

Supplementary Information

Electrolyte Tuning with Low Concentration Additive for Dendrite Suppression in Lithium Metal Anodes

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I. Experimental Section

Electrolyte preparation. Baseline electrolyte was prepared by dissolving 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma Aldrich, 99.95 %) salt and 1 wt. % lithium nitrate (LiNO_3 , Sigma Aldrich, 99.99 %) in a 1:1 v/v mixture of 1,3-dioxolane (DOL, Sigma Aldrich, 99.8 %) and 1,2-dimethoxyethane (DME, Sigma Aldrich, 99.5%). Similarly, the novel additive added electrolyte was prepared first by experimenting with multiple concentrations of gadolinium (III) nitrate ($\text{Gd}(\text{NO}_3)_3$) added in the baseline electrolyte solution followed by magnetic stirring. All steps above were carried out in an argon (Ar) filled glovebox with water and oxygen content below 0.1 ppm.

Electrode preparation. LFP cathode slurry was prepared by mixing LFP (LiFePO_4 , Xiamen Tmax, China, particle size 0.55 μm) active material, Super P conductive carbon (Alfa Aesar, 99 %) as conductive additive, and polyvinylidene fluoride (PVDF, Sigma Aldrich, $M_w \sim 534,000$) as binder at 8:1:1 weight ratio in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich, 99.5 %) solvent. The powders were first dry mixed with mortar and pestle and then added into the pre-dispersed NMP + PVDF. This cathode slurry solution was stirred for ~ 12 h. Then, the lump-free slurry was coated on aluminum (Al) foil (Xiamen Tmax, China, 0.0016 mm thick) current collector using mini tape casting coater (MTI Corp.). The coatings were dried in a vacuum oven at 120 $^\circ\text{C}$ overnight for solvent evaporation. Thus, the obtained dry cathode strips were cut into circular discs of 12 mm diameter by disc cutter which achieved active material mass loading of ~ 4 mg cm^{-2} . Similar procedure was followed for preparing NMC 111 ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) cathodes with a cathode loading of ~ 2.8 mg cm^{-2} for testing high voltage electrolyte stability.

LMAs were prepared by polishing Li chips (15.6mm diameter and 0.25 mm thick, Xiamen Tmax, China) using 1500 grit sized sandpapers attached to a rotary tool set (Dremel, USA) in Ar

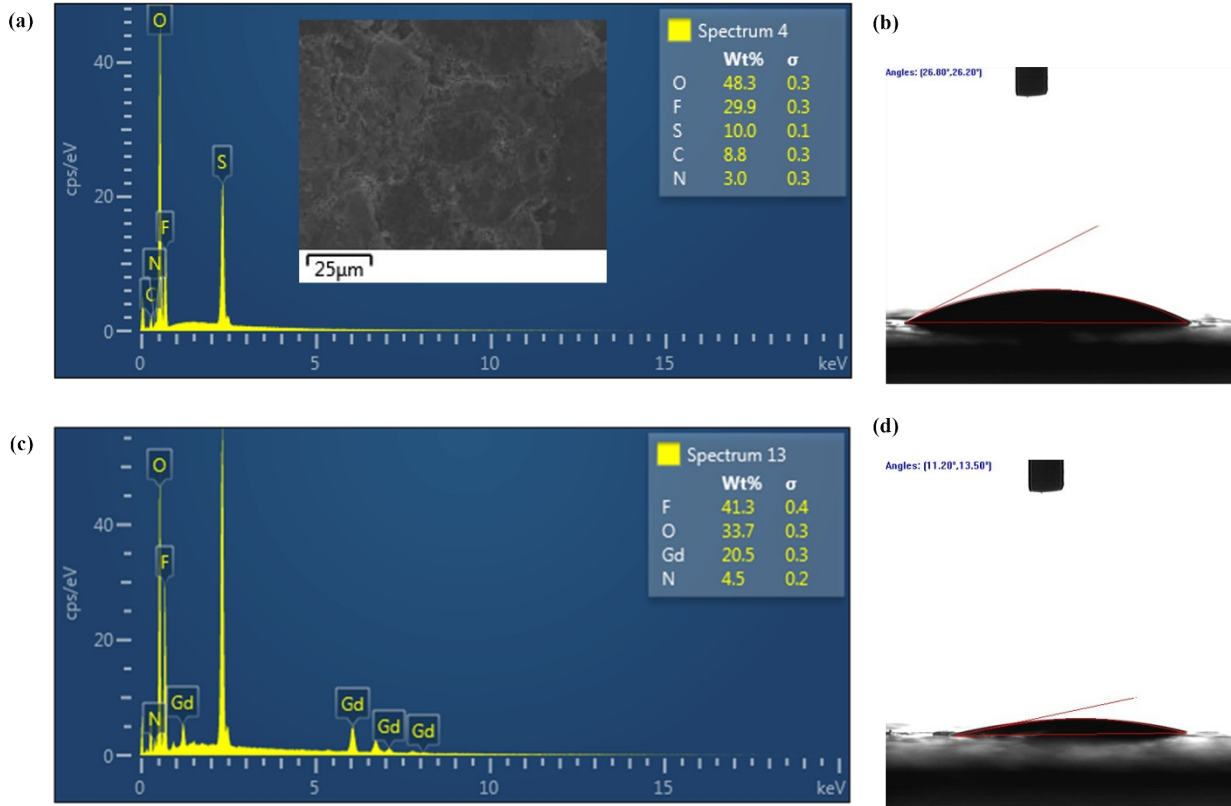
environment. After uniform polishing, they were immediately used to assemble coin-cells with the polished side facing the separator.

Fabrication of Li-symmetrical cells and full cells. CR2032 coin cell batteries were assembled in both symmetrical and full cell designs. For Li symmetrical cell, polished Li metal chips were stacked onto each other with 25 μm thick Celgard separator (Xiamen Tmax, China) sandwiched in the middle. In each of these cells, 60 μl of electrolytes were used to prepare Li symmetrical cells without and with the gadolinium nitrate additive, respectively. In addition, the full cells were assembled using prepared LFP or NMC 111 cathodes and Li metal anode material. All symmetrical and full cells were pressed using a manual hydraulic coin cell crimping press (Xiamen Tmax, China). The full assembly process was carried out in an Ar-filled glovebox.

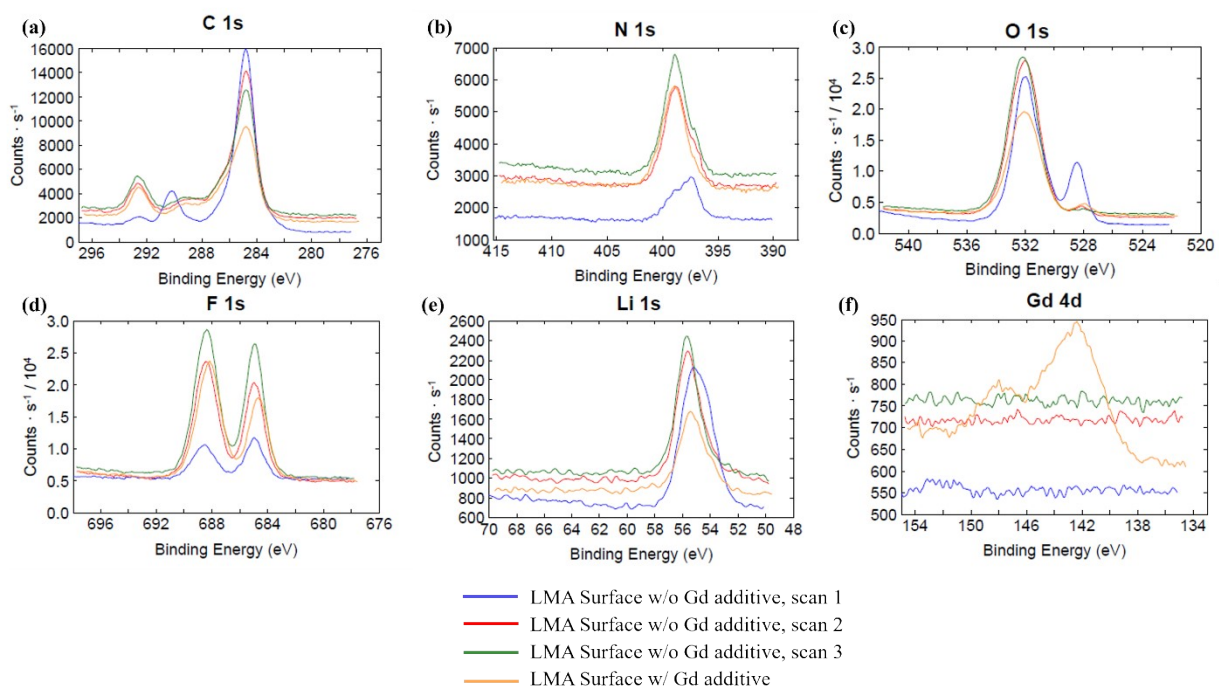
Characterizations. The morphology of Li deposition and LMAs surface after cycling was observed in SEM images using a Hitachi S-4300N scanning electron microscope equipped with energy-dispersive spectroscopy (EDS) capability. The X-ray photoelectron spectroscopy (XPS) analysis was performed using a VersaProbe 4 scanning XPS microprobe from Physical Electronics, Minnesota. The samples were transferred to the XPS microprobe under inert environment through a transfer vessel mounted on a load-lock, evacuated to $\sim 2 \times 10^{-6}$ Torr before moving into the XPS analysis chamber. The electrochemical impedance spectroscopy (EIS) was performed using an Ametek VERSASTAT3-200 potentiostat electrochemical workstation from Princeton Applied Research. The signals were measured over a working frequency range of 100 KHz to 0.1 Hz with an amplitude of 10 mV. Similarly, LSV and CV were measured using a Biologic SP-150 potentiostat at voltages ranging 0 to 5V and 2 to 4.5 V at scan rate of 0.5 mV s^{-1} versus Li/Li^+ , respectively. Galvanostatic charge/discharge cycling measurement of coin cells were performed using a Neware battery analyzer system. The full cells with LFP cathodes were

cycled at different current densities ($1\text{ C} = 170\text{ mA g}^{-1}$) in a voltage range of 2.5 to 4.2 V and the ones with NMC111 cathodes underwent similar C-rate profiles ($1\text{ C} = 200\text{ mA g}^{-1}$) between 2.7 – 4.3 V versus Li/Li^+ at ambient conditions.

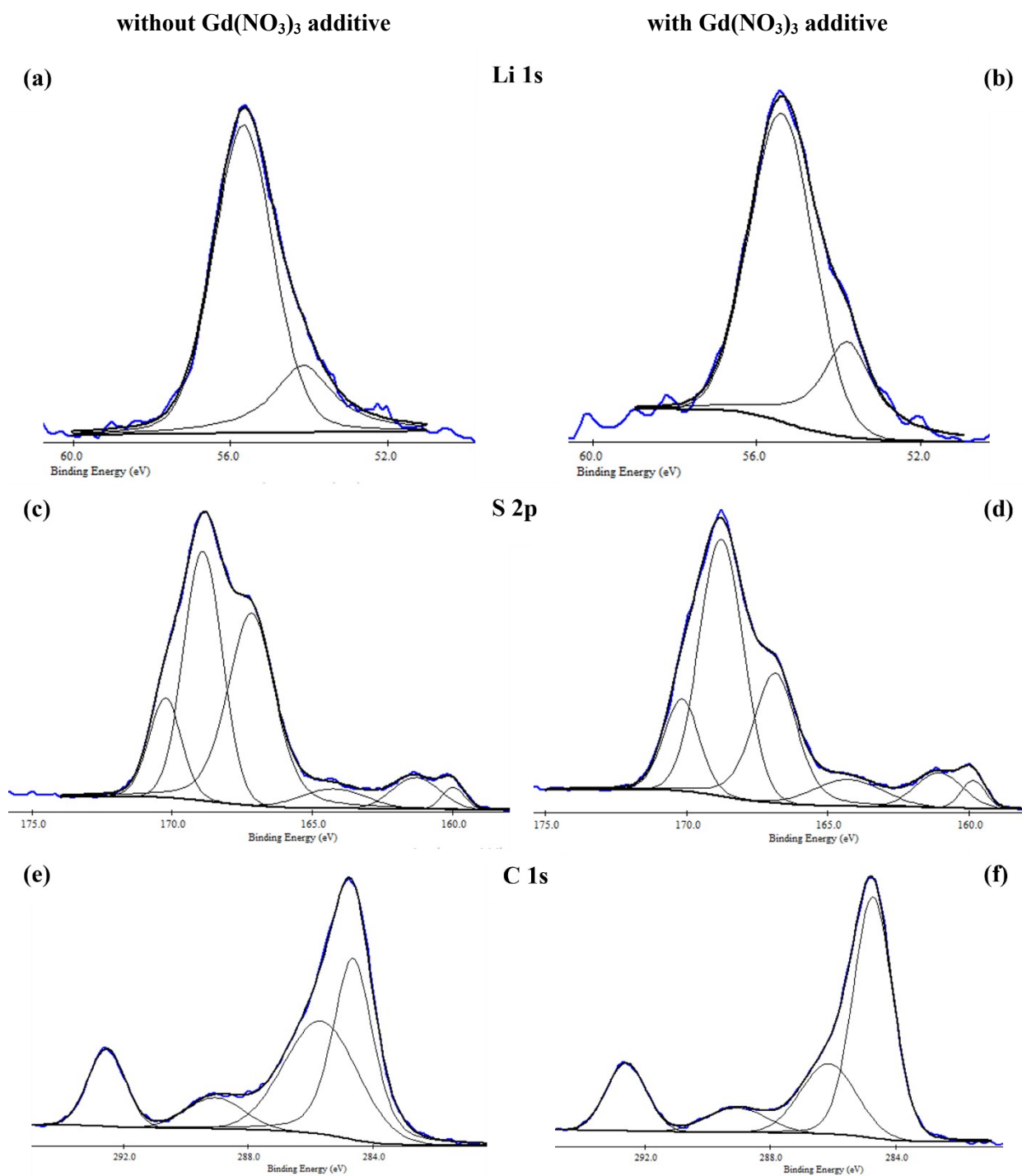
II. Supplementary Figures



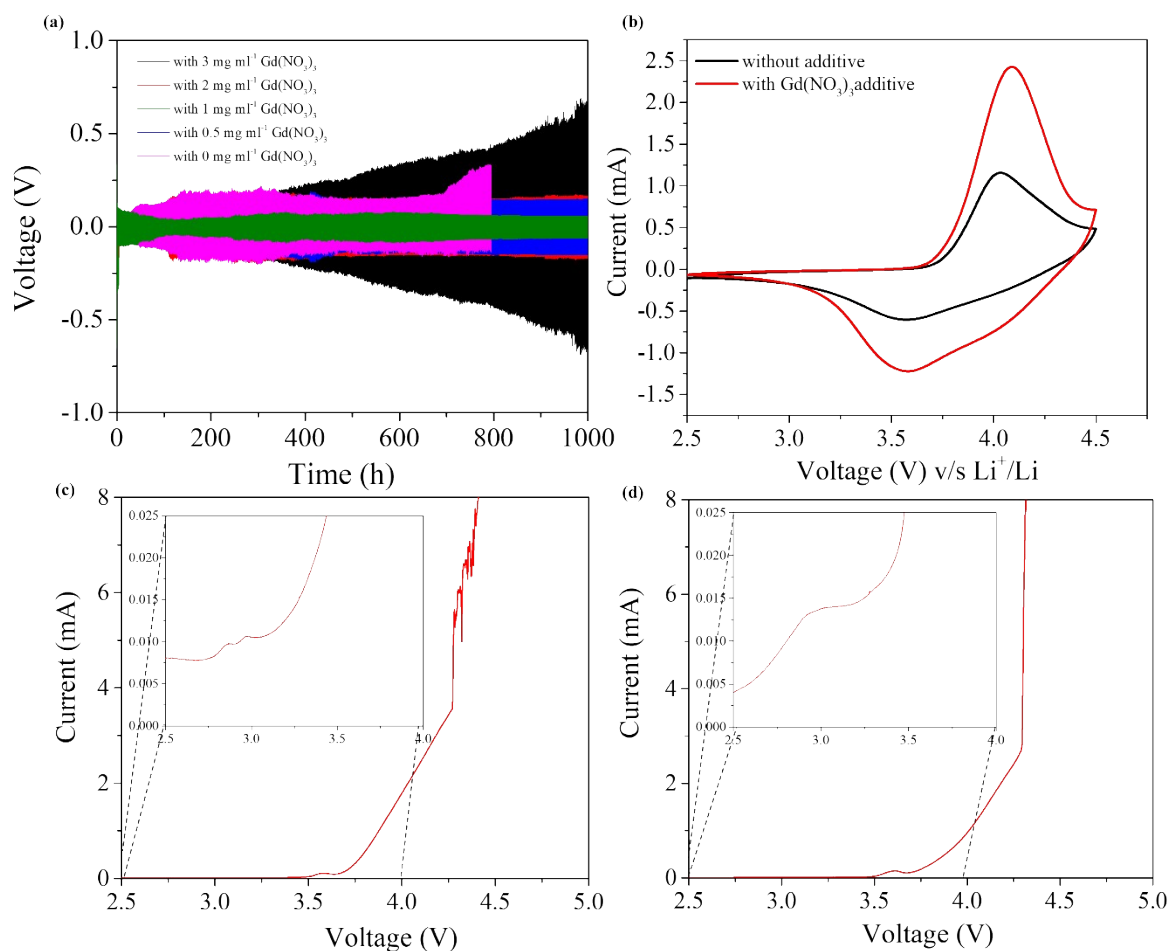
Supplementary Figure S1. EDS analysis of LMA surfaces cycled (a) without electrolyte additive, and (c) with $\text{Gd}(\text{NO}_3)_3$ additive. Contact angle measurements of electrolytes on Li metal surface (b) without $\text{Gd}(\text{NO}_3)_3$ additive, and (d) with $\text{Gd}(\text{NO}_3)_3$ additive.



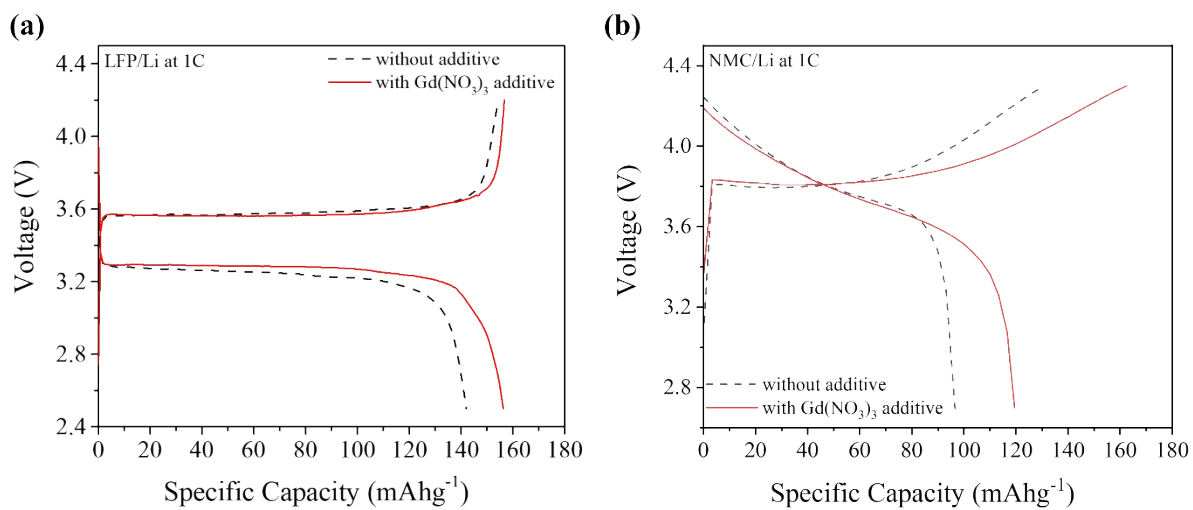
Supplementary Figure S2. Raw XPS spectra for (a) C 1s, (b) N 1s, (c) O 1s, (d) F 1s, (e) Li 1s and (f) Gd 4d of LMA surface cycled without and with Gd(NO₃)₃ additive in the electrolyte. Multiple scans of LMA surface w/o Gd additive were carried out and depicted by different colors.



Supplementary Figure S3. Fitted XPS spectra of (a, b) Li 1s, (c, d) S 2p, and (e, f) C 1s for post-cycling LMA surfaces without and with Gd(NO₃)₃ additive.



Supplementary Figure S4. (a) Additive concentration optimization experiments by cycling Li symmetrical cells with different $\text{Gd}(\text{NO}_3)_3$ additive amount in the electrolyte; (b) Cyclic voltammetry curves for Li/NMC 111 full cells with and without $\text{Gd}(\text{NO}_3)_3$ additive; LSV for Li/NMC 111 full cells cycled in electrolyte (c) without, (d) with $\text{Gd}(\text{NO}_3)_3$ additive, inset shows the enlarged plot from 0-0.0025 mA current.



Supplementary Figure S5. Initial Charge-Discharge curves of (a) LFP/Li and (b) NMC/Li cells

III. Supplementary Tables

Supplementary Table S1. Mass fractions obtained from EDS analysis

Element	Without Gd(NO ₃) ₃ additive	With Gd(NO ₃) ₃ additive
F	29.90 %	30.00 %
O	48.30 %	24.48 %
N	3.00 %	3.27 %
S	10.00 %	11.39 %
C	8.80 %	15.94 %
Gd	0.00 %	14.92 %
Total	100.00 %	100.00 %

Supplementary Table S2. Elements obtained from different XPS analysis spectra.

XPS spectra	Without Gd additive		With Gd(NO ₃) ₃ additive	
	Atom %	Weight %	Atom %	Weight %
C 1s	27.6	21.99	30.1	24.20
N 1s	4.1	3.81	5.4	5.06
O 1s	23.3	24.74	20.8	22.28
F 1s	20.5	25.84	18.2	23.15
S 2p	7.4	15.74	6.8	14.60
Li 1s	17.1	7.88	18.5	8.60
Gd 4d	0.0	0.00	0.2	2.11
Total	100.0	100.0	100.0	100.0

Supplementary Table S3. R_{ct} values at different cycle numbers for NMC/Li full cells.

Cycle number	Without additive	With $Gd(NO_3)_3$ additive
0	286.85 Ω	184.49 Ω
5	700 Ω	439.87 Ω
10	734.71 Ω	490.89 Ω
50	515 Ω	477 Ω
100	500 Ω	286.94 Ω