Electronic Supplementary Material (ESI)

S1. Methods

Molecular dynamics (MD) simulation: We used the relaxed system as a starting configuration. As it is before system relaxation MD, energy minimization was carried out with a composite protocol of steepest descent using termination gradients of 100 $kJ\ (mol \cdot nm)$. A 10 ns NPT relaxation run at 298K for the equilibrium MD simulation. The Nose´-Hoover thermostat was used to maintain the equilibrium temperature at 298 K, and periodic boundary conditions were imposed on all three dimensions [1]. The Particle Mesh-Ewald method was used to compute long-range electrostatics within a relative tolerance of $1x10^{-6}$ [2,3]. A cut-off distance of 1nm was applied to real-space Ewald interactions. The same value was used for van der Waals interactions. The LINCS algorithm was applied to constrain bond lengths of hydrogen atoms [4]. A leap-frog algorithm was used with a time step of 1 fs [5].

S2. Figures and Tables

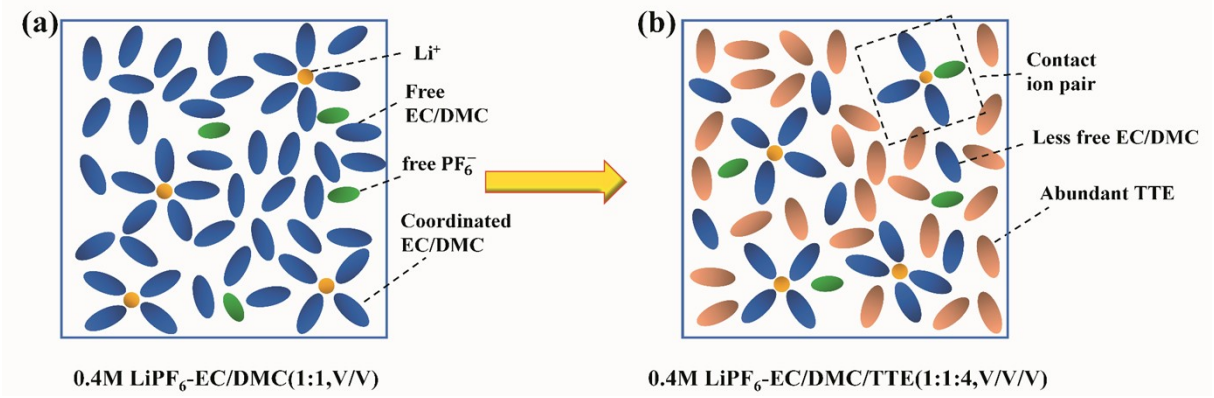

Fig. S1 The schemes of the Li^+-solvation structures in the 0.4M $LiPF_6$-EC/DMC (1:1, v/v) and 0.4M $LiPF_6$-EC/DMC/TTE (1:1:4, v/v/v)

Table S1 The compositions of electrolytes for all-atom MD simulation.

	PF_6^-	Li^+	EC	DMC	TTE	Box size (nm)
0.4M-11	48	48	900	704	0	6.14*6.14*6.14
0.4M-111	48	48	600	469	265	6.04*6.04*6.04
0.4M-112	48	48	450	352	398	6.00*6.00*6.00
0.4M-113	48	48	360	281	477	5.98*5.98*5.98
0.4M-114	48	48	300	234	530	5.96*5.96*5.96

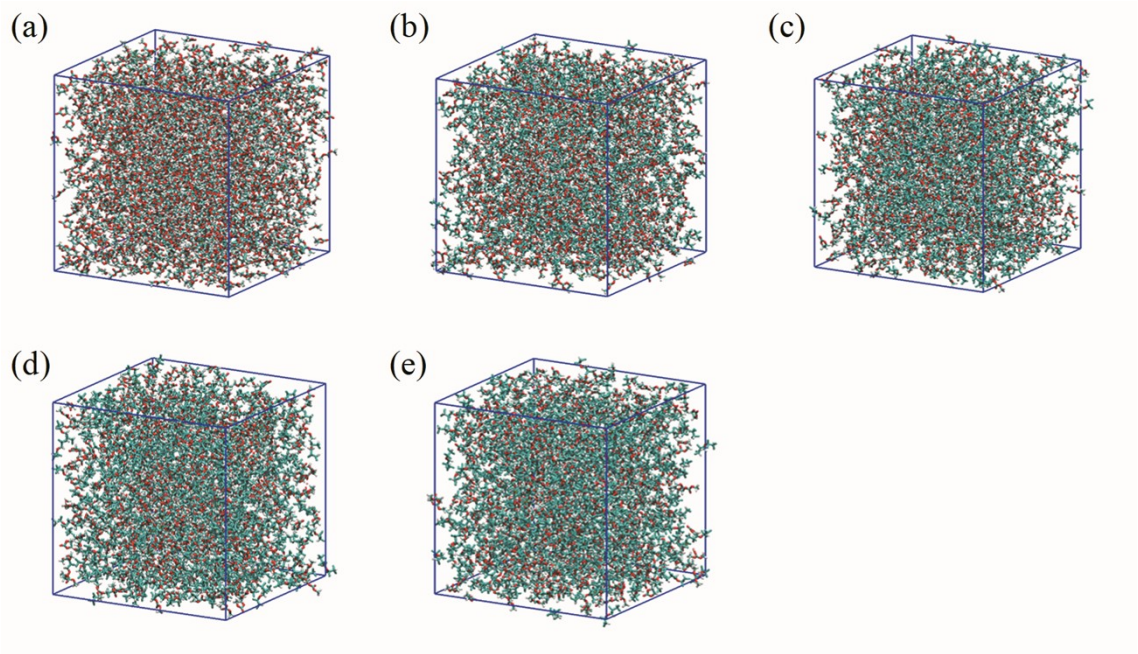

Fig. S2 All-atom MD simulation snapshots of (a)0.4M-11, (b)0.4M-111, (c)0.4M-112, (d)0.4M-113, (e)0.4M-114. Color code: H, White; O, Red; C, Pale blue; Li, Dull yellow; P, Green; F, Dark blue.

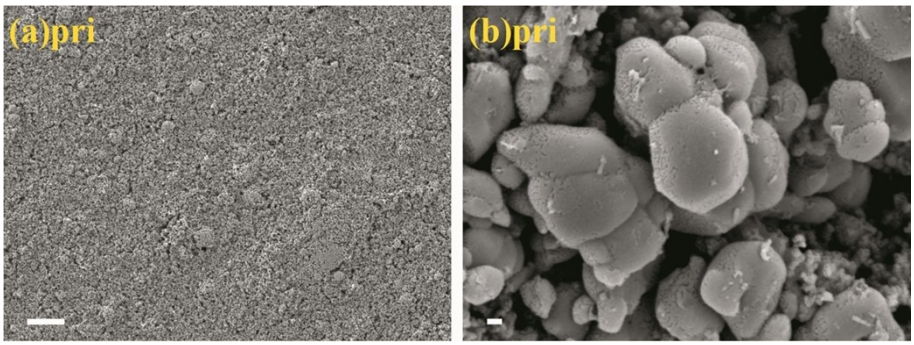

Fig. S3 Top view of LFP cathode before cycling (a) and morphology of LFP particles before cycling (b). Scale bars, 10μm (a) and 100nm (b).

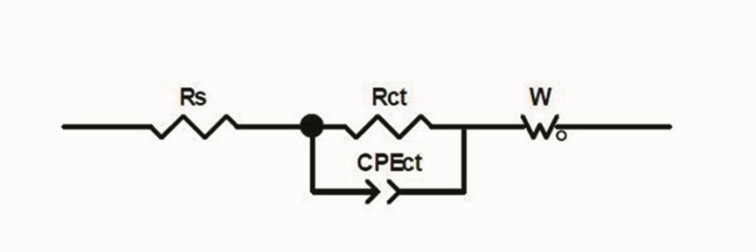

Fig. S4 Equivalent circuit used for fitting the EIS of Li||LFP cells.

Table S2 EIS fitting results for Li||LFP cells with different electrolytes.

Li||LFP cells	**After 3 cycles**		**After 302 cycles**	
	Rs(Ω)	**Rct(Ω)**	**Rs(Ω)**	**Rct(Ω)**
0.4M-11	3.33	175.1	52.07	379.6
0.4M-111	3.57	75.62	6.77	235.5
0.4M-112	3.8	71.4	6.23	178
0.4M-113	4.1	38.54	6.57	47.5
0.4M-114	5.43	26	7.80	31.13
1M-11	3.58	112.1	8.66	239.6

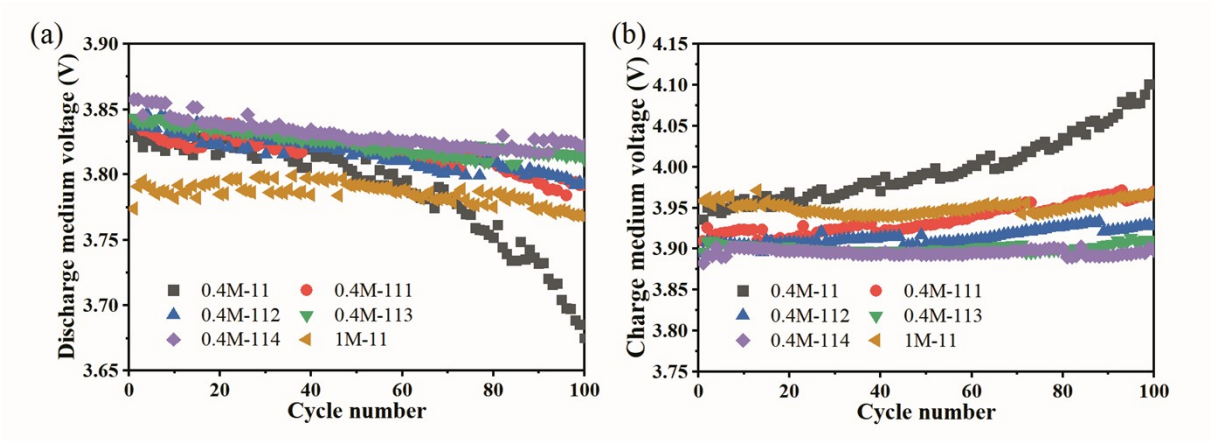

Fig. S5 The discharge medium voltages (a) and charge medium voltages (b) of the Li||NCM811 cells with different electrolytes at 1C.

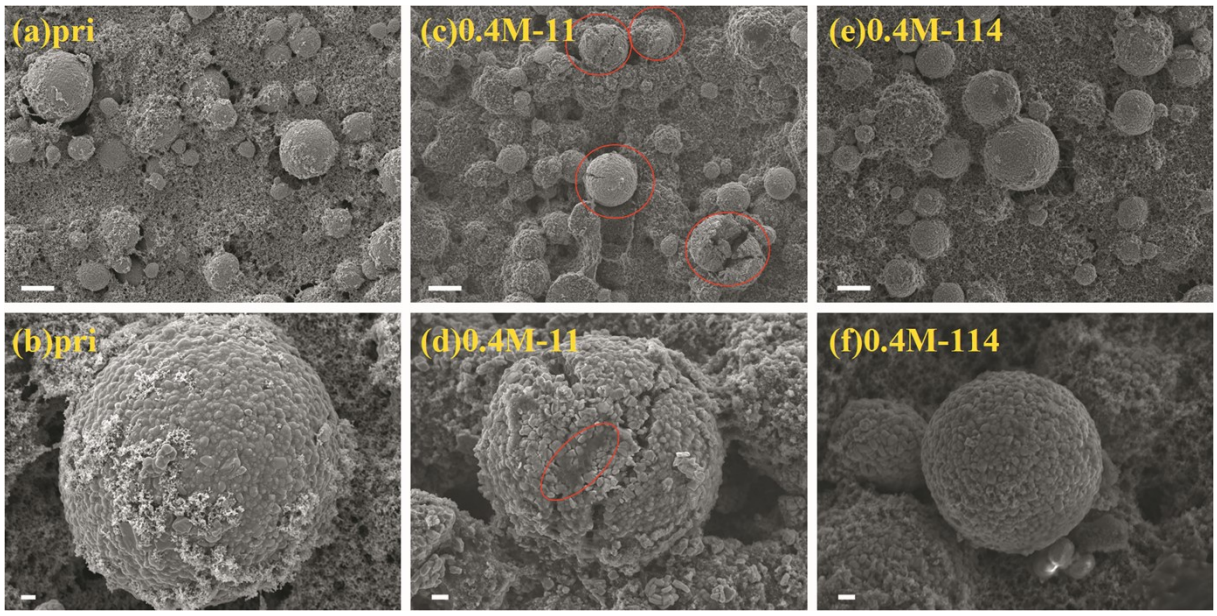

Fig. S6 Morphologies of NCM811 cathodes before cycling (a, b) and after 100 cycles in the 0.4M-11(c, d) and 0.4M-114 electrolyte (e, f). Scale bars, 10μm (a, c, e) and 1μm (b, d, f).

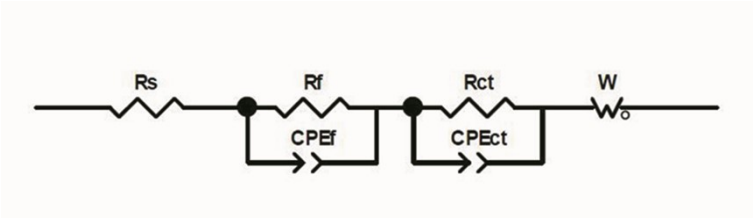

Fig. S7 The equivalent circuit used for fitting the EIS of Li||NCM811 cells.

Table S3 EIS fitting results for Li||NCM811 cells with different electrolytes.

Li||NCM811 cells	**After 4 cycles**			**After 103 cycles**		
	R_s(Ω)	**R_f(Ω)**	**R_{ct}(Ω)**	**R_s(Ω)**	**R_f(Ω)**	**R_{ct}(Ω)**
0.4M-11	3.74	15.56	135.7	18.24	48.07	277.8
0.4M-111	4.30	16.16	109.1	9.86	29.86	213
0.4M-112	4.92	21.76	103	8.70	26.51	163.1
0.4M-113	6.13	21.03	64.71	7.37	21.23	112.6
0.4M-114	6.62	22.88	53.97	6.38	16.2	92.46
1M-11	4.16	22.84	79.18	9.91	24.2	171.5

References

[1] J. Berendsen, H. J.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, *J. Chem. Phys.* **1984**, *81*, 3684.

[2] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, L. G. Pedersen, *J. Chem. Phys.* **1995**, *103*, 8577.

[3] L. G. Astrakas, C. Gousias, M. Tzaphlidou, in *J. Appl. Phys.*, **2012**.

[4] B. Hess, H. Bekker, H. J. C. Berendsen, J. G. E. M. Fraaije, *J. Comput. Chem.* **1997**, *18*, 1463.

[5] W. F. Van Gunsteren, H. J. C. Berendsen, *Mol. Simul.* **1988**, *1*, 173.