Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2020

Supplementary Information

Investigation of the cathodic interfacial stability of a nitrile electrolyte and its performance with a high-voltage $LiCoO_2$ cathode

Fang Xian,[‡a] Jiedong Li,[‡b] Zhenglin Hu,[b] Qian Zhou,[b] Chen Wang,[b] Chenglong Lu,[b] Zhongyi Zhang,[a] Shanmu Dong,b,* Chunbo Mou,[a],* Guanglei Cuib,*

[a] *School of Material Science and Engineering, Qingdao University, Qingdao 266071, PR China.* E-mail: mouchunbo2008@126.com;

[b] *Qingdao Industrial Energy Storage Research Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, PR China*

E-mail: dongsm@qibebt.ac.cn; cuigl@qibebt.ac.cn

*Corresponding author.

‡:These authors contribute equally to this work.

Experimental section

1.1 Electrolyte and electrode preparation

Succinonitrile (SN), bis(trifluoromethylsulphonyl)imide (LiTFSI), and lithium difluoro(oxalato)borate (LiDFOB) (all in battery-grade purity) were all purchased from MacKLin. 1,2-dimethoxyethane (DME) was obtained from Sigma. 2.5 M LiTFSI/SN electrolyte was prepared, which corresponded to a SN/LiTFSI mass ratio of 1:0.75. A mass fraction of 4 wt% of LiDFOB (about 0.5 M) was used as the additive of 2 M LiTFSI/SN (mass ratio: 0.6:1) electrolyte. Above mixture was stirred at room temperature to obtain homogeneous electrolyte at room temperature. Commercial electrolyte of 1 M $LiPF_6$-EC/DMC (1:1 v/v) was provided by Aladdin. All experiments were conducted in a glove box filled with Ar with O_2 and H_2O content below 0.01 ppm. Li mental was provided commercially from China Energy Lithium. $LiCoO_2$ power was purchased from MGL power technology co., ltd. $LiCoO_2$ cathode was made by grinding 80 wt% $LiCoO_2$ powder, 10 wt% Super P (Aladdin) and 10 wt% polyvinylidene difluoride (PVDF, Alfa Aesar). $Li_4Ti_5O_{12}$ anode was made by grinding 80 wt% $Li_4Ti_5O_{12}$ powder (Sigma Corporation), 10 wt% Super P and 10 wt% polyvinylidene difluoride. The PVDF dissolved in N-methyl-2-pyrrolidone (NMP, Sinopharm Chemical ReagentCo., Ltd) in advance was prepared as the binder.

1.2 Electrocemical measurements

Coin-type (CR2032) cells ($LiCoO_2$|Li, $LiCoO_2$|$Li_4Ti_5O_{12}$) were assembled in an argon glove box with O_2 and H_2O content below 0.01 ppm. Glass fiber was used as the separator. The loading amount of active material of the cathode electrode is 1.22 mg/cm^2. The cycling performance of $LiCoO_2$|Li coin cells with a rate of 0.5 C were carried on a LAND test system (Wuhan LAND Electronic Co. Ltd., China).

1.3 Characterization

X-ray photoelectron spectroscopy (XPS) was employed to detect the surface components on the $LiCoO_2$ cathode and it was performed on a Thermo Scientific ESCALab 250Xi. For the XPS study, electrochemical cycling was performed with the following cathodes: the pristine $LiCoO_2$; After $LiCoO_2$|Li battery charging to 4.7 V with commercial liquid electrolyte of 1 M $LiPF_6$-EC/DMC (1:1 v/v), the disassembled

$LiCoO_2$ cathode was soaked in 2.5 M LiTFSI/SN electrolyte for 48 h with no further treatment, named SCLCO. The DCLCO was the charged $LiCoO_2$ cathode soaked in LiDFOB-containing electrolyte for 48 h with no further treatment. In-situ XRD spectra were recorded in the range of 10°-90° and collected with a speed of 10° min^{-1}. The in-situ XRD patterns were collected with Cu-Kα radiation (λ =1.5406 Å) on an Ultima IV of Rigaku. In-situ FTIR spectra measurement were conducted on a fourier transform infrared spectrometer (Nicolet iS 50).

SUPPLEMENTARY FIGURES

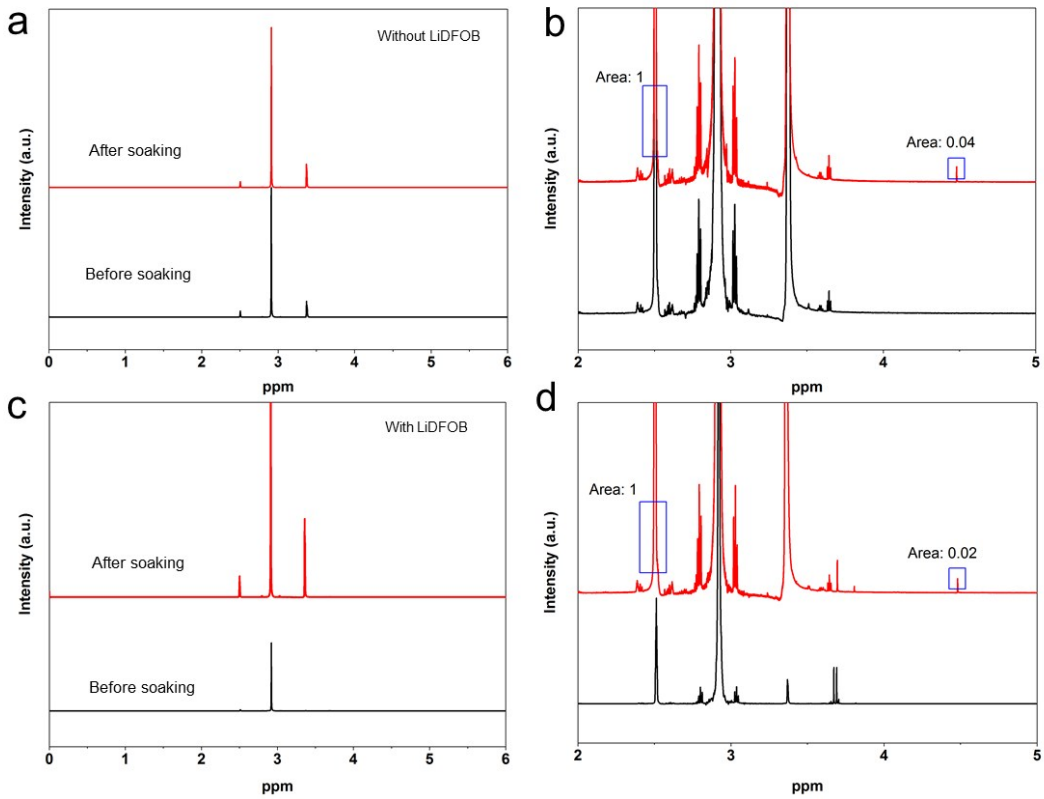

Figure S1. (a) ^1H NMR spectra of LiDFOB-absent electrolyte before and after soaked with charged $LiCoO_2$ cathode; (b) Corresponding enlarged view of (a); (c) ^1H NMR spectra of LiDFOB-containing electrolyte before and after soaked with charged $LiCoO_2$ cathode; (d) Corresponding enlarged view of (c).

Nuclear magnetic resonance (NMR) analyses were conducted on a Bruker 300-MHz NMR spectrometer. Samples for NMR spectroscopy were prepared in an Ar-filled glove box. For NMR tests, each micromagnetic tube included 30 μL of electrolyte and

600 μL of deuterated reagent (DMSO). The electrolyte soaked with charged $LiCoO_2$ cathode was placed at 60 °C for 48 hrs. ^1H NMR resonances were referenced to SN at 2.8 ppm.

NMR testing was further carried out to disclose the changes of electrolyte. As shown in Figure S1a, 2.5 M LiTFSI/SN electrolytes before and after soaked with charged $LiCoO_2$ cathodes were prepared and ^1H NMR spectra were acquired. The ^1H NMR spectrum of the original electrolyte contained three peaks. Figure S1b was the corresponding enlarged view, the singlet at 2.5 ppm are from the solvent residual peak of $(CD_3)_2SO$, and one set of peaks at 2.8 ppm are characteristic of the $-CH_2-$ in SN. When electrolyte was soaked with charged $LiCoO_2$, a peak at 4.5 ppm was present in the ^1H NMR spectrum, suggesting that SN reacted with charged $LiCoO_2$ cathode, generating side products. When we used the deuterated reagent (DMSO) as a standard, the amount (in the figure, the amount was reflected by the size of the peak area) of the by-product produced by the reaction of SN and charged $LiCoO_2$ cathode was 0.04. The same NMR experiments were performed for the electrolyte with LiDFOB salt, as shown in Figure S1c and S1d, the amount of by-product produced was significantly reduced (0.02), which contributed to the protective film generating from the LiDFOB on $LiCoO_2$ interface restrained the parasitic reaction of Co^{4+} ion and SN.

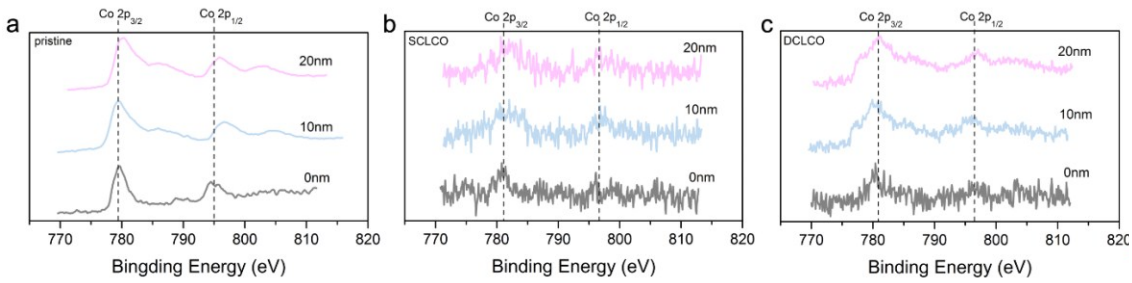

Figure S2. XPS etching spectra of Co 2p for different depths of (a) Pristine $LiCoO_2$ and treated $LiCoO_2$ electrode: (b) SCLCO was the charged $LiCoO_2$ cathode soaked in LiDFOB-absent electrolyte for 48 h with no further treatment; (c) DCLCO was the charged $LiCoO_2$ cathode soaked in LiDFOB-containing electrolyte for 48 h with no further treatment.

The Co2p photoemission spectrum etching for different depths of different samples were shown in Figure S2. Visually, for the pristine $LiCoO_2$ electrode, the peaks of Co

$2p_{3/2}$ and $Co2p_{1/2}$ were clearly observed. However, when charged $LiCoO_2$ electrode was soaked in LiDFOB-absent electrolyte and LiDFOB-containing electrolyte, named as SCLCO and DCLCO respectively, the Co signal peak intensity was much weaker than pristine $LiCoO_2$ sample. It was noted that the Co signal peak of SCLCO sample was still weak even etching for 20 nm, which might result from the side reaction between SN and Co^{4+} and the serious Co dissolution of $LiCoO_2$ cathode after soaking with LiDFOB-absent electrolyte. However, after DCLCO sample etching for 10 nm, the relatively clear Co peak reappeared, suggesting that LiDFOB salt may decompose to form CEI film on surface of $LiCoO_2$ electrode and suppress Co dissolution.

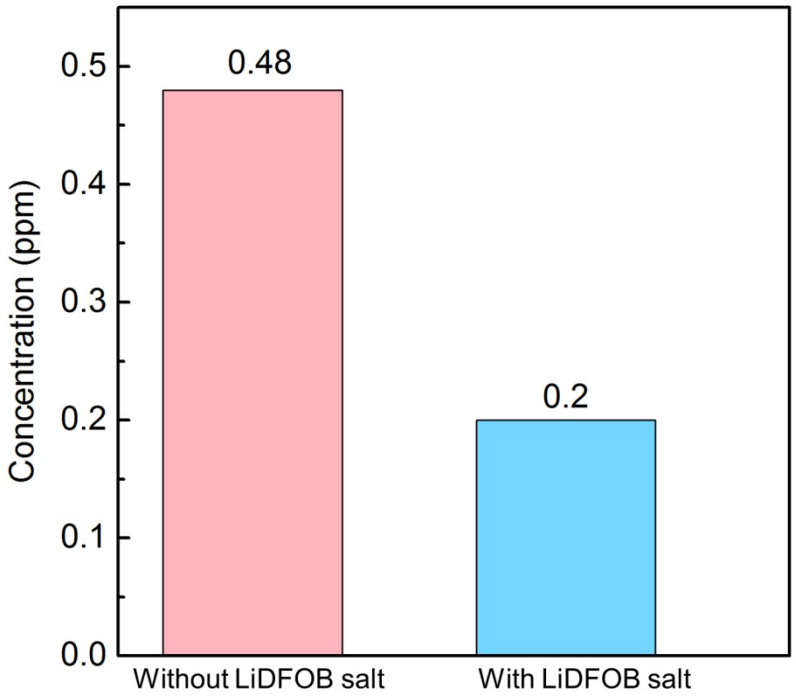

Figure S3. A comparison of Co dissolution behavior of cycled $LiCoO_2$ cathode dissembled from $LiCoO_2$|Li cells with LiDFOB-absent and LiDFOB-containing electrolytes.

To understand the Co dissolution behavior of cycled $LiCoO_2$ cathode using electrolytes with/without LiDFOB salt, the cathode was disassembled from cycled $LiCoO_2$|Li battery in charged state and soaked in DME at 60 ^{o}C for 48 hrs. The amount of Co ions was measured by inductively coupled plasma (ICP)-mass spectrometry (MS). The results showed that Co ion content was 0.2 ppm from the cycled $LiCoO_2$ cathode with the LiDFOB-containing electrolyte, which was much lower than that of LiDFOB-

absent electrolyte, suggesting that the formed cathode interface film induced by LiDFOB salt, could suppress the dissolution of Co element.

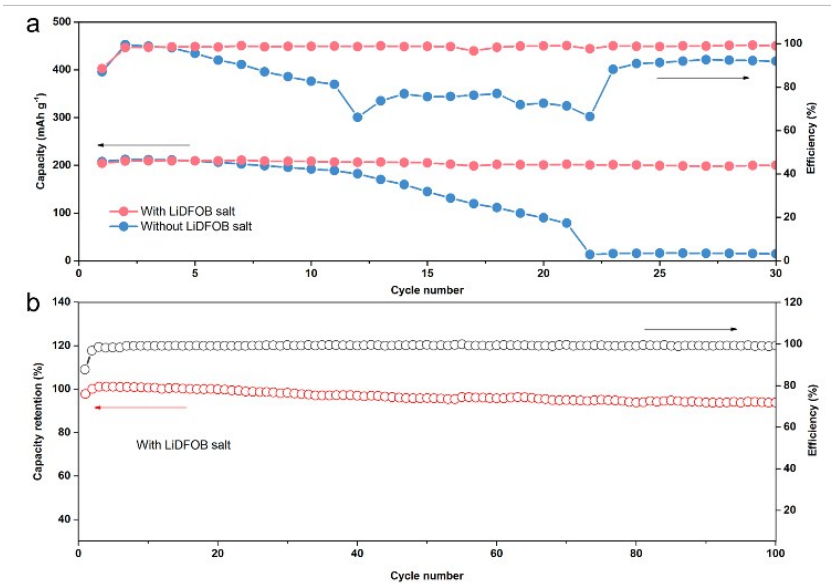

Figure S4. (a) Cycle performance of $LiCoO_2$|Li cell cycled in LiDFOB-absent or LiDFOB-containing electrolytes under a voltage range of 3-4.7 V; (b) Discharge capacity retention of $LiCoO_2$|Li cell cycled in LiDFOB-containing electrolyte under a voltage range of 3-4.6 V.

In order to evaluate the unique function of LiDFOB salt in the electrolyte, we conducted a cycling test on a $LiCoO_2$|Li half-cell (Fig. S4a, Fig. S6). Impressively, a comparison of the cell performance showed that with LiDFOB-absent electrolyte, the capacity and coulombic efficiency of cell fade extremely rapidly during initial cycles, and after 20 cycles, the capacity even dropped to zero. Conversely, with LiDFOB-containing electrolyte, it was clear that the cycling performance of half cells was markedly improved to stable operation until 30 cycles. The electrochemical long cycle performance of $LiCoO_2$|Li cell was further performed to evaluate the effect of LiDFOB salt (Fig. S4b, Fig. S5). Cells exhibited impressive cycling stability and capacity retention of about 94 % for 100 cycles under the cut-off voltages of 3-4.6 V (vs Li/Li^+). These results demonstrated the important role of LiDFOB salt for achieving better cycling performance.

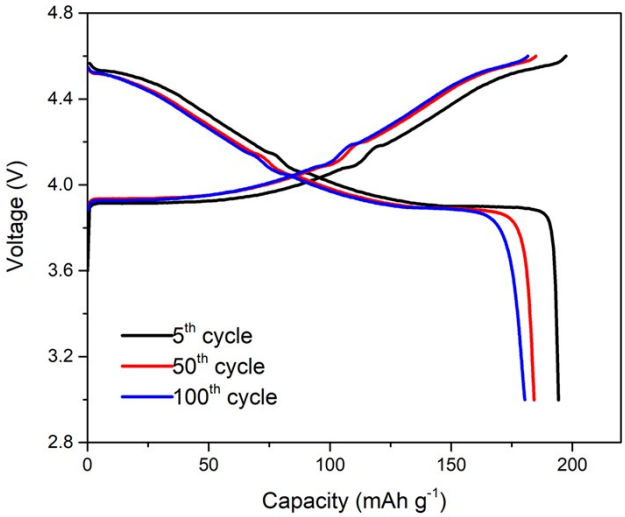

Figure S5. Charge-discharge curves of $LiCoO_2$|Li cell cycled in LiDFOB containing electrolyte under a voltage range of 3-4.6 V.

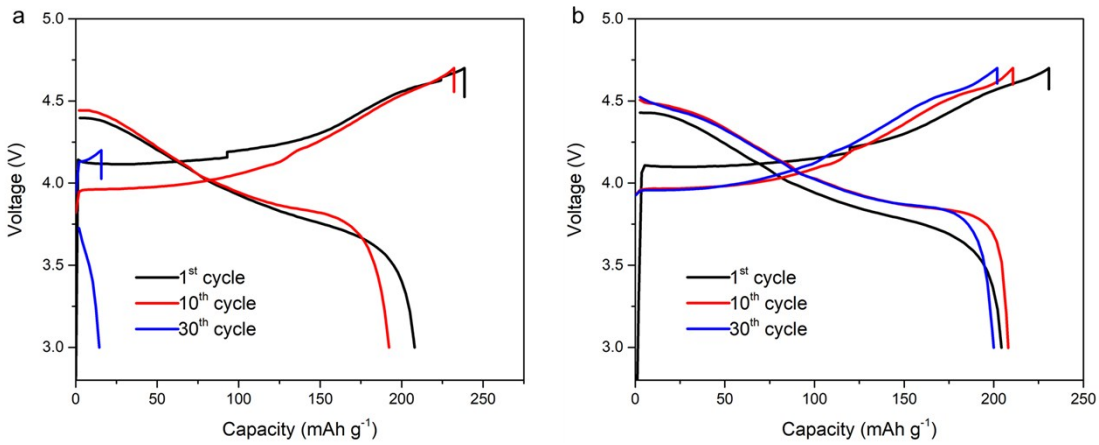

Figure S6. Charge-discharge curves of $LiCoO_2$|Li cell cycled in (a) LiDFOB-absent and (b) LiDFOB-containing electrolytes under a voltage range of 3-4.7 V.

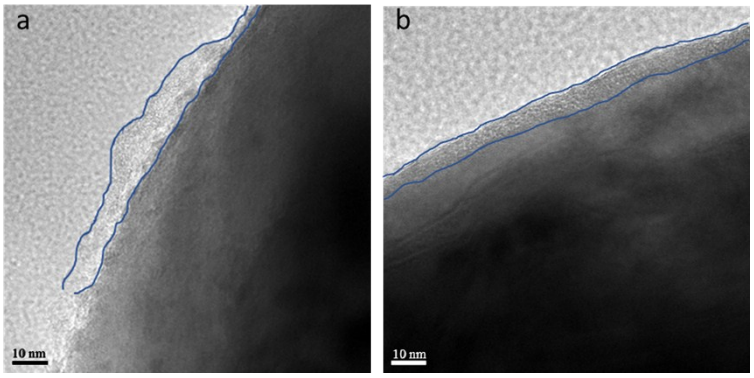

Figure S7. TEM images of cycled $LiCoO_2$ cathode disassembled from $LiCoO_2$|Li cells with (a) LiDFOB-containing and (b) LiDFOB-absent electrolyte;

Figure S7 shows TEM images of 30th cycled $LiCoO_2$ electrode in different electrolytes. There was not a uniform film formed on the surface of $LiCoO_2$ cycled with LiDFOB-absent electrolyte (Figure S7a). The thickness of some part of the film even more than 10 nm, which may be due to serious side reactions between the SN electrolyte and the lithium cobaltate cathode. For $LiCoO_2$ electrode cycled with LiDFOB-containing electrolyte (Figure S7b), there was a uniform, thinner and compact CEI layer on the $LiCoO_2$ surface. The TEM results indicated the protective film generating from LiDFOB-containing electrolyte on $LiCoO_2$ interface may restrain the parasitic reaction of Co4+ ion and SN solvent.

Table S1

Co concentration of different etching depth on pristine $LiCoO_2$ cathode and $LiCoO_2$ cathode soaked with different electrolytes.

Sample	0 nm (%)	10 nm (%)	20 nm (%)
pristine	0.81	4.09	5.02
SCLCO	0.22	0.19	0.28
DCLCO	0.24	0.76	1.04