# **Supporting Information**

# Increasing Poly(ethylene oxide) Stability to 4.5 V by Surface Coating of the Cathode

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#### **Experimental Procedures**

Synthesis of LiCoO<sub>2</sub> powders. LiCoO<sub>2</sub> powders were prepared with Li<sub>2</sub>CO<sub>3</sub> (99.9%) and Co<sub>3</sub>O<sub>4</sub> (99.9%) as precursors by a solid reaction process. 5 wt% excess of Li<sub>2</sub>CO<sub>3</sub> was added to make up for the lithium loss during sintering. Precursors were mixed with an Agate mortar. Then mixtures were sintered at 1,000 °C for 10 h for pre-sintering. After that, the mixtures were ground again in Agate mortar for a second time. Finally the mixture was sintered at 1000 °C for 10 h to obtain LiCoO<sub>2</sub> powders.

**LATP coating of cathode particles.** LATP coated LiCoO<sub>2</sub> powders were prepared by a mechanical mixing method. After mixing LiCoO<sub>2</sub> powders with corresponding 1 wt % LATP powders, the obtained mixture was sintered at 700  $^{\circ}$ C for 5 hours to obtain LATP coated LiCoO<sub>2</sub>.

**Preparation of electrodes.** PEO and PVDF with a mass ratio of 2:1 were dissolved in N-methylpyrrolidone (NMP) to prepare a binder solution, the solid concentration of which is 50mg/ml. LiCoO<sub>2</sub>, Super P and binder solution were slurried at a mass ratio of 75:10:15 and uniformly mixed in an Agate mortar. Then, the slurry was coated on an aluminum foil by doctor bladecoating. Then the electrode was heated at 55 °C for 6 hours for pre-drying and punched into circular rings with outer diameter of 12mm and inner diameter of 4mm with an electrode "punch". Finally, the perforated electrodes were weighed and then dried under vacuum at 120 °C for 6 hours for further drying. LATP coated LiCoO<sub>2</sub> electrodes were prepared in the same way. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes were made in a same way while the anodes were punched into 14-mmdiameter disks to match with cathodes.

#### Cell assembly and differential electrochemical mass spectrometry (DEMS) setup.

DEMS cell assembly: The specially designed DEMS cell was assembled in an Ar filled glovebox  $(O_2 \text{ and } H_2O \text{ below } 0.1 \text{ ppm}, \text{MBraun})$ . The DEMS cell is made of 304 stainless steel. O-rings and FEP films were put between the various parts of the battery for insulation. An PTFE sleeve was put into the cavity of the cell for insulation. Counter electrode, PEO film, perforated cathode and perforated gasket were put into the cell in sequence. A spring with high stiffness coefficient was put between gasket and upper shell to make the cell impacted. The upper shell of the cell is directly connected to DEMS.

DEMS setup: Hiden Analytical HPR-40 DEMS bench-top gas analysis system with direct membrane inlet probe was used for online gas analysis. After connecting the instrument, the cell was heated to 60 °C by a temperature controller and kept at this temperature for 24 hours. The intelligent temperature controller is the AI-207D2GH type from Xiamen Yudian automation technology co., LTD. Gas detecting was started at least 5 hours earlier than the start of battery charging to ensure the reliable measurement of baseline. Volatile molecules with molecular mass of 2 (H<sub>2</sub>), 16 (CH<sub>4</sub>), 18 (H<sub>2</sub>O), 26 (C<sub>2</sub>H<sub>2</sub>), 28 (CO, C<sub>2</sub>H<sub>4</sub>), 30 (C<sub>2</sub>H<sub>6</sub>, HCHO), 32 (O<sub>2</sub>, CH<sub>3</sub>OH), 44 (CO<sub>2</sub>, CH<sub>3</sub>CHO) and 46 (CH<sub>3</sub>CH<sub>2</sub>OH, HCOOH) were set to be monitored online.

Coin cell assembly: Unmodified LiCoO<sub>2</sub> and Li<sub>1.4</sub>Al<sub>0.4</sub>Ti<sub>1.6</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP)-coated LiCoO<sub>2</sub> electrodes were tested in 2032-type coin cells with PEO membrane and lithium metal anode. Coin cells were assembled in the same Ar filled glovebox (O<sub>2</sub> and H<sub>2</sub>O below 0.1 ppm, MBraun).

## **Electrochemical testing:**

DEMS cell: The DEMS cell was preserved at 60 °C for 24 hours before test to achieve good contact between electrode and electrolyte. For the active material-free cell, a constant current

charging was applied with a current of 10  $\mu$ A (8.85  $\mu$ A cm<sup>-2</sup>), followed by a constant voltage charging for 5 hours at the voltages of 4.2 V and 4.4 V, respectively. For the final step, the constant current charging cannot reach the designed voltage of 4.6V due to the severe decomposition of PEO electrolyte (voltage fluctuate at around 4.5 V), and the gas generation was recorded until the complete short-circuit of the cell. LiCoO<sub>2</sub>|PEO|Li cell and LATP-LiCoO<sub>2</sub>|PEO|Li cell were cycled between 3.0 - 4.2 V, 3.0 - 4.4 V, 3.0 - 4.6 V and 3.0 - 4.8 V for 2 cycles successively with a constant current of 27.4 mA g<sup>-1</sup>. The LiCoO<sub>2</sub>|PEO|LTO full cell was tested between 1.0 V and 3.2 V to compare with the result of half-cell result of 3.0 - 4.2 V.

Coin cell: Coin cells were preserved at 60 ° C for 12 hours before test to achieve good contact between electrodes and electrolyte. Then, the cells were charged at a constant current of 18.5 mA  $g^{-1}$  to 4.5 V and then the voltage was held for 10 minutes followed by discharging to 3.0 V at 18.5 mA  $g^{-1}$  at 60 °C.



**Figure S1.** Voltage profiles of modified LiCoO<sub>2</sub> half cells at first two cycles tested with 2032type coin cell and specially designed DEMS cell in the voltage range of 3.0 - 4.2 V with a constant current of 14 mA g<sup>-1</sup> at the first cycle and 28 mA g<sup>-1</sup> for the second cycle at 60 °C.



**Figure S2.** Continuous scan of mass-to-charge ratio (m/z) signals from 0 to 140 in a profile mode during violent decomposition stage of bare LiCoO<sub>2</sub>|PEO-LiTFSI|Li cell.

**Table S1.** The highlighted m/z values with strong signals as shown in Figure S2 and their assignments to the possible volatile molecules or fragment ions that may be generated during decomposition of PEO.

m/z	Possible molecules or fragment ions	m/z	Possible molecules or fragment ions
1	$\mathrm{H}^{+}$	30	НСНО
2	$H_2$	31	$^{+}CH_{2}OH$
14	$N^{+}, CH_{2}^{+}$	32	O <sub>2</sub> , CH <sub>3</sub> OH
15	$\mathrm{CH_{3}^{+}}$	43	$\mathrm{CH}_3\mathrm{CO}^+$
17	$\mathrm{HO}^+$	44	CO <sub>2</sub> , CH <sub>3</sub> CHO
18	$H_2O$	45	<sup>+</sup> COOH
19	$H_3O^+$	58	CH <sub>3</sub> COCH <sub>3</sub> , CH <sub>3</sub> CH <sub>2</sub> CHO
26	$C_2H_2$	88	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>
27	$^{+}C_{2}H_{3}$	112	CH2=CHCOCH2COCH3
28	$N_2$ , CO, $C_2H_4$	120	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH
29	$\mathrm{CHO}^+$ , $\mathrm{CH}_3\mathrm{CH}_2^+$	132	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>2</sub> COOH

For m/z signals with relatively high values, there may be multiple isomers corresponding to them, but only some of them are given here. Because the real situation could be more complicated which needs further explorations.



Scheme S1. Possible mechanism of HTFSI attacking PEO chains leading to chain scissions and producing volatile molecules.



**Figure S3.** Voltage profile and corresponding DEMS mass signals m/z = 2 (H<sub>2</sub>), 16 (CH<sub>4</sub>), 18 (H<sub>2</sub>O), 26 (C<sub>2</sub>H<sub>2</sub>), 28 (CO, C<sub>2</sub>H<sub>4</sub>), 30 (C<sub>2</sub>H<sub>6</sub>, HCHO), 32 (O<sub>2</sub>, CH<sub>3</sub>OH), 44 (CO<sub>2</sub>, CH<sub>3</sub>CHO) and 46 (CH<sub>3</sub>CH<sub>2</sub>OH, HCOOH) detected in bare LiCoO<sub>2</sub>|PEO-LiTFSI|LTO full cell cycled between 1.0-3.2V for 3 cycles with a constant current of 27.4 mA g<sup>-1</sup> and followed by a quiescence process at 60 °C.

#### **Computational methods**

All DFT calculations were performed with the Vienna ab initio simulation package (VASP) with projector augmented-wave (PAW) approach.<sup>1-2</sup> For the structure relaxation of molecule PEO monomer, LiTFSI, HTFSI and electrode material LiCoO<sub>2</sub>, we adopt the exchange-correlation functional of General Gradient Approximation (GGA) type in the parameterization by Perdew-Burke-Ernzerhof (PBE).<sup>3</sup> The relaxation of molecule structure was done in a cubic cell of 30Å×30Å×30Å. A slab model with 20Å vacuum and five layers of LiCoO<sub>2</sub> of the surface dimension 3×5 was adopted for the simulation of molecule absorbed on the surface of electrode LiCoO<sub>2</sub>. The (104) surface of LiCoO<sub>2</sub> was chosen since it was experimentally observed existing in the material and the surface oxygen is exposed on this surface.<sup>4</sup> For the calculation of model structures' total energy Hubbard U type correction was adopted to address the electron correlation for the 3d electrons of Co with an effective U value of 4.9 eV.<sup>5</sup> For all calculations the cutoffs of wave function and charge density are 500 and 756 eV, respectively. A k-mesh with the density of one point per ~0.03Å<sup>-3</sup> was generated using the Monkhorst-Pack method to ensure the precision of the calculated total energy. For the relaxations of model structures, the forces felt by each of the atoms were well converged below  $0.005 \text{eV} \cdot \text{Å}^{-1}$ .

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