Supplementary Information

Investigation of the cathodic interfacial stability of a nitrile electrolyte and its performance with a high-voltage LiCoO$_2$ cathode

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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$_2$O content below 0.01 ppm. Li metal 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$_4$Ti$_5$O$_{12}$ anode was made by grinding 80 wt% Li$_4$Ti$_5$O$_{12}$ powder (Sigma Corporation), 10 wt% Super P and 10 wt% polyvinylidene difluoride. The PVDF dissolved in N-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd) in advance was prepared as the binder.

1.2 Electrochemical measurements
Coin-type (CR2032) cells (LiCoO$_2$|Li, LiCoO$_2$|Li$_4$Ti$_5$O$_{12}$) were assembled in an argon glove box with O$_2$ and H$_2$O 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 ($\lambda = 1.5406$ 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) $^1$H NMR spectra of LiDFOB-absent electrolyte before and after soaked with charged LiCoO$_2$ cathode; (b) Corresponding enlarged view of (a); (c) $^1$H 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 LiCoO2 cathode was placed at 60 °C for 48 hrs. $^1$H 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 LiCoO2 cathodes were prepared and $^1$H NMR spectra were acquired. The $^1$H 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$_3$)$_2$SO, and one set of peaks at 2.8 ppm are characteristic of the -CH$_2$- in SN. When electrolyte was soaked with charged LiCoO2, a peak at 4.5 ppm was present in the $^1$H NMR spectrum, suggesting that SN reacted with charged LiCoO2 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 LiCoO2 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 LiCoO2 interface restrained the parasitic reaction of Co$^{4+}$ ion and SN.

![Figure S2](image)

**Figure S2.** XPS etching spectra of Co 2p for different depths of (a) Pristine LiCoO2 and treated LiCoO2 electrode: (b) SCLCO was the charged LiCoO2 cathode soaked in LiDFOB-absent electrolyte for 48 h with no further treatment; (c) DCLCO was the charged LiCoO2 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 LiCoO2 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 °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 Co$^{4+}$ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 nm (%)</th>
<th>10 nm (%)</th>
<th>20 nm (%)</th>
</tr>
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<tr>
<td>pristine</td>
<td>0.81</td>
<td>4.09</td>
<td>5.02</td>
</tr>
<tr>
<td>SCLCO</td>
<td>0.22</td>
<td>0.19</td>
<td>0.28</td>
</tr>
<tr>
<td>DCLCO</td>
<td>0.24</td>
<td>0.76</td>
<td>1.04</td>
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