Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Insights into Lithium Inventory Quantification of $LiNi_{0.5}Mn_{1.5}O_4$-Graphite Full Cells

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Table S 1 Summary of Lithium inventory quantification study

No.	System	Li inventory quantification			Conclusion
		Cathode	Anode	Electrolyte	
1	NCM-811/Gr	XRD	/	/	High temperature causes severe capacity loss to NCM-811[1].
2	NCM-811/Gr	Differential voltage analysis	Differential voltage analysis	/	Active Li loss at the anode SEI dominants the capacity loss[2].
3	Gr/Li	/	MS titration	/	Plated Li causes extra SEI formation[3].
4	NMC532/Gr	/	/	ICP-MS	Li^+ in electrolyte has not been consumed or has been consumed at the same rate as the solvent[4].
This work	LNMO/Gr	XRD	TGC	ICP-MS	SEI growth is the dominant reason for active Li inventory loss in LNMO/graphite cell

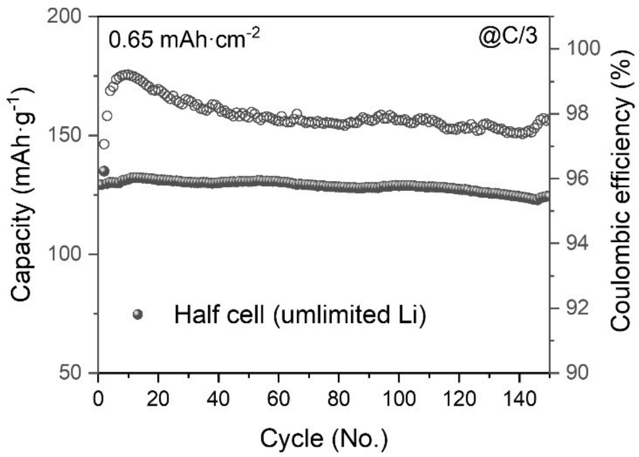

Figure S 1 Half cell cycling performance of (a) LNMO and (b) Graphite. Cycling conditions:3.5-4.85V with Gen2 electrolyte.

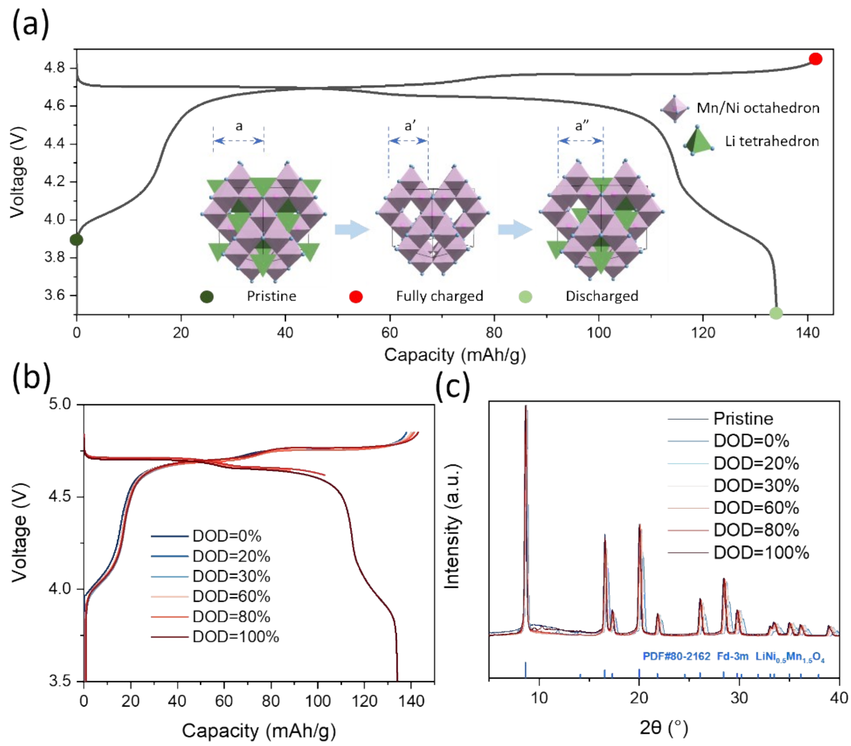

Figure S 2 (a) LNMO half cell 1st charge-discharge profile with corresponded structural change; (b) Charge-discharge profiles of LNMO half cell stopped at different DOD% and (c) Corresponding XRD spectra.

A set of cells was selected with a controlled DOD, changes in capacity are attributed to the active Li in the cathode. When the cell is discharged to X% DOD, minimal CEI formation occurs during the first cycle. Therefore, the remaining capacity in the cathode can be calculated as the theoretical capacity minus the difference between the charge and discharge capacities:

Remained capacity (DOD X%) = Theoretical capacity– (charge capacity - discharge capacity)

Obtaining the remained capacity and lattice parameters at different DODs enables the calibration curve for the cathode active Li inventory.

Table S2 Li inventory in cathode

Sample	Delivered discharge capacity (mAh/g)	Remained capacity (mAh/g)	Kinetically Trapped capacity (mAh/g)
After 1 cycle	112.83	122	~10
After 140 cycles	88.42	104	~16

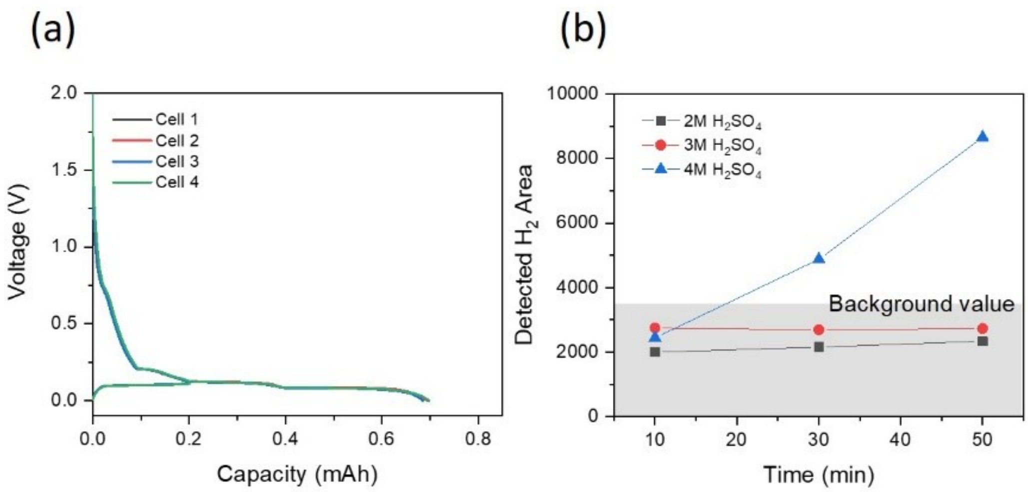

Figure S 3 (a) Charge and discharge profile of Li||Gr for solvent optimization;(b) TGC results of Cu current collector with H_2SO_4 solutions.

Table S3 TGC results of different titration solvents with the Li_xC_6 sample from Figure S3a.

Solvent	Total discharge capacity (mAh)	Charge capacity (mAh)	Remaining capacity (mAh)	Estimated value (mAh)	Actual Capacity from Titration (mAh)	Ratio
H_2O	0.6957	0.2000	0.4957	0.4261	0.3537	83.0%
0.5M H_2SO_4	0.6915	0.2000	0.4915	0.4224	0.3683	87.2%
2M H_2SO_4	0.6841	0.2000	0.4841	0.4157	0.3961	95.3%
4M H_2SO_4	0.6978	0.2000	0.4978	0.4280	0.4203	98.2%

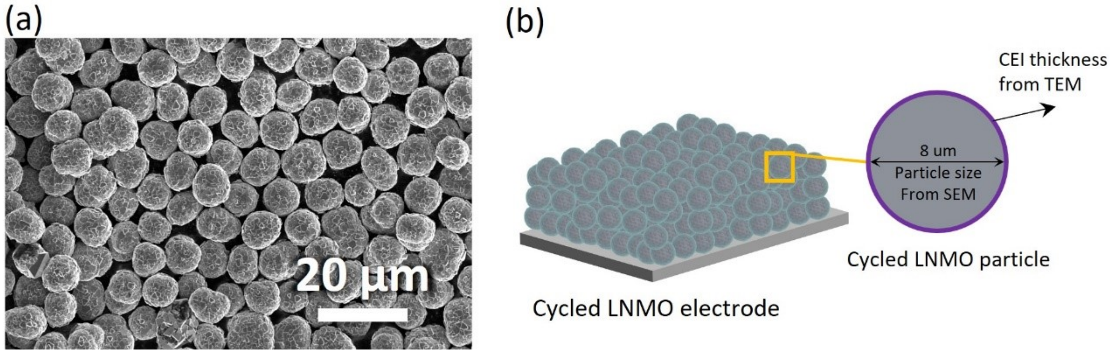

Figure S 4 (a) SEM image of LNMO cathode. The particle size is 8 um. (b) Model Schematic for the CEI estimation, the estimation value of Li inventory in the CEI is listed in the Table S4.

Table S4 Estimation of Li inventory in the CEI

	Value	Unit		Value	Unit
Density of LiF	2.64	g/cm^3	**Mass of single LNMO particle**	1.21E-09	g
Density of LNMO	4.50	g/cm^3	**Active mass of LNMO electrode**	1.36E-02	g/cm^2
Single LNMO particle size	8.00	um	**Number of LNMO particle**	1.12E07	$count/cm^2$
Volume of single LNMO particle	2.68E-10	cm^3			
1st cycle CEI			**140th cycle CEI**		
CEI thickness from TEM	1.5	nm	**CEI thickness from TEM**	3.5	nm
Volume of single LNMO particle+CEI	2.68E-10	cm^3	**Volume of single LNMO particle+CEI**	2.69E-10	cm^3
Volume LiF in single LNMO particle	3.02E-13	cm^3	**Volume LiF in single LNMO particle**	7.04E-13	cm^3
Mass of LiF in single LNMO particle	7.97E-13	g	**Mass of LiF in single LNMO particle**	1.86E-12	g
Total mass of LiF	8.93E-06	g/cm^2	**Total mass of LiF**	2.08E-05	g/cm^2
Mole of Li	3.44E-07	mol/cm^2	**Mole of Li**	8.02E-07	mol/cm^2
Related Li amount	9.20E-03	mAh/cm^2	**Related Li amount**	2.15E-02	mAh/cm^2

***1mAh=3.7368E-05 mol Li; Assumption: all the CEI is composed of LiF**

The calculation of the Li amount consumed in the CEI after 140 cycles is based on the TEM results and morphology of the LNMO. The LNMO has a sphere morphology with a particle size of 8 µm. Therefore, the mass of **a single LNMO particle** is:

$$Mass_{LNMO} = Density_{LNMO} \times Volume_{LNMO} = 4.5\ g \cdot cm^{-3} \times 2.68 \times 10^{-10} c$$

g

The **total number of LNMO particles** is calculated based on the active mass on the electrode:

$$Total_{LNMO} = Active\ mass_{LNMO} \times Mass_{LNMO} = 1.36 \times 10^{-2}\ g{\cdot}cm^{-2} \div 1.2$$
$$g = 1.12 \times 10^{7}\ particle{\cdot}cm^{-2}$$

The CEI thickness is 3.5 nm from TEM if we assume all the particles are covered by the 3.5nm CEI and that the CEI is composed of LiF. **The mass of LiF on a single LNMO particle** is.

$$Mass_{LiF} = (Volume_{LNMO+CEI} - Volume_{LNMO}) \times Density_{LiF} = (2.69 \times 1$$
$$2.68 \times 10^{-10}\ cm^{3}) \times 2.64 g{\cdot}cm^{-3} = 1.86 \times 10^{-12} g$$

The **total mass of LiF on the electrode** is:

$$Total\ Mass_{LiF} = Mass_{LiF} \times Total_{LNMO} = 1.86 \times 10^{-12} g \times 1.12 \times 10^{7}\ particle$$
$$= 2.08 \times 10^{-5} g{\cdot}cm^{-2}$$

The related Li mAh/cm^2 amount is:

$$Li\ amount\ in\ CEI = Total\ Mass_{LiF} \div Molecular\ Mass_{LiF} \div 3.7368 \times 10^{-5} = 2.15 \times 10^{-2}\ mAh{\cdot}cm^{-2}$$

The ratio of CEI Li compared to total Li (2 mAh · cm^{-2}):

$$2.15 \times 10^{-2}\ mAh{\cdot}cm^{-2} \div 2\ mAh{\cdot}cm^{-2} = 1\%$$

A similar approach is applied to calculate the 1st cycle Li amount in CEI.

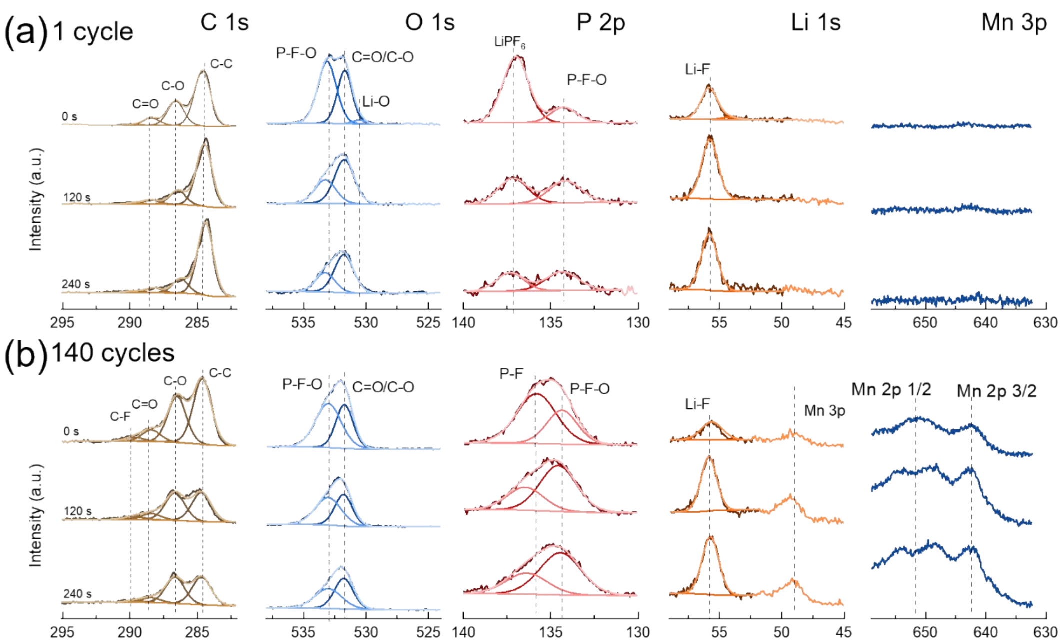

Figure S 5 XPS depth profile spectra of Gr anode after different cycles.

Table S5 Li inventory evolution in LNMO-Gr full cell upon cycling

Sample	Active Li in cathode (mAh/g)	Li kinetically trapped in cathode (mAh/g)	Li trapped in anode (mAh/g)	Electrolyte Li amount	Interphase Li* (mAh/g)
After 1 cycle	112.83	10	5.7	~5×10^{-4} mol	~18.5
After 140 cycles	88.4	16	3.3	＜5×10^{-4} mol	＞39.3

The Li inventory calculation:

At the Pristine state, active Li is only present in the cathode, and the amount is 147 $mAh\cdot g^{-1}$ (2 $mAh\cdot cm^{-2}$). After 140 cycles the Li inventory in each part is:

On the cathode side, after 140 cycles, the XRD shows the remaining capacity of the cathode is 104 $mAh\cdot g^{-1}$, of which 88.4 $mAh\cdot g^{-1}$ (60%) is reversible Li from the discharge capacity, the remaining 15.6 $mAh\cdot g^{-1}$ (10%) is kinetically trapped Li. The CEI Li is 1% based on previous calculations.

On the anode side, after 140 cycles, the TGC results show the Li trapped in the anode is 33 $mAh\cdot g^{-1}$ (2%).

The residual lithium from the cathode, with a capacity of 39.69 $mAh\cdot g^{-1}$ (27%), is consumed in the formation of SEI. Additionally, since Li from the electrolyte also contributes to SEI formation, the total amount of SEI formed exceeds 27%.

A similar approach is used to calculate the Li inventory in 1st cycle sample.

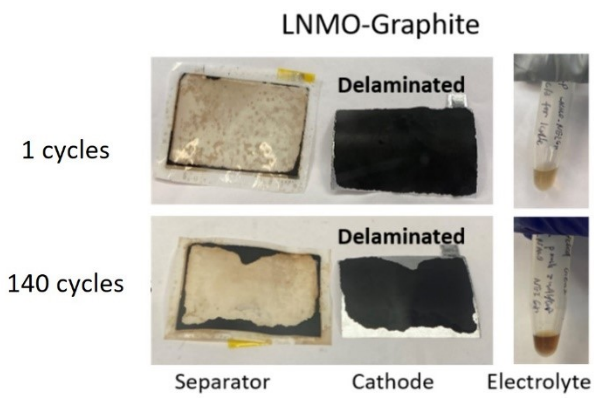

Figure S 6 Optical images of cycled LNMO-Gr pouch cells after disassembly.

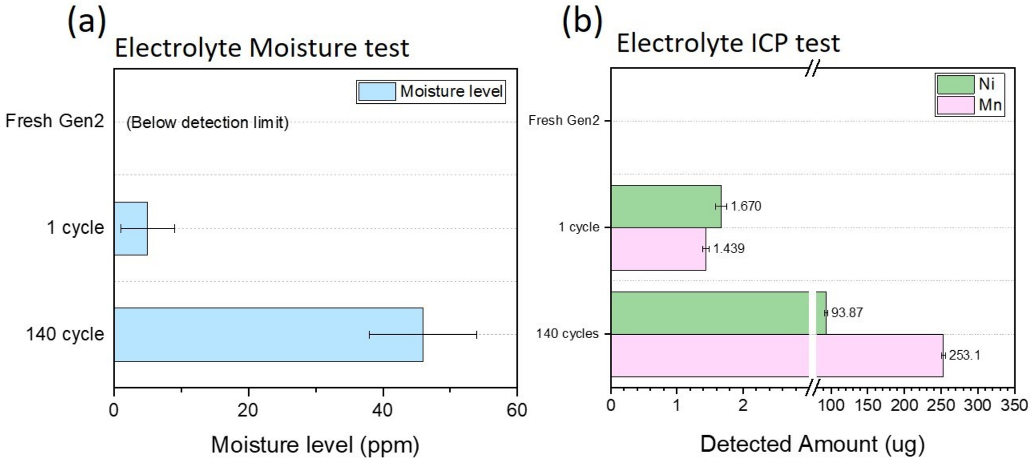

Figure S 7 Cycled electrolyte (a) Moisture test and (b) ICP-MS results of cycled electrolyte

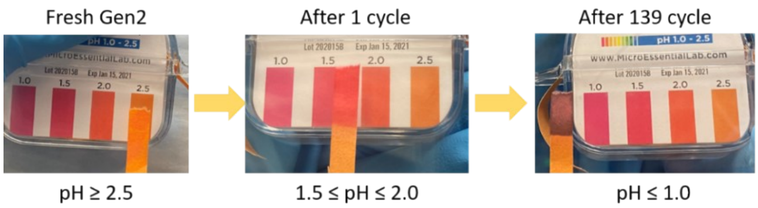

Figure S 8 pH value check on cycled electrolyte from LNMO-Gr pouch cell

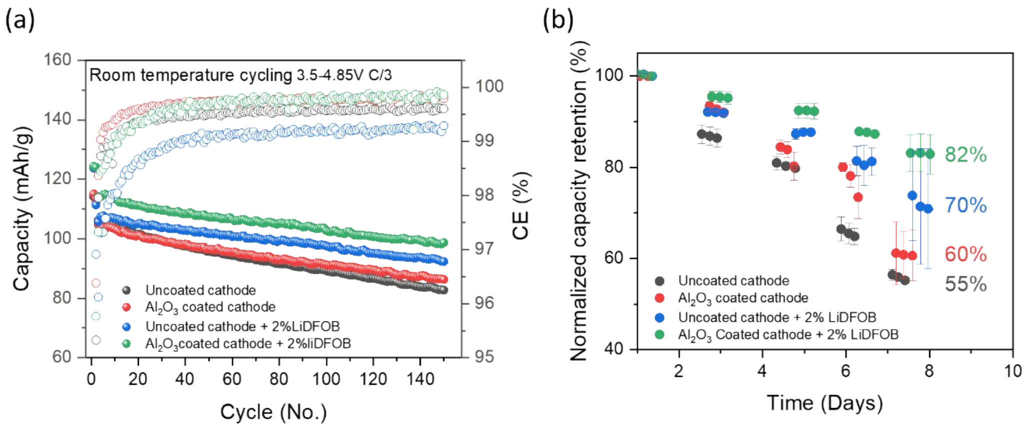

Figure S 9 (a) Room temperature coin cell cycling performance and (b) high temperature storage test of LNMO-Gr system with different improvement methods. The cell storage at 55 ℃ @100% SOC every 3 cycles.

References

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