

Supplementary material

A non-flammable electrolyte for long-life lithium ion batteries operating over a wide temperature range

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Experiment

Preparation of electrolyte and electrode

GBL, LiPF₆ and LiODFB (Zhangjiagang Guotai-Huarong Co., Ltd) were used as received. FPPN (TCI (Shanghai) Development Co., Ltd) was further dried with 4Å molecular sieves. Electrolytes of 1M LiPF₆-EC/DMC/DEC (1:1:1, vol. % ratio, Shanghai Songjing High-tech Co., Ltd) (marked as LBE 302) and 1M LiPF₆-EC/DMC/DEC +4 wt% FPPN (marked as LBE 302 +4 wt% FPPN) were used as the reference electrolytes. Electrolytes of 1 M LiPF₆-GBL (marked as LiPF₆-GBL), 1 M LiPF₆-GBL/FPPN (96:4 wt%) (marked as LiPF₆-GBL/FPPN (96:4)) and 1M LiPF₆-GBL/FPPN (96:4 wt%) + 2 wt% LiODFB (marked as LiPF₆-GBL/FPPN (96:4) + 2 wt% LiODFB) electrolytes were gained by dissolving 1 M LiPF₆ in the mixture of GBL and FPPN in a 96:4 wt% ratio. The LiODFB-containing electrolyte was prepared by adding 2 wt% LiODFB to the LiPF₆-GBL/FPPN (96:4) electrolyte. The water content of each of the electrolytes was determined by Karl-Fisher titration (Metrohm 73KF coulometer), and the value was limited in 30 ppm. An argon glove box is used to conduct the preparation of electrolyte (H₂O < 0.1ppm, O₂ < 0.1ppm).

The compositions of electrodes are listed in Table S1. In the glove box, full cells were assembled with LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode (NCM cathode), graphite anode and PE separator.

Table S1 Compositions of electrode.

	LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂ cathode	Graphite anode
Active materials	94.5 wt%	92 wt%
Carbon black	2.5 wt%	3 wt%
Binder	3 wt% polyvinylidene fluoride (PVDF)	2.5 wt% carboxy methyl cellulose (CMC) 2.5 wt% styrene butadiene rubber (SBR)
Current collector	aluminum foil	copper foil

Average electrode loading	8.8 mg cm ⁻²	4.7 mg cm ⁻²
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Flammability test

According to the reported method, the flammability test was implemented.¹ 1 g electrolyte was instilled into a lump of glass fiber cotton (0.2 g). The soaked glass fiber cotton was ignited by a flame of the lighter, and the flame contacted with the cotton until 10 s had passed. Once the flame of the lighter was removed, the flame of the electrolyte was timed until it extinguished.

SEM-EDS and XPS characterization

Scanning electron microscopy (SEM, NOVA NanoSEM NPE218) was used to observe the surface morphology of electrodes. Energy-Dispersive Spectroscopy (EDS, RISE-MAGNA) was used to watch the distribution of elements on the surface of electrodes. XPS measurements were conducted with an AXIS Ultra DLD instrument using aluminum K X-ray radiation. After cycling, disassembly of cells was implemented in an argon glove box. For LBE 302 electrolyte, the cycled electrodes were soaked in DMC solvent overnight and washed by DMC in order to remove the salt residue and EC. After that, the cycled electrodes were dried for 3 days under vacuum at 60 °C. The electrodes cycled in GBL-based electrolytes were prepared by using GBL instead of DMC.

Electrochemical measurements

Electrochemical tests were implemented by using CR-2016 coin cells to evaluate the electrochemical performances of electrolytes in graphite/NCM full cells. To ensure the sufficient infiltrate of electrolyte into the electrodes, cells were stayed for 16 hours before the charge-discharge (C-D) tests. The test procedure consisted of three-cycle activation of full cell at 0.1C, which was regarded as the formation step of the cells. Afterwards, full cells were cycled between 2.5 V to 4.2

V at a constant current. The current rate was calculated according to the loading mass of cathode materials and the nominal capacity of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (165 mAh g^{-1}). A three-cycle activation of full cell was performed at 0.1C, which was called as the formation step. A Land CT2001A cell test instrument was used for the C-D tests.

The linear sweep voltammetry (LSV) measurement was performed on a CHI660D electrochemistry workstation. Here, a 3 mm diameter glassy carbon electrode, which was polished with alumina paste ($d=0.3 \mu\text{m}$, Beijing Innochem Technology Co., Ltd), was used as WE and metallic lithium as reference/counter electrode. The tests of electrochemical impedance spectroscopy (EIS) and LSV were conducted on a CHI660D electrochemistry workstation. Conductivity of all the electrolytes was applied by a DDS-11A conductivity meter at 25 °C. Viscosity was obtained by using a viscometer (DV-III ULTRA, Brookfield Engineering Laboratories, Inc).

- 1 P. Murmann, X. Mönnighoff, N. von Aspern, P. Janssen, N. Kalinovich, M. Shevchuk, O. Kazakova, G.-V. Röschenthaler, I. Cekic-Laskovic and M. Winter, *Journal of The Electrochemical Society*, 2016, **163**, A751-A757.

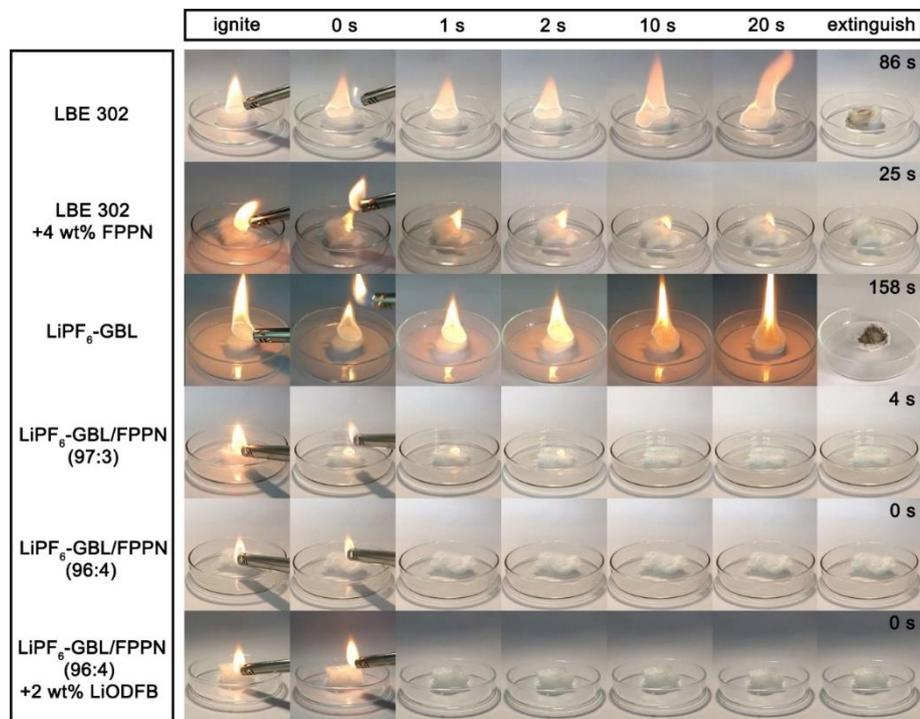


Fig. S1 flammability test of different electrolytes.

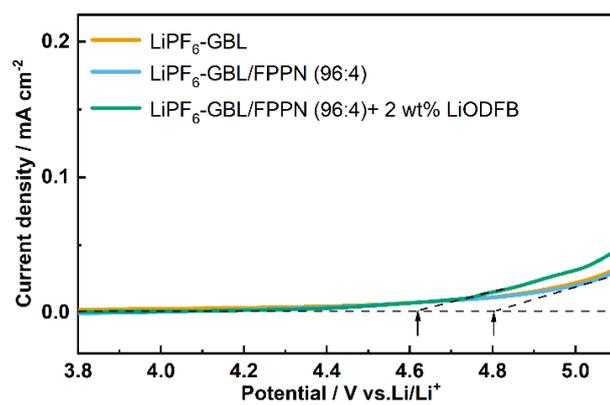


Fig. S2 LSV curves of different electrolyte.

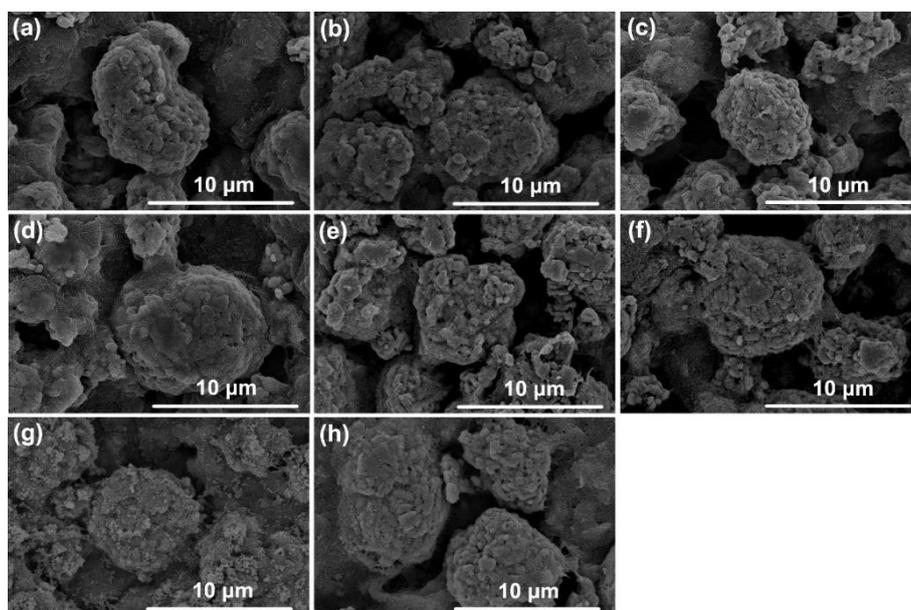


Fig. S3 SEM images of (a) pristine cathode and the cycled cathodes with (b) LBE 302, (c) LBE 302 + 4 wt% CPN, (d) LiPF₆-GBL, (e) LiPF₆-GBL/CPN (96:4) and (f) LiPF₆-GBL/CPN (96:4) + 2 wt% LiODFB electrolytes after formation step and cycled cathodes with (g) LBE 302 and (h) LiPF₆-GBL/CPN (96:4) + 2 wt% LiODFB electrolytes after 500 cycles test.

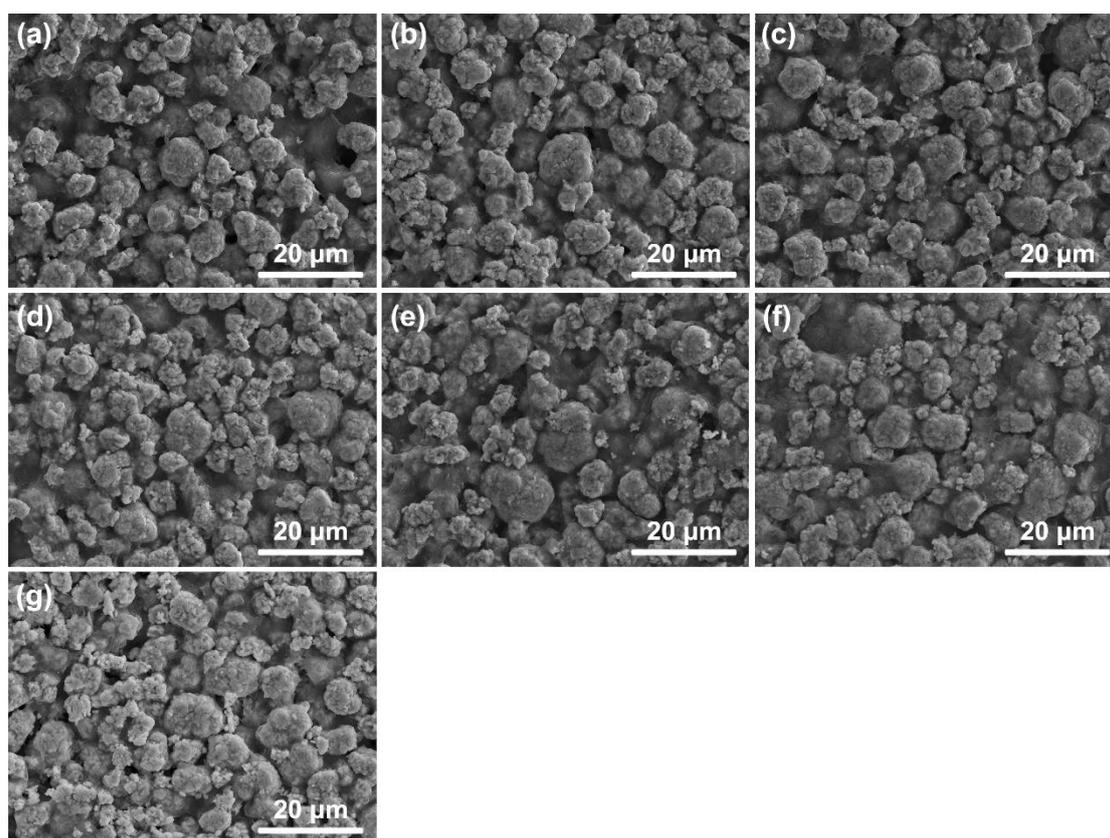


Fig. S4 SEM images of cycled anodes with (a) LBE 302, (b) LBE 302 + 4 wt% FPPN, (c) LiPF₆-GBL, (d) LiPF₆-GBL/FPPN (96:4) and (e) LiPF₆-GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after formation step, and the cycled anodes with (f) LBE 302 and (g) LiPF₆-GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after 500 cycles test.

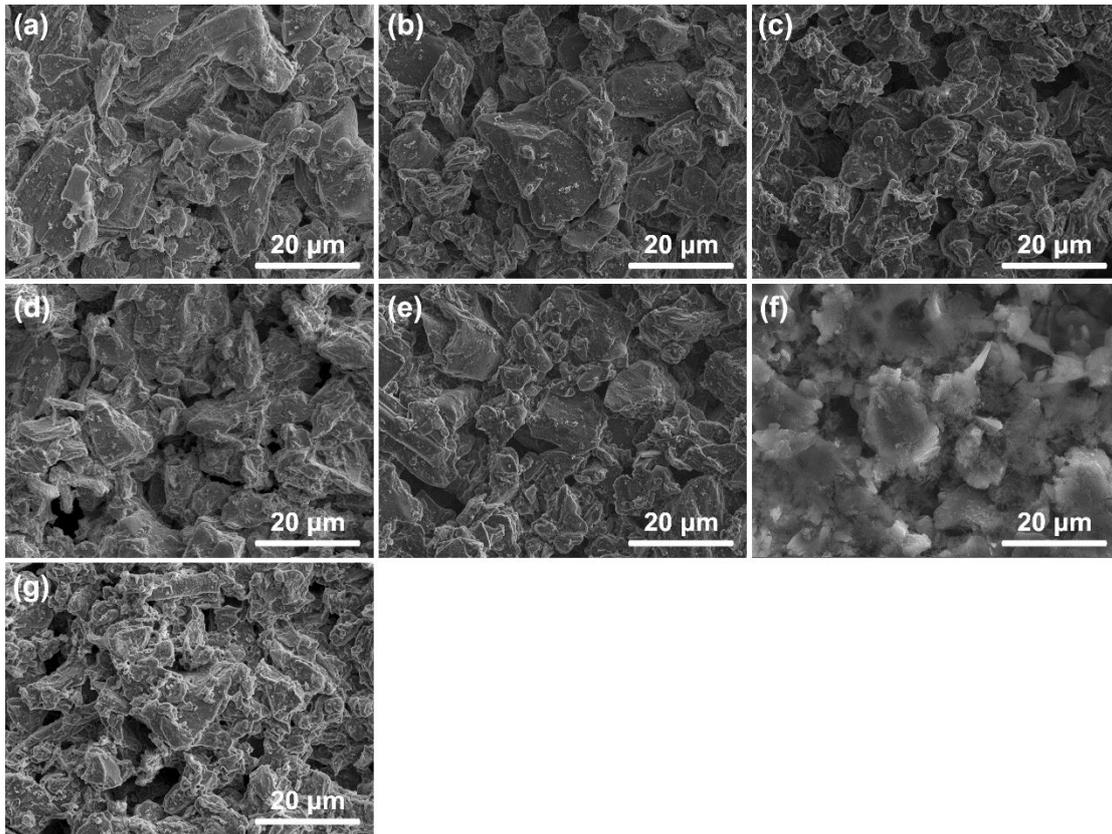


Fig. S5 SEM images of cycled anodes with (a) LBE 302, (b) LBE 302 + 4 wt% FPPN, (c) LiPF_6 -GBL, (d) LiPF_6 -GBL/FPPN (96:4) and (e) LiPF_6 -GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after formation step, and the cycled anodes with (f) LBE 302 and (g) LiPF_6 -GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after 500 cycles test.

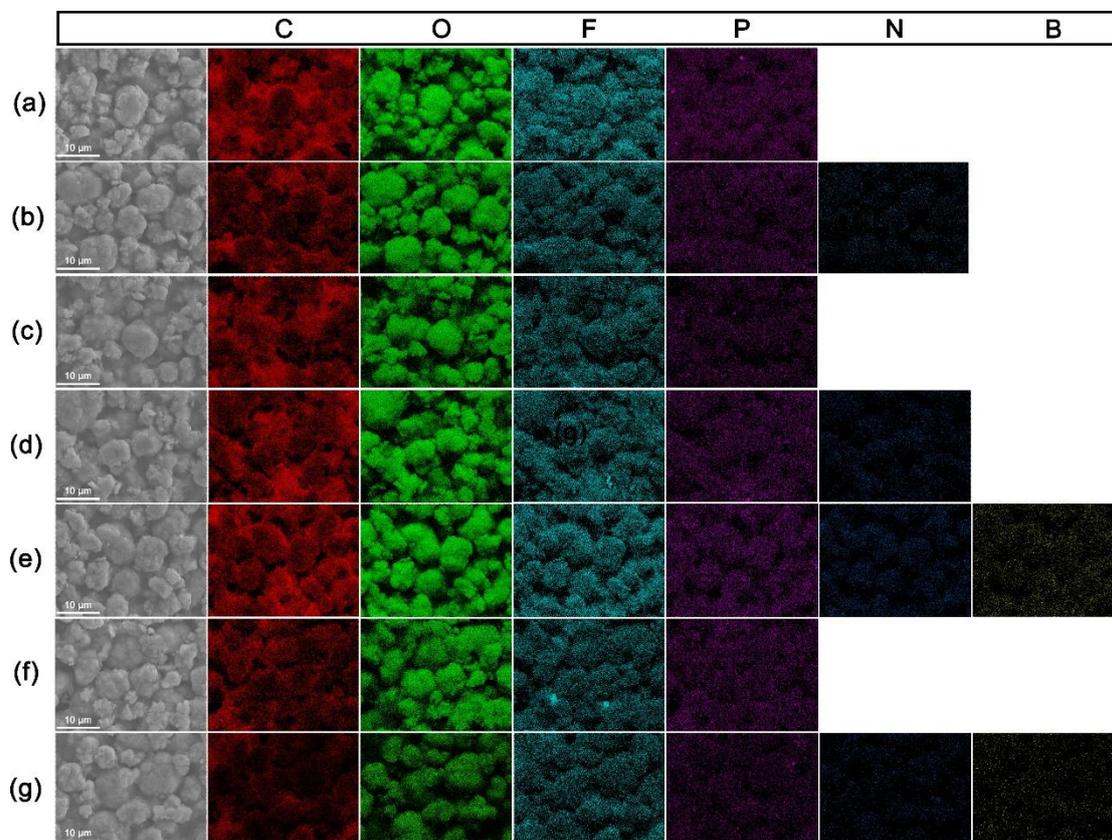


Fig. S6 EDS mapping results of element C, O, F, P, N and B on the cycled cathodes with (a) LBE 302, (b) LBE 302 + 4 wt% FPPN, (c) LiPF₆-GBL, (d) LiPF₆-GBL/FPPN (96:4) and (e) LiPF₆-GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after formation step and the cycled cathodes with (f) LBE 302 and (g) LiPF₆-GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after 500 cycles test.

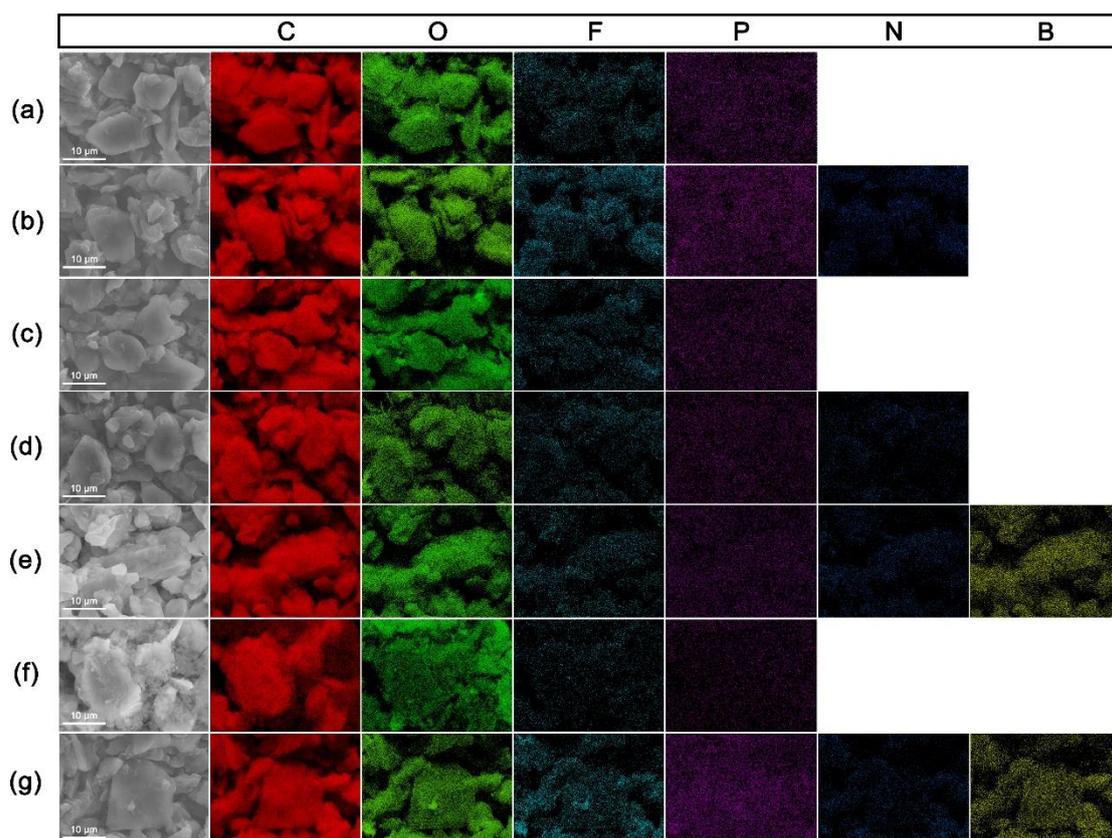


Fig. S7 EDS mapping results of element C, O, F, P, N and B on the cycled anodes with (a) LBE 302, (b) LBE 302 + 4 wt% FPPN, (c) LiPF₆-GBL, (d) LiPF₆-GBL/FPPN (96:4) and (e) LiPF₆-GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after formation step and the cycled anodes with (f) LBE 302 and (g) LiPF₆-GBL/FPPN (96:4) + 2 wt% LiODFB electrolytes after 500 cycles test.

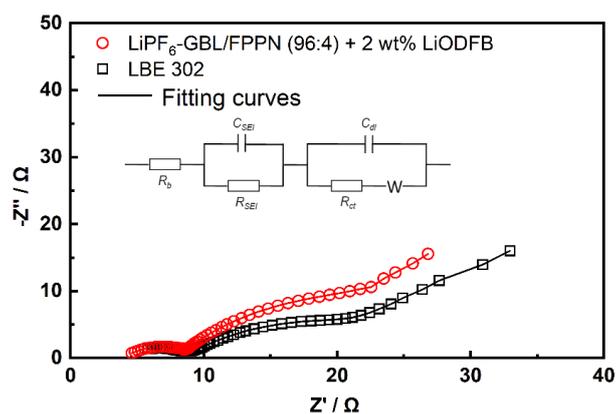


Fig. S8 EIS plots after formation step (3 cycles at 0.1C).

Table S2 Resistance parameters calculated from the EIS plots.

Electrolyte	R_b / Ω	R_{SEI} / Ω	R_{ct} / Ω
LiPF ₆ -GBL/FPPN (96:4) + 2 wt% LiODFB	4.6	4.0	14.3
LBE 302	5.3	3.3	13.1