>6</sub> + (25%) TMP, (E): EC + DEC + (50%) TMP, (F): EC + DEC + LiPF<sub>6</sub> + (50%) TMP, (G): EC + DEC + (75%) TMP, (H): EC + DEC + LiPF<sub>6</sub> + (75%) TMP, (I): TMP, (J): LiPF<sub>6</sub> + TMP.



**Figure S9.** <sup>7</sup>Li DOSY NMR spectra of the following solutions: (B) EC + DMC + LiPF<sub>6</sub>, (D) EC + DEC + LiPF<sub>6</sub> + (25%) TMP, (F: EC + DEC + LiPF<sub>6</sub> + (50%) TMP, (H) EC + DEC + LiPF<sub>6</sub> + (75%) TMP, (J) LiPF<sub>6</sub> + TMP.



**Figure S10.** <sup>31</sup>P DOSY NMR spectra of the following solutions: (D) EC + DEC + LiPF<sub>6</sub> + (25%) TMP, (F) EC + DEC + LiPF<sub>6</sub> + (50%) TMP, (H) EC + DEC + LiPF<sub>6</sub> + (75%) TMP, (J) LiPF<sub>6</sub> + TMP, (I) TMP.

## 4. <sup>1</sup>H, <sup>7</sup>Li and <sup>31</sup>P DOSY corrections

Solutions	<sup>1</sup> H <sub>Tol</sub> Diff <sup>(a)</sup>	<b>∆</b> <sup>(b)</sup>	<sup>1</sup> H <sub>Tol</sub> [Diff.] <sup>(c)</sup>	<sup>1</sup> H <sub>EC</sub> Diff. <sup>(a)</sup>	<sup>1</sup> H <sub>EC</sub> [Diff.] <sup>(c)</sup>	<sup>1</sup> H <sub>DEC(CH2)</sub> Diff. <sup>(a)</sup>	<sup>1</sup> H <sub>DEC(CH2)</sub> [Diff.] <sup>(c)</sup>	<sup>1</sup> H <sub>TMP</sub> Diff. <sup>(a)</sup>	<sup>1</sup> H <sub>TMP</sub> [Diff.] <sup>(c)</sup>
A : EC + DEC	11.01	1	11.01	9.62	9.62	9.14	9.14	n/a	n/a
$B : EC + DEC + LiPF_6$	5.96	1.85	11.01	3.75	6.92	3.90	7.21	n/a	n/a
D : (25%) TMP + EC + DEC + LiPF <sub>6</sub>	6.28	1.75	11.01	4.57	8.01	4.45	7.81	1.96	3.43
D : (50%) TMP + EC + DEC + LiPF <sub>6</sub>	6.33	1.74	11.01	5.34	9.29	5.07	8.81	2.33	4.05
H : (75%) TMP + EC + DEC + LiPF <sub>6</sub>	4.72	2.33	11.01	4.02	9.38	3.73	8.71	2.12	4.94
J : (100%) TMP + LiPF <sub>6</sub>	5.10	2.16	11.01	n/a	n/a	n/a	n/a	2.54	5.49
I : TMP	9.18	1.20	11.01	n/a	n/a	n/a	n/a	6.98	8.38

**Table S3.** <sup>1</sup>H Diffusion coefficients (10<sup>-10</sup> m<sup>2</sup> s<sup>-1</sup>) after corrections.

<sup>(a)</sup>: Experimental <sup>1</sup>H Diffusion Coefficients from DOSY measurements;

(b): Correction factor; determined by <sup>1</sup>H NMR DOSY experiments according to equation 2 (see Supplementary Paragraph 6)

<sup>(c)</sup>: <sup>1</sup>H Diffusion Coefficients after corrections.



Solutions	<b>∆</b> <sup>(a)</sup>	<sup>7</sup> Li Diff. <sup>(b)</sup>	<sup>7</sup> Li [Diff.] <sup>(c)</sup>
A : EC + DEC	1	n/a	n/a
$B : EC + DEC + LiPF_6$	1.85	1.73	3.21
D : (25%) TMP + EC + DEC + LiPF <sub>6</sub>	1.75	1.81	3.17
D : (50%) TMP + EC + DEC + LiPF <sub>6</sub>	1.74	2.15	3.74
H : (75%) TMP + EC + DEC + LiPF <sub>6</sub>	2.33	1.60	3.74
J : (100%) TMP + LiPF <sub>6</sub>	2.16	1.48	3.19
I : TMP	1.20	n/a	n/a

**Table S4.** <sup>7</sup>Li Diffusion coefficients ( $10^{-10}$  m<sup>2</sup> s<sup>-1</sup>) after corrections.

<sup>(a)</sup>: Correction factor; determined by <sup>1</sup>H NMR DOSY experiments according to equation 2 (see Supplementary Paragraph 6);

<sup>(b)</sup>: Experimental <sup>1</sup>H Diffusion Coefficients from DOSY measurements; <sup>(c)</sup>: <sup>1</sup>H Diffusion Coefficients after corrections.



Solutions	<b>∆</b> (a)	<sup>31</sup> P <sub>TMP</sub> Diff. <sup>(b)</sup>	<sup>31</sup> P <sub>TMP</sub> [Diff.] <sup>(c)</sup>
A : EC + DEC	1	n/a	n/a
$B : EC + DEC + LiPF_6$	1.85	n/a	n/a
D : (25%) TMP + EC + DEC + LiPF <sub>6</sub>	1.75	0.28	0.50
D : (50%) TMP + EC + DEC + LiPF <sub>6</sub>	1.74	0.42	0.73
H : (75%) TMP + EC + DEC + LiPF <sub>6</sub>	2.33	0.34	0.80
J : (100%) TMP + LiPF <sub>6</sub>	2.16	0.43	0.93
I : TMP	1.20	1.17	1.41

Table S5.  $^{31}P$  Diffusion coefficients (10 $^{-10}$  m<sup>2</sup> s<sup>-1</sup>) after corrections.

<sup>(a)</sup>: Correction factor; determined by <sup>1</sup>H NMR DOSY experiments according to equation 2 (see Supplementary Paragraph 6);

(b): Experimental <sup>1</sup>H Diffusion Coefficients from DOSY measurements; (c): <sup>1</sup>H Diffusion Coefficients after corrections.



#### 5. Coordination ratio "α" and coordination number of lithium by DOSY NMR experiments

Solutions	Composition <sup>(a)</sup>	<sup>1</sup> H D <sub>Tol</sub> <sup>(b)</sup>	<sup>1</sup> H D <sub>EC</sub> <sup>(b)</sup>	<sup>1</sup> H D <sub>DEC(CH2)</sub> <sup>(b)</sup>	<sup>1</sup> Н <sub>ТМР</sub> <sup>(b)</sup>	<sup>7</sup> Li D <sup>(b)</sup>	$\alpha_{\rm EC}^{(c)}$	$\alpha_{\text{DEC}}^{(c)}$	$\alpha_{\text{TMP}}^{(c)}$
A : EC:DEC	1:1	11.01	9.62	9.14	n/a	n/a			
B : EC:DEC:LiPF <sub>6</sub>	7.5:4.1:1	5.96	3.75	7.21	n/a	1.73	0.42 <u>+</u> 0.01	0.33 <u>+</u> 0.01	n/a
C:25%TMP:EC:DEC	1:1.5:1.5	10.26	8.96	8.32	7.46	n/a			
D:25%TMP:EC:DEC:LiPF <sub>6</sub>	2.1:5.6:3.1: 1	6.28	4.57	7.81	3.43	1.81	0.25 <u>+</u> 0.01	0.19 <u>+</u> 0.01	0.95 <u>+</u> 0.01
E : 50%TMP:EC:DEC	1.5:1:1	10.02	8.78	8.20	7.24	n/a			
F: 50%TMP:EC:DEC:LiPF <sub>6</sub>	4.2:3.7:2.1:1	6.33	5.34	8.81	4.05	2.15	$0.06 \pm 0.01$	0.04 <u>+</u> 0.01	0.92 <u>+</u> 0.01
G : 75%TMP:EC:DEC	6:1:1	9.24	8.22	7.78	6.74	n/a			
H:75%TMP:EC:DEC:LiPF <sub>6</sub>	6.4:1.9:1:1	4.72	4.02	8.71	4.94	1.60	0.07 <u>±</u> 0.01	$0.10 \pm 0.01$	0.72 <u>+</u> 0.01
I:100%TMP	1	9.18	n/a	n/a	8.38	n/a			
J : 100%TMP:LiPF <sub>6</sub>	8.5:1	5.10	n/a	n/a	5.49	1.48	n/a	n/a	0.56 <u>+</u> 0.01

**Table S6.** Coordination ratio  $\alpha$  of electrolytes EC, DEC and TMP in the solutions A to J.

<sup>(a)</sup>: Determined by considering the molar ratios in a 1 M LiPF<sub>6</sub> (or unsalted) solution prepared from a mixture of TMP+EC+DEC (v:v:v%, where v = volume) (see Table S1); <sup>(b)</sup>: <sup>1</sup>H Diffusion Coefficients have been extrapolated from <sup>1</sup>H DOSY measures and reported in units of  $10^{-10}$  m<sup>2</sup>/s;

<sup>(c)</sup>: The errors were calculated considering the 2% typical inaccuracy limit of the diffusion NMR techniques.

Solutions	Composition <sup>(a)</sup>	Coordination Number of Li <sup>(b)</sup>	%Li coordinated with TMP <sup>(c)</sup>	%Li coordinated with EC <sup>(c)</sup>	%Li coordinated with DEC <sup>(c)</sup>	structures presupposed Li(DEC/EC) <sub>x</sub> (TMP/TEP) <sub>y</sub>
A : EC:DEC	1:1					n/a
B : EC:DEC:LiPF <sub>6</sub>	7.5:4.1:1	4.5 <u>+</u> 0.1	0	69.95	30.05	Li(DEC/EC) <sub>4</sub> (TMP/TEP) <sub>0</sub>
C : 25%TMP:EC:DEC	1:1.5:1.5					n/a
D:25%TMP:EC:DEC:LiPF <sub>6</sub>	2.1:5.6:3.1: 1	4.0 <u>±</u> 0.1	50.07	35.15	14.78	Li(DEC/EC) <sub>2</sub> (TMP/TEP) <sub>2</sub>
E : 50%TMP:EC:DEC	1.5:1:1					n/a
F: 50%TMP:EC:DEC:LiPF <sub>6</sub>	4.2:3.7:2.1:1	4.2 <u>±</u> 0.1	92.66	5.32	2.02	Li(DEC/EC)≈0(TMP/TEP)≈4
G:75%TMP:EC:DEC	6:1:1					n/a
H:75%TMP:EC:DEC:LiPF <sub>6</sub>	6.4:1.9:1:1	4.8 <u>+</u> 0.1	95.19	2.75	2.06	Li(DEC/EC)≈0(TMP/TEP)≈4
I:100%TMP	1					n/a
J : 100%TMP:LiPF6	8.5:1	4.8 <u>+</u> 0.1	100	0	0	Li(DEC/EC)0(TMP/TEP)4

**Table S7.** Coordination number of Li in the solutions A to J.

<sup>(a)</sup>: Determined by considering the molar ratios in a 1 M LiPF<sub>6</sub> (or unsalted) solution prepared from a mixture of TMP+EC+DEC (v:v:v%, where v = volume) (see Table S1);

<sup>(b)</sup>: Coordination numbers of Li were calculated by multiplying the coordination ratios of the electrolyte solutions by their molar ratios;

<sup>(c)</sup>: Determined from the coordination number of lithium and the coordination ratios of the electrolyte compositions.

#### 6. Supplementary discussion.

As reported in the main text of the article, Li-coordination by phosphates leads to an upfield shift of the <sup>31</sup>P signals due to a major degree of d-orbital occupancy in the P-O bonds once Li<sup>+</sup> ion is coordinated to O=P (Fig. S6). However, since such a  $d_{\pi}$ -p<sub> $\pi$ </sub> bond-back donation phenomenon does not take place in the carbonate species, the main contribution to the observed <sup>13</sup>C NMR outcomes derives primarily from electronegativity. Therefore, a deshielding effect has been observed from the free DEC/EC species to the Li<sup>+</sup>-coordinated analogues (Fig. S4).

Corrections to the original diffusion NMR data presented in Supplementary Paragraph 4 have been carried out in order to minimize temperature and viscosity effects on the different solutions. In fact, it makes no sense to compare diffusion coefficients related to one (or more) species deriving from solutions that are different from each other in composition / concentration / ratio of their components. Solutions dissimilar for their composition or concentration may cause viscosity changes (and have different temperatures) affecting thus the corresponding diffusion coefficient values. A descriptive example is reported in Table S2 (third column) wherein the diffusion coefficient data for toluene differ considerably depending on the electrolyte solution in which toluene is dissolved, despite its mass is supposed to remain constant. Here, corrections to the original diffusion coefficient values allow several electrolyte solutions to be compared in a more accurate manner. Of note, toluene has now the same diffusion coefficient in all solutions (see diagram below Table S3). The diagrams gathered from Tables S3-S5 have been attained as follows. <sup>1</sup>H diffusion coefficients have been reported according to the Stokes-Einstein equation, 1, where D is diffusion coefficient, *k* is the Boltzmann constant, *T* is the temperature (in kelvin),  $\eta$  is the viscosity, and *r* is the hydrodynamic radius:

$$D = \frac{k T}{6 \pi \eta r}$$
(1)

By using toluene as internal reference, we can introduce a correction factor,  $\Delta_X$  (2), corresponding to the ratio between the diffusion coefficient of toluene in the solution A and that in a solution X (with X = A to J, see the first column in Table S2). Since toluene slightly interacts with the polar electrolyte solution, the corresponding hydrodynamic radius ( $r_{Tol}$ ) does not vary changing solution. Therefore,  $r_{Tol A} = r_{Tol X}$  and the correction factors  $\Delta_X$  appear as a constant that depends exclusively on the temperature and the viscosity of the two A and X solutions.

$$\Delta_X = \frac{D_{TolA}}{D_{TolX}} = \frac{\frac{k T_A}{6 \pi \eta_A r_{TolA}}}{\frac{k T_X}{6 \pi \eta_A r_{TolX}}} = \frac{T_A \eta_X}{T_X \eta_A}$$
(2)<sup>4</sup>

or 
$$\frac{T_X}{\eta_X} = \frac{T_A}{\Delta_X \eta_A}$$
 (3)

Diffusion coefficients for the electrolytes EC, DEC and TMP in the solution X ( $D_{el} x$ ) can be determined according to a modified Stokes-Einstein equation (5):

$$D_{el X} = \frac{K T_X}{6 \pi \eta_X r_{el X}} = \frac{K T_A}{6 \pi \Delta_X \eta_A r_{el X}}$$
(4)

$$\left[\Delta_{X} D_{el X}\right] = \frac{K T_{A}}{6 \pi \eta_{A}} \frac{1}{r_{el X}}$$
(5)

If diffusion coefficients  $D_{el X}$  (equation 4) rely on temperature, viscosity as well as hydrodynamic radius of the electrolyte in the solutions X, the modified diffusion coefficients (equation 5) are dependent exclusively on

the hydrodynamic radius, since  $T_A/\eta_A$  is a constant. In this way, the effect of temperature and viscosity changes can be bypassed and a direct comparison of diffusion coefficients could be meaningful. We can display thus a diagram where "revised" <sup>1</sup>H diffusion coefficients (*i.e.* [ $\Delta_X D_{el X}$ ]) have been related to the percentage of TMP (% vol.) in the solution X (see Table S3 and the below chart). Despite <sup>7</sup>Li and <sup>31</sup>P NMR spectra have not an internal standard (like toluene for <sup>1</sup>H NMR measures), a similar procedure however has been adopted using the same  $\Delta_X$  correction factor already used for <sup>1</sup>H NMR DOSY experiments (see Tables S4 and S5).

Together with the chemical shift information, the self-diffusion coefficients obtained from <sup>1</sup>H, <sup>7</sup>Li and <sup>31</sup>P NMR DOSY enable us to more details on the Li<sup>+</sup> solvation. Concerning to the chart of <sup>1</sup>H Diff. *vs.* % vol. TMP, we can observe that <sup>1</sup>H TMP diffusion coefficients increase according to the percentage of phosphate in the electrolyte composition. This is due to the major portion of the free phosphate in solution, which is consistent with the  $\alpha_{TMP}$  calculated in Table S6. A similar trend has been depicted in the chart <sup>31</sup>P Diff. *vs.* % vol. TMP, where <sup>31</sup>P Diff. of TMP molecules augments as the percentage of TMP increases. In the case of <sup>7</sup>Li Diff. *vs.* % vol. TMP, no meaningful changes of the <sup>7</sup>Li coefficient diffusions have been observed (the slight fluctuation of the data trend around 3.5  $10^{-10}$  m<sup>2</sup>/s may be easily related to the limit error of the DOSY technique). This indicates that the TMP concentration does not affect the diffusion and therefore the size of the aggregate around Li<sup>+</sup> is supposed to remain constant. Although we cannot provide a direct diffusion-molecular weight correlation from DOSY NMR data<sup>5,6</sup> (internal reference are not possible because of the shape and density of the electrolyte solutions), on the base of the literature,<sup>7-12</sup> we may postulate that the most plausible structure is a separate ion pair with a general composition Li(DEC/EC)<sub>x</sub>(TMP)<sub>y</sub> (x+y=<4) according to the phosphate to lithium molar ratio (see Figure 2c).

Concerning the calculation of coordination ratio  $\alpha$  and coordination number of Li (Tables S6 and S7 in Supplementary Paragraph 5), we followed a procedure already reported by Amine *et al.*<sup>4</sup>

Indeed, we suppose that the experimentally observed electrolyte diffusion coefficient in a Li-salted solution  $(D_{exp})$  is the average of the diffusion coefficients of the electrolyte in dissociated  $(D_{free \ el})$  and Li-coordinated form  $(D_{Li-coord \ el})$ , where  $\alpha$  is the ratio of the coordinated electrolyte (equation 6).

$$D_{exp} = D_{Li-coord \ el} * \alpha + D_{free \ el} * (1 - \alpha)$$
(7)

## 7. Supporting Information file Bibliography

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