Supporting Information

Influence of Bis(2,2,2-Trifluoroethyl) Carbonate Flame Retarding Co-Solvent on Interfacial Chemistry in Carbonate Ester Lithium-Ion Battery Electrolytes

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Figure S1. Galvanostatic cycling (discharge) over 100 cycles for NMC622|graphite cells with 95 % and 100 % TFEC electrolytes, saturated with LiPF₆ (<1 M).



Figure S2. Photographs of flammability tests for electrolytes containing 30 %, 50 % and 0 % (LP57) TFEC. Lowering of the fume hood sash caused the flame for the 30 % TFEC electrolyte to extinguish so was categorised as flame retarding, while the 50 %TFEC electrolyte did not light at all and was categorised as non-flammable. The self-extinguishing time (SET) could only be determined for LP57 as 61.5 s g^{-1} and is therefore classed as flammable.



Figure S3. Coulombic efficiency over 200 cycles for NMC622|graphite cells with electrolytes containing up to 90 % TFEC. The shaded area represents standard deviation of two samples; LP57 is only a single sample.

Electrolyte	Conductivity at approx. room temperature / mS cm ⁻¹
LP57	9.14 (25.3 °C)
30 % TFEC (1 M LiPF ₆)	5.46 (27.6 °C)
50 % TFEC (1 M LiPF ₆)	4.08 (28.3 °C)
70 % TFEC (1 M LiPF ₆)	2.33 (27.1 °C)
90 % TFEC (saturated, <1 M LiPF ₆)	0.84 (26.2 °C)

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		TFEC	EC	EMC	LiPF ₆	TFEC:Li	EC:Li	EMC:Li
90% TFEC	Volume (ml)	0.90	0.03	0.07	-			
	Mass (g)	1.36	0.04	0.07	< 0.152			
	Amount (mmol)	6.01	0.46	0.68	< 1.00	< 6.01	< 0.46	< 0.68
70% TFEC	Volume (ml)	0.70	0.09	0.21	-			
	Mass (g)	1.06	0.12	0.21	0.152			
	Amount (mmol)	4.68	1.37	2.04	1.00	4.68	1.37	2.04
50% TFEC	Volume (ml)	0.50	0.15	0.35	-			
	Mass (g)	0.76	0.20	0.35	152.00			
	Amount (mmol)	3.34	2.28	3.40	1.00	3.34	2.28	3.40
30% TFEC	Volume (ml)	0.30	0.21	0.49				
	Mass (g)	0.45	0.28	0.49	152.00			
	Amount (mmol)	2.00	3.19	4.75	1.00	2.00	3.19	4.75
0% TFEC	Volume (ml)	0.00	0.30	0.70				
	Mass (g)	0.00	0.40	0.71	152.00			
	Amount (mmol)	0.00	4.56	6.79	1.00	0.00	4.56	6.79

Table S2. Calculations of solvent-lithium molar ratios, assuming room-temperature densities of 1.51, 1.34 and 1.01 g/ml for TFEC, EC and EMC, respectively, as reported by the manufacturer.



Figure S4. Cyclic voltammograms showing the reduction peaks of TFEC containing electrolytes in Li|Graphite cells.



Figure S5. Galvanostatic cycling over 200 cycles for a NMC622|graphite cells with electrolytes containing up to 70 % tris(2,2,2-trifluoroethyl) phosphate (TFEP) and 1 M LiPF₆.



Figure S6. C 1s, F 1s, O 1s, P 2p, and Li 1s X-ray photoelectron spectra, measured at 2.35 keV excitation energy, for a graphite electrode cycled in LP57 (4 cycles).



Figure S7. O 1s X-ray photoelectron spectra, measured at two excitation energies, for graphite electrodes cycled to 4 cycles in electrolytes with up to 90% TFEC.



Figure S8. Li 1s X-ray photoelectron spectra, measured at two excitation energies, for graphite electrodes cycled to 4 cycles in electrolytes with up to 90% TFEC. Shaded areas indicate density attributed to intercalated lithium.



Figure S9. P 2p X-ray photoelectron spectra, measured at two excitation energies, for graphite electrodes cycled to 4 cycles in electrolytes with up to 90% TFEC.

Table S3. Fitting specification for X-ray photoelectron spectra.

<u>1487 eV</u>		<u>30 % TFEC</u>			<u>50 % TFEC</u>			<u>70 % TFEC</u>			<u>90 % TFEC</u>	
		FWHM			FWHM			FWHM			FWHM	
C 1s	BE / eV	/ eV	% Area	BE / eV	/ eV	% Area	BE / eV	/ eV	% Area	BE / eV	/ eV	% Area
Li _x C	283.19	1.17	0.27	283.19	0.77	0.57	283.14	0.84	3.41	283.06	0.92	2.97
C=C	284.18	0.80	0.01	284.02	0.54	3.56	283.87	0.60	1.15	283.83	0.64	0.87
C–C	284.85	0.95	0.00	285.00	0.92	10.33	285.00	0.89	6.02	285.00	0.80	4.04
C0	285.72	1.21	74.65	285.70	1.28	50.66	285.70	1.32	52.43	285.70	1.38	59.51
C=O	287.41	1.40	12.85	287.35	1.33	14.98	287.35	1.40	17.54	287.35	1.40	12.83
0–C=0	288.35	1.53	3.57	288.38	1.43	8.11	288.51	1.63	8.82	288.50	1.66	10.11
Inorg. CO ₃ ²⁻	289.91	0.92	0.18	290.00	1.23	3.14	289.75	0.96	1.61	289.86	0.96	1.98
Polycarbonates	290.51	0.87	5.89	290.53	1.17	3.90	290.70	1.49	6.00	290.66	1.34	3.87
C–F ₂	291.88	1.26	1.09	291.87	1.29	1.55	291.82	1.38	0.81	291.98	0.53	0.46
C–F ₃	294.00	0.88	1.48	293.86	1.02	3.21	293.85	1.06	2.21	294.02	1.11	3.37
F 1s												
LiF	685.90	1.45	22.73	685.87	1.45	30.95	685.87	1.53	53.10	685.91	1.49	57.82
PF _x	687.73	1.56	52.87	687.60	1.64	33.78	687.69	1.70	26.49	687.73	1.70	17.53
C–F	689.03	1.93	24.40	689.04	1.96	35.27	689.04	2.00	20.41	689.17	2.00	24.65
O 1s												
Li ₂ O	529.50	2.00	0.44	529.50	1.80	0.53	529.50	2.00	0.95	529.03	1.95	3.52
P=O	532.28	1.61	4.65	532.40	1.73	10.43	532.30	1.80	42.36	532.26	1.80	34.39
C=0/CO ₃ ²⁻	533.40	1.28	38.65	533.28	1.56	47.98	533.20	1.78	30.42	533.20	1.60	33.72
P0/C0	534.71	1.76	56.26	534.66	1.80	41.06	534.52	1.79	26.26	534.68	1.80	28.38

<u>2984 eV</u>	<u>30 % TFEC</u>			<u>50 % TFEC</u>			<u>70 % TFEC</u>			<u>90 % TFEC</u>		
		FWHM			FWHM			FWHM			FWHM	
C 1s	BE / eV	/ eV	% Area	BE / eV	/ eV	% Area	BE / eV	/ eV	% Area	BE / eV	/ eV	% Area
Li _x C	283.19	0.94	0.35	283.15	0.75	0.74	283.20	0.86	8.23	283.16	1.04	9.92
C=C	284.48	0.77	10.77	284.11	0.79	10.19	283.91	0.79	6.35	284.01	0.80	4.25
C–C	285.00	0.92	5.52	284.98	1.30	11.47	285.00	1.03	7.64	285.00	1.06	6.24
C0	285.83	1.60	52.02	285.77	1.55	46.86	285.78	1.47	49.82	285.75	1.54	53.95
C=0	287.36	1.40	10.81	287.35	1.40	11.43	287.35	1.39	11.16	287.35	1.40	9.29
0-C=0	288.49	1.40	7.78	288.39	1.62	7.74	288.59	1.68	8.69	288.52	1.51	7.36
Inorg. CO ₃ ²⁻	289.75	1.13	2.90	289.88	1.49	4.42	289.85	0.76	1.79	289.75	0.93	2.90
Polycarbonates	290.66	1.15	4.39	290.70	1.18	3.01	290.70	1.41	4.02	290.65	1.22	2.95
C–F ₂	291.81	1.28	2.35	291.80	1.05	1.72	291.81	0.97	1.15	292.03	0.99	0.67
C–F ₃	294.06	1.67	3.12	293.95	1.22	2.43	294.01	1.13	1.14	294.10	1.43	2.48
F 1s												
LiF	686.06	1.60	60.13	685.97	1.63	57.53	686.04	1.60	67.19	686.00	1.60	67.30
PF _x	687.82	1.70	16.60	687.75	1.70	17.64	687.85	1.69	16.30	687.85	1.70	13.95
C–F	689.30	2.00	23.26	689.16	2.00	24.83	689.15	2.00	16.51	689.29	2.00	18.75
O 1s												
Li ₂ O	529.50	2.00	1.56	529.50	1.77	0.06	529.50	1.99	2.03	529.14	2.00	9.13
P=O	532.40	1.51	10.94	532.40	1.72	17.59	532.24	1.80	42.14	532.20	1.80	39.25
C=O/CO ₃ ²⁻	533.54	1.80	59.87	533.47	1.80	53.75	533.36	1.61	34.22	533.29	1.66	31.67
P0/C0	535.02	1.80	27.62	534.93	1.80	28.60	534.78	1.80	21.62	534.78	1.80	19.95

<u>2350 eV</u>	<u>LP57</u>							
		FWHM						
C 1s	BE / eV	/ eV	% Area					
C=C	284.00	0.64	7.27					
C–C	284.81	1.01	3.90					
C–O	286.20	1.60	58.65					
C=O	287.35	1.40	17.03					
0-C=0	288.55	1.07	4.70					
Inorg. CO ₃ ²⁻	289.75	1.50	3.69					
Polycarbonates	290.80	1.16	2.77					
C–F ₂	291.80	1.53	1.99					
F 1s								
LiF	686.50	1.48	62.96					
PF _x	687.55	1.49	28.16					
C–F	689.30	1.73	8.88					
O 1s								
Li₂O								
P=O	532.20	1.80	13.79					
C=O/CO ₃ ²⁻	533.73	1.80	52.29					
P-0/C-0	535.09	1.80	33.92					