Supporting Information For:

High-voltage and intrinsically safe supercapacitors based on a trimethyl phosphate electrolyte

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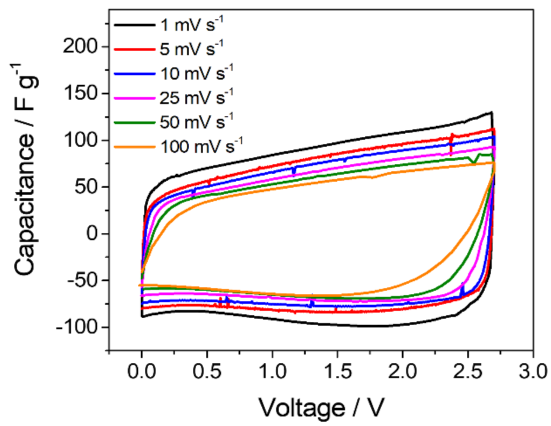

Fig. S1. Cyclic voltammetry of the TMP electrolyte at different scan rate ranging from 1 to 100 mV s^{-1}.

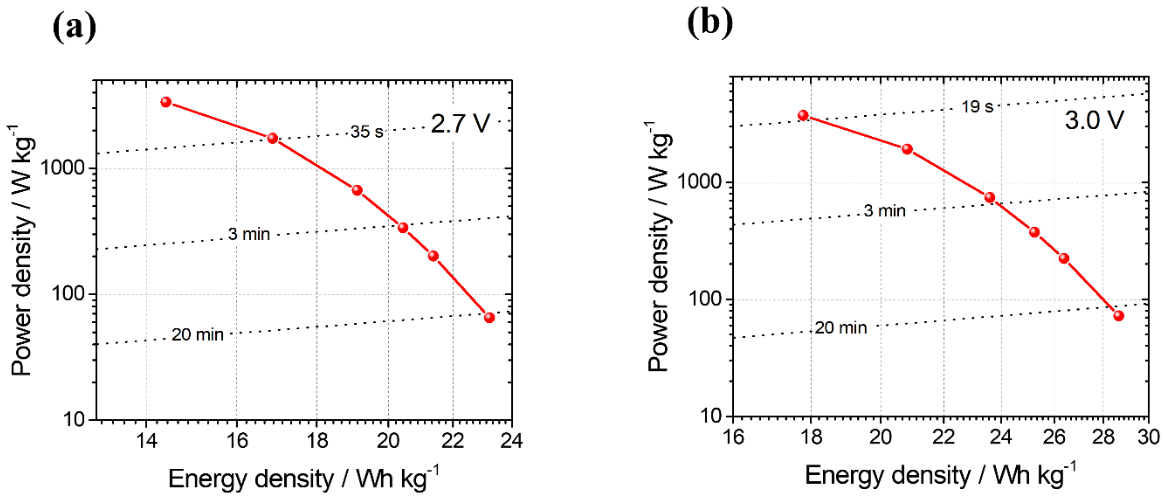

Fig. S2. Ragone plot of EDLCs at the cutoff voltage of 2.7 V (a) and 3.0 V (b).

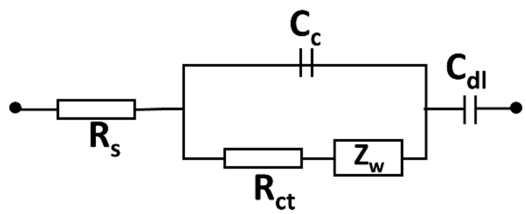

Fig. S3. The equivalent circuit model for the Nyquist plot; where, R_s and R_{ct} denote the electrolyte resistance and charge transfer resistance, respectively. C_c and C_{dl} indicate the interfacial contact capacitance and electric double layer capacitance, respectively. Z_w is the Warburg impedance.

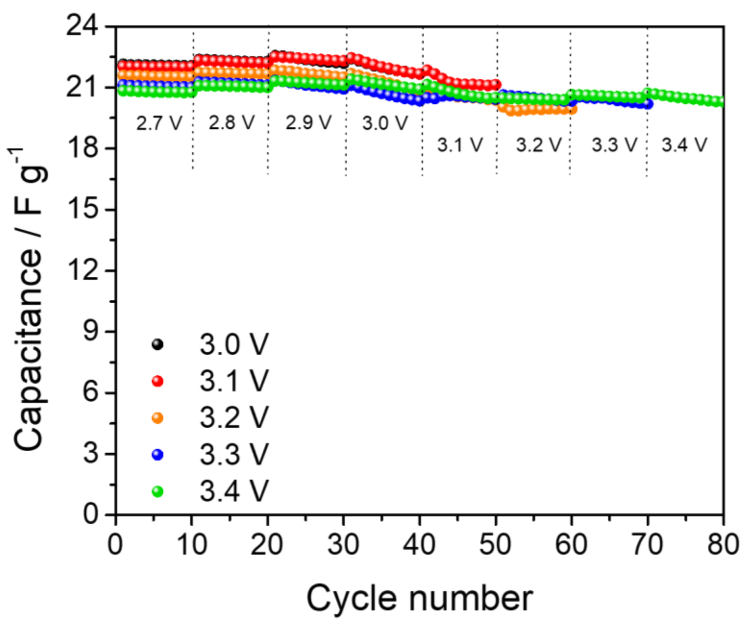

Fig. S4. Discharge capacitance of the cell from 2.7 V to the upper voltage.

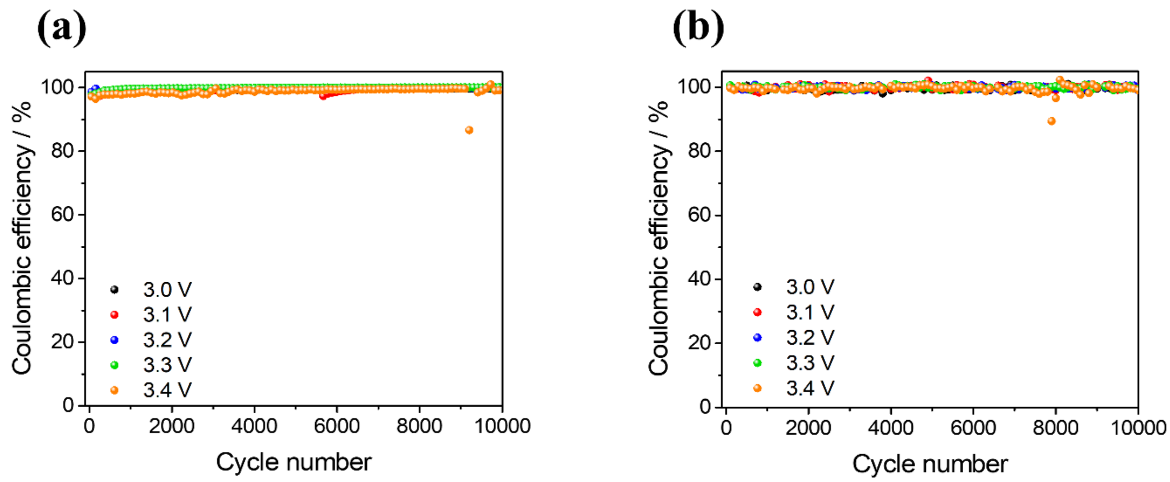

Fig. S5. Coulombic efficiency during charge–discharge cycling test carried out at different working voltages and a current density of 0.1 A g^{-1} (a) and 2.5 A g^{-1} (b).

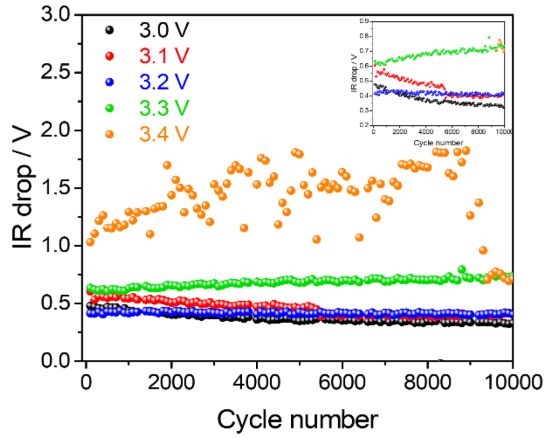

Fig. S6. Internal ohmic drops during charge–discharge cycling test carried out at different working voltages and a current density of 2.5 A g^{-1}.

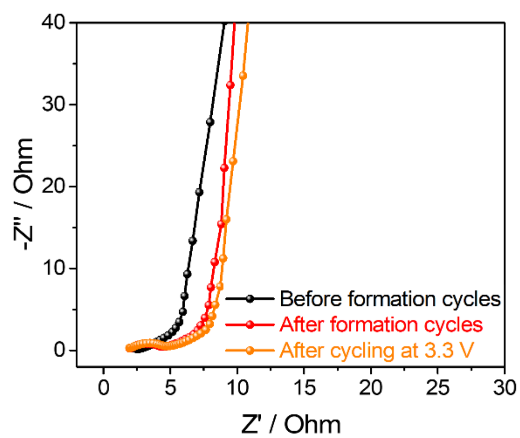

Fig. S7. Nyquist plots of the EDLCs before and after formation cycles, as well as after cycling test, which was performed after the formation cycles, at the voltage of 3.3 V.

Table S1 The Van der Waals volume and effective molecular radius of the solvents[a].

Molecule	Van der Waals volume (Å^3)	Relative volume (%)	Radii (Å)	Relative radii (%)
TPP	278.69	100	4.05	100
TBP	262.43	94.1	3.97	98.0
TEP	162.32	58.2	3.38	83.4
TMP	112.27	40.2	2.99	73.8

[a] All details regarding the calculation methodology are mentioned in the ref[1,2].

Table S2 The resistances and capacitance obtained from fitting of the EIS spectra.

Rs	R_{ct}	C_{dl}
1.45 Ω	1.20 Ω	0.329 F

Table S3 Comparison of properties and performances of TMP electrolyte and conventional PC, and AN-based electrolytes.

	PC-based electrolyte[a]	AN-based electrolyte[a]	TMP-based electrolyte[b]
Capacitance (F g^{-1})	24.0	25.6	23.9
Potential window (V)	4.85	5.07	5.90
Ionic conductivity (mS cm^{-1})	12.1	45.5	10.0
Cycling durability (%)[c]	87.5	87.9	83.2
Safety (s g^{-1})[d]	166	138	0

[a] Ref[1,2]

[b] This work.

[c] Capacitance retention of the cells with the given electrolyte systems after floating test for 1000 h at a voltage of 3.0 V.

[d] The safety of the electrolyte was determined by the SET values. The SET values were defined by normalizing the combustion time against the electrolyte mass (refer to characterization section).

REFERENCE

1. H. V. T. Nguyen, K. Kwak and K. K. Lee, *Electrochim. Acta*, 2019, **299**, 98-106.
2. H. V. Nguyen, A. Bin Faheem, K. Kwak and K. K. Lee, *J. Power Sources*, 2020, **463**, 10.