Supporting Information

Nitrofullerene, a \( C_{60} \)-based Bifunctional Additive with Smoothing and Protecting Effects for Stable Lithium Metal Anode

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1. Experimental Procedures

**Materials:** Li foil (400 μm φ 14 mm, China Energy Lithium Co., Ltd.), C_{60} (XIAMEN FUNANO Co., Ltd., China, 99%), chlorobenzene (CB, 99%, Aladdin), lithium hexafluorophosphate (LiPF_6), ethylene carbonate (EC), and diethyl carbonate (DEC) were purchased from Guangzhou Tinci Materials Technology Co., Ltd. lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99%, Sigma-Aldrich), 1,3-dioxolane (DOL, 99.5%, Sigma-Aldrich), 1,2-dimethoxyethane (DME, 99.5%, Sigma-Aldrich). Commercial LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 electrode was supplied by Jiangxi Anchitech Company (China). All these materials used without further purification.

**Materials Characterization:** SEM observations were carried out with field-emission SEM (SIRION200). TEM and HRTEM images were observed by Talos F200X (Thermo Fisher Scientific). FT-IR spectra measured on a Bruker Vertex 70 FTIR spectrometer. TGA was tested by Pyris1 TGA (PerkinElmer Instruments. Co., Ltd.). XPS performed on an AXIS-ULTRA DLD-600W (SHIMADZU-KRATOS. Co., Ltd.). EPMA and X-ray Wavelength Dispersive Spectrometer (WDS) were carried out with EPMA-8050G (SHIMADZU-KRATOS. Co., Ltd.). *In-situ* optical observations carried out by a transparent quartz cuvette (width of 10 mm). Optical microscope (Phenixoptics XSP-36, 100X-1600X) with matched camera applied to record the Li stripping/plating process. HPLC was monitored with LC-16 (SHIMADZU-KRATOS. Co., Ltd.) equipped with an analytical Buckyprep column (Ø4.6×250 mm) (Test condition: 20 μL injection volume, 1.0 mL min^{-1} toluene flow, 40°C and 330 nm detection wavelength).
**Synthesis of nitrofullerene:** Nitro-C$_{60}$ was synthesized according to the previously reported procedure.\(^1\) Briefly, C$_{60}$ powders (500 mg) was dissolved in chlorobenzene (500 mL) stirred for 1 h at ambient temperature, and then an abundant stream of NO$_2$ was injected into the solution for 3 h (Cu and concentrated nitric acid as a precursor). After removing the solvent by rotary evaporation, the precipitate was sequentially washed with n-hexane for three times, and finally dried under vacuum at 50 °C for 12 h to afford 448 mg product.

**Electrochemical measurements:** The electrolyte was 1M LiPF$_6$ in EC/DEC (1: 1, vt%) or 1M LiTFSI in DOL/DME (1: 1, vt%) with/without C$_{60}$(NO$_2$)$_6$ (1 mM, 5 mM or 10 mM). Particularly, 1M LiTFSI in DOL/DME (1: 1, vt%) with 5 or 30 mM LiNO$_3$ was prepared as a control experiment. Besides, 1M LiPF$_6$ in EC/DEC (1: 1, vt%) with 5mM C$_{60}$/ 30 mM LiNO$_3$/ 5 mM C$_{60}$+30 mM LiNO$_3$ also was prepared as a control experiment. The amount of electrolyte is controlled as 50 μL (Li-Li, Li-Cu, Li-S cells and Li-NCM622 cells with thin Li metal) or 12 μL (Li-NCM622 cells with lean electrolyte). The electrochemical performance of the samples was conducted on Land battery test instrument. Li-Li symmetrical cells assembled with two Li foils. Li-Cu half cells assembled with the Cu foil and Li foils by stripping up to 1 V (vs. Li$^+$/Li). The Se$_x$S$_{1-x}$PAN cathode was made by blending Se$_x$S$_{1-x}$PAN power, Ketjen black, PVDF with a weight ratio of 8: 1: 1 (9: 0.5: 0.5 for high loading electrode) to form the slurry, and then coated on the Al foil. After drying at 80 °C under vacuum overnight, the obtained electrodes with areal mass loadings controlled to be 1.5 mg cm$^{-2}$ (8.0 or 10.6 mg cm$^{-2}$ for high loading electrode), and the cells were galvanostatically cycled.
between 1 and 3 V. Element analysis results indicated the weight of S, Se, C, N, H is 35.521%, 7.252%, 42.36%, 13.74%, 1.127%, respectively. The corresponding theoretical specific capacity calculated is 1507 mAh g⁻¹ based on the contents of S and Se. Li-NCM full cells used commercial LiNi₀.6Co₀.2Mn₀.2O₂ electrode with mass loading of 20 mg cm⁻² as the cathode and Li foil as the anode, then the cells were galvanostatically cycled between 2.8 and 4.3 V. Electrochemical impedance spectrometry (EIS) (100 kHz to 0.1 Hz) and cyclic voltammetry (CV) (the rate of 0.1 mV s⁻¹) measurements were conducted using Solartron electrochemical workstation. Tafel plots were measured using a CHI 600D, at a scan rate of 1 mV s⁻¹.

**Computational details:** DFT calculation is within the generalized gradient approximation (GGA) from Perdew, Burke, and Ernzerhof (PBE) by VASP code. As for Li surface and its derivatives, a 4×4×1 k-point sampling was used containing 24 Li atoms in 6 layers and appropriate atoms by the number of layer with the vacuum thickness of 1.5 nm. The k-point meshes of 7×7×7 were used for Li with BCC structure and gamma point for C₆₀ molecule and its derivatives. The plane-wave cutoff energy is 520 eV and an energy tolerance of 10⁻⁵ eV atom⁻¹ was used for the convergence. The maximum tolerance for force along any Cartesian component was 0.05 eV Å⁻¹. The final morphology is determined by the model when the lowest total surface energy of the crystal is reached.
2. Supporting Figures

**Video S1.** *In-situ* optical microscope observation of Li deposition in the carbonate electrolyte.

**Video S2.** *In-situ* optical microscope observation of Li deposition in the carbonate electrolyte with 5 mM C\textsubscript{60}(NO\textsubscript{2})\textsubscript{6} additive.

![Figure S1](image1.png)

**Figure S1.** Photograph of nitro-C\textsubscript{60} and pure C\textsubscript{60} dissolve in a) the carbonate electrolyte and b) the ether electrolyte.

![Figure S2](image2.png)

**Figure S2.** a) FT-IR and b) TGA of the nitrofullerene.

**Note:** FT-IR spectrum of product shows typical NO\textsubscript{2} vibrations at 1568, 1338 and 810 cm\textsuperscript{-1} and C\textsubscript{60} vibrations at 686 and 543 cm\textsuperscript{-1}, which indicates that the structure of the product is C\textsubscript{60}(NO\textsubscript{2})\textsubscript{x}, and the average molecular formula can be further calculated according to the weight loss (decomposition of NO\textsubscript{2}) of TGA after heating.\textsuperscript{2-4}
**Figure S3.** Cycling performance of the Li-Li symmetric cells in the carbonate electrolyte with different concentrations of $C_{60}(NO_2)_6$.

**Figure S4.** Photograph of nitro-$C_{60}$ dissolve in the carbonate electrolyte with different concentrations (Test temperature: 25 °C) a) 1 mM, b) 5 mM, c) 10 mM, d) 25 mM, e) 50 mM, f) 100 mM.

**Note:** As shown in the photograph, precipitation appears in the 100 mM nitro-$C_{60}$ solution, indicating that its maximum solubility is greater than 50 mM but less than 100 mM in the carbonate electrolyte.

**Figure S5.** SEM a) surface and b) cross-sectional images of Li morphology in the carbonate electrolyte with 10 mM $C_{60}(NO_2)_6$ additive after 50 cycles. (Insert figure is the photograph of cycled Li)
Figure S6. EIS for the cycled Li-Li symmetric cell in the carbonate electrolyte a) without and b) with C₆₀(NO₂)₆ additive. c) The equivalent circuit of Nyquist plots.

Figure S7. SEM surface and cross-sectional images of cycled Li morphology in the carbonate electrolyte after 200 cycles a,b) without and c,d) with C₆₀(NO₂)₆ additive at the Li-Li symmetric cells with 0.5 mA cm⁻², 0.5 mAh cm⁻². (Insert figures is the photographs of cycled Li)

Figure S8. Cycling performance of the Li-Li symmetric cells in the carbonate electrolyte without/with 5 mM C₆₀(NO₂)₆ additive (0.5 mA cm⁻², 1 mAh cm⁻²).
**Figure S9.** SEM surface and cross-sectional images of Li morphology in the ether electrolyte after 100 cycles. a,e) 1M LiTFSI in DOL+DME, b,f) 1M LiTFSI in DOL+DME+5 mM LiNO₃, c,g) 1M LiTFSI in DOL+DME+30 mM LiNO₃, d,h) 1M LiTFSI in DOL+DME+5 mM C₆₀(NO₂)₆. (Insert figures is the photographs of cycled Li)

**Figure S10.** Coulombic efficiency of Li||Cu cells in the carbonate electrolyte without/with C₆₀(NO₂)₆ (0.5 mA cm⁻², 0.5 mAh cm⁻²).

**Figure S11.** a) Coulombic efficiency of Li||Cu cells in the carbonate electrolyte without/with C₆₀(NO₂)₆ (0.1 mA cm⁻², 0.5 mAh cm⁻²) and b) corresponding polarization curves.
**Figure S12.** SEM images and photographs of Li depositing on Cu foils in the carbonate electrolyte after 100 cycles a) without and b) with C_60(NO_2)_6 additive at 0.1 mA cm\(^{-2}\), 0.5 mAh cm\(^{-2}\).

![SEM images and photographs of Li depositing on Cu foils](image)

**Figure S13.** Photographs of the devices undergoing *in-situ* plating/stripping test, a) Li foil and electrolyte in the transparent cuvette and b) optical microscope observation.

![Photographs of the devices undergoing *in-situ* plating/stripping test](image)

**Figure S14.** The polarization curves of *in-situ* optical microscope observation.

![Polarization curves](image)

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<th>Li (001) face</th>
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**Figure S15.** Optimized geometries for calculating the binding energy of Li-Li (001) and Li-C_{60} interface.

![Optimized geometries](image)
**Figure S16.** Discharge/charge curves of Li-S batteries in the carbonate electrolyte a) without and b) with C$_{60}$(NO$_2$)$_6$ additive. (Cathode loading: 1.5 mg cm$^{-2}$, 2 C)

**Figure S17.** Discharge/charge curves of Li-S batteries in the carbonate electrolyte a) without and b) with C$_{60}$(NO$_2$)$_6$ additive. (Cathode loading: 10.6 mg cm$^{-2}$, C/5)

**Figure S18.** Charge/discharge curves of Li-NCM622 full cells in the carbonate electrolyte a) without and b) with C$_{60}$(NO$_2$)$_6$ additive. (Cathode loading: 20 mg cm$^{-2}$, lean electrolyte: 3 g Ah$^{-1}$, C/3)
Figure S19. SEM surface and cross-sectional images of Li morphology in the carbonate electrolyte after 200 cycles a,b) without and c,d) with C_{60}(NO_2)_6 additive in the Li-S full cells at 2 C.

Figure S20. SEM surface and cross-sectional images of cycled Li morphology in the carbonate electrolyte a, b) without and c, d) with C_{60}(NO_2)_6 additive in the Li-NCM622 full cells at C/3.

Figure S21. Cycling performance of Li-NCM622 full cells at C/3. (Cathode loading = 20 mg cm^{-2}, thin Li metal = 50 μm, 1 C = 180 mAh g^{-1})
Figure S22. Cycling performance of the Li-Li symmetric cells in the carbonate electrolyte with different additives (0.5 mA cm$^{-2}$, 0.5 mAh cm$^{-2}$).

Figure S23. Cycle performance of high loading Li-S batteries with different additives at C/2 (Cathode loading = 8.0 mg cm$^{-2}$, 1 C = 1507 mAh g$^{-1}$).

3. References


