Supplementary information

Constructing "Li-rich Ni-rich" cathodes for high-energy-density Li-ion batteries

Biao Li^{1,2}, Gwenaëlle Rousse^{1,2,3}, Leiting Zhang⁴, Maxim Avdeev^{5,6}, Michaël Deschamps^{2,7}, Artem M. Abakumov⁸, Jean-Marie Tarascon^{1,2,3*}

¹Chimie du Solide-Energie, UMR 8260, Collège de France, 75231 Paris Cedex 05, France.

²Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France.

³Sorbonne Université, 4 Place Jussieu, 75005, Paris, France.

⁴Battery Electrodes and Cells, Electrochemistry Laboratory, Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen-PSI, Switzerland. (*Present address: Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden.*)

⁵School of Chemistry, The University of Sydney, Sydney, New South Wales, Australia.

⁶Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, Kirrawee DC, New South Wales, Australia.

⁷CNRS, CEMHTI UPR3079, Université d'Orléans, Orléans, France

⁸Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel str. 3, 121205 Moscow, Russia.

* Corresponding author: jean-marie.tarascon@college-de-france.fr



Figure S1. SEM images of $Li_{1+y}Ni_{(3-5y)/3}Mo_{2y/3}O_2$ (y=0, 0.03, 0.06, 0.09). It can be seen that, with the addition of Li and Mo, the primary particle size is getting smaller prominently.



Figure S2. Lattice parameters of $Li_{1+y}Ni_{(3-5y)/3}Mo_{2y/3}O_2$ (*y*=0, 0.03, 0.06, 0.09, and 0.12) determined from Rietveld refinement.



Figure S3. HAADF-STEM image of two adjacent twinned domains of the O3 structure (marked as 1 and 2) with the corresponding Fourier transforms taken from the encircled areas. The Fourier transforms are indexed with the R-3m O3-type structure; they clearly demonstrate different orientation of the 00*l* reciprocal lattice rows confirming mirror twin. The common reflection row of the two twin domains is along the 104 reflection (marked with dashed lines in the Fourier transforms and the experimental ED pattern). This indicates (104) as the twin plane (marked with the dashed line in the image). Contributions of the ED patterns from two twin domains gives rise to weak reflections due to multiple diffraction (marked with squares in the experimental ED pattern).



Figure S4. XRD patterns and electrochemistry of non-Li-rich LiNi_{1-y}Mo_yO₂ (y=0.02, 0.04, 0.06, 0.08) compounds. (a-d) XRD patterns. (e-l) Electrochemical cycling curves and their corresponding dQ/dV profiles. The first discharge capacity and first-cycle Coulomb efficiency are annotated beside the cycling curves.



Figure S5. (a) Half-cell cycling performance of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$. The cells were cycled at 0.8C/1C (1C=200 mA g⁻¹) at room temperature (25±1°C) in half cell with Li as anode. (b) Full cell cycling performance of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ at 25°C. A commercial graphite anode (Umicore) having a composition of 91.5% graphite and 8.5% PVDF, with a loading of ~7 mg cm⁻², was used to construct the full cell. The cathode material consists of 80% active materials and 20% carbon Super P, with a loading of ~10 mg cm⁻². The N/P ratio was around 1.1 calculated based on a capacity of 360 mA h g⁻¹ for graphite and 230 mA h g⁻¹ for Li_{1.09}Ni_{0.85}Mo_{0.06}O₂.



Figure S6. Rate performance (a, charge and b, discharge) for $Li_{1+y}Ni_{(3-5y)/3}Mo_{2y/3}O_2$ (y=0, 0.03, 0.06, 0.09, and 0.12).



Figure S7. Electrochemical performance of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ in the voltage window of 2.0-4.8V. **a**, Galvanostatic cycling curve of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ between 2.0 and 4.8V at a current density of 20 mA g⁻¹ at room temperature. The cycling performance is shown as inset. **b**, 5th cycle showing the mild voltage hysteresis with an energy efficiency of ~91%. **c**, The evolution of discharge curves with normalized capacity, showing negligible voltage decay. **d**, dQ/dV plots during cycling showing stable redox peaks.



Figure S8. DSC results of sample LiNiO₂, Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ and Li_{1.12}Ni_{0.8}Mo_{0.08}O₂ charged to 4.3 V. The total heat flow is indicated for each sample. The heat flow peaks at ~210 °C of Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ and Li_{1.12}Ni_{0.8}Mo_{0.08}O₂ are largely suppressed compared with that of LiNiO₂. However, additional peaks around 130-160 °C emerged due to unknown sources (probably originate from the interaction of Mo-rich phase with electrolyte).



Figure S9. The energy density (cathode active material based) and energy efficiency of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ during cycling at C/10.



Figure S10. a, Electrochemical curve of the first 3 cycles of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ at C/10 in the voltage range of 2.7-4.3V. **b**, Cycling performance at C/2 in the range of 2.7-4.3V.



Figure S11. Comparison of electrochemical performance of different loadings of cathode electrode. Green curve: 80% AM and 20% carbon super P with a loading of 6-8 mA/cm². Pink curve: 96% AM and 4% carbon super P with a loading of 10-12 mA/cm². Increasing the loading apparently influence the stability especially at the beginning of cycling. However, considering that the material is Co-free and the introduction of Li and Mo should decrease the electronic conductivity, we think this limitation is acceptable and can be improved in the future based on compositional design and morphology control.



Figure S12. Comparison of the *in situ* XRD evolution between LiNiO₂ and Li_{1.09}Ni_{0.85}Mo_{0.06}O₂. (a-b) *In situ* XRD patterns for LiNiO₂ and Li_{1.09}Ni_{0.85}Mo_{0.06}O₂, respectively. (c-d) XRD patterns (16-23°) at the end of charge in 2^{nd} cycle (2C4.3V) for LiNiO₂ and Li_{1.09}Ni_{0.85}Mo_{0.06}O₂, respectively. The pattern of charged LiNiO₂ shows a bifurcation of (003) peak with the co-existence of Li-rich and Li-poor phases due to bulk fatigue, whereas the pattern of charged Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ only shows a single-phase. Note that during the 1st charge the (003) peak shifts in a larger magnitude in LiNiO₂ than that of Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ because the former delivers higher charging capacity. While for the 2^{nd} charge, it is because LiNiO₂ has a bifurcation and hence pushes the Li-poor phase more shifted.



Figure S13. *In situ* XRD for LNO (BASF). **a**, cycling curve of LNO during the first three cycles. 15 mA g^{-1} was used for the H2-H3 phase transition region otherwise 20 mA g^{-1} was used. A short relaxation was done at the end of charge in first two cycles in order to capture the XRD pattern of the fully charged state. A constant voltage charge was applied in the end of charge at 3^{rd} cycle with a cutoff current of C/100 (2 mA g^{-1}). The region where XRD patterns were collected was highlighted by color-coded shaded area. **b**, XRD patterns and their corresponding contour plots during the H2-H3 phase transition of the first 3 cycles. XRD pattern was collected around every 12 min and only in the range of 15-23° to have a high resolution. **c**, Comparison of the XRD patterns at the end of every cycle. Note that for 3^{rd} cycle, the pattern is taken from the end of constant-current charging process.

While the 1st cycle shows almost a complete phase transition behavior, a bifurcation starts to appear in the 2nd cycle and aggravates at 3rd cycle (Fig.S13b,c). Even by holding the voltage at 4.3V at 3rd charge process, the "Li-rich" phase cannot fully disappear (Fig.S13b, 3rd cycle). Therefore, we believe this socalled "bulk fatigue" behavior does happen for LNO, but whose extent highly depends on the cycling rate and synthetic conditions, as apparently our synthesized LNO shows more prominent bifurcation behavior (2nd cycle).



Fig. S14 HAADF-STEM images of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ in the charged (a) and discharged (b) states. Electron diffraction patterns are shown as inserts, the c-axes of twinned domains of the O3 structure are marked.



Fig. S15 Rietveld refinement of SXRD pattern of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ after 50 cycles at 0.2C between 2.0-4.3V.



Figure S16. Redox mechanism of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$. **a**, the 1st cycle curve with marked SoCs where samples were taken for Ni K-edge XAS measurements. **b**, Ni K-edge XANES during 1st cycles. **c**, Mo K-edge XANES of pristine and 1st discharged samples. **d**, GITT curve of 2nd cycle. Oxygen oxidation and reduction region were highlighted to show the redox inversion behavior.

From Fig. S16b we can see that Ni is the main redox-active species, which changes reversibly and symmetrically between charge and discharge processes. However, Ni K-edge shifts in a larger magnitude for "pristine \rightarrow 1C3.9V" compared with "1C3.9V \rightarrow 1C4.3V" while both periods have similar capacities (Fig.S16b, inset), indicating that Ni³⁺/Ni⁴⁺ redox dominates at the beginning, whereas, most probably, oxygen redox is also active in high voltage region. This O activity can come from σ -type Ni3*d*-O2*p* interactions but may also from O 2*p* lone-pair states as the LiNiO₂-domain was confirmed to be slightly Lirich (Li_{1.04}Ni_{0.93}Mo_{0.03}O₂).

Another signature evidence of O redox activity from lone-pair states is the large hysteresis observed in the end of discharge, as identified from the GITT analysis (Fig.S16d). Typically, Ni-doped Li-rich materials will have such voltage hysteresis associated with redox inversion (i.e. Ni reduction happens before O reduction during discharge) as shown in our recent paper¹. This behavior can also be found in similar systems like Fe² and Ni-doped³ Li₄MoO₅ compounds that also feature out a low-voltage oxygen-redox plateau during discharge with large hysteresis.

There is no Mo⁶⁺ reduction during discharge as inferred from the Mo K-edge XAS (Fig.S16c). This agrees well with NMR signal for Li_4MoO_5 domain that shows no chemical shift upon cycling, since, once Mo reduction happens, the generated Mo³⁺/Mo⁴⁺/Mo⁵⁺ species should not be diamagnetic. Besides, Mo redox with large voltage hysteresis is hard to understand if this is the true case.

It may be noted that the activation of anionic redox happens at a relatively lower potential (4.1-4.3V) than some reported compounds, such as Ni-substitued Li_2TiO_3 system (~4.4V). In the case of Li_4MoO_5 , due to the high valence of Mo^{6+} , the number of Li^+ surrounding one specific O ion should be larger than Ti^{4+} for local charge balance. This leads to less positive charges around O 2*p* lone-pair states and hence less Coulombic attraction, pushing the O 2*p* lone-pair electrons to higher energy, and hence the lower activation potential.



Figure S17. Extending the study to other transition metal ions. a,b, the XRD pattern and cycling curves (inset shows the cycling stability) of $Li_{1.1}Ni_{0.7}Ti_{0.2}O_2$ compound, respectively. c,d, the XRD pattern and cycling curves (inset shows the cycling stability) of $Li_{1.08}Ni_{0.84}Nb_{0.08}O_2$ compound, respectively. Note that in both cases, the XRD patterns show a similar feature of the reversal of the relative intensity of (003) and (104) diffraction peaks, highlighting a possible layered-disorder intergrowth alike Li-Ni-Mo-O compounds. Therefore, these two cases by Ti⁴⁺ and Nb⁵⁺, as representatives of tetravalent and pentavalent transition metal ion doping, validate the feasibility of constructing Li-rich Ni-rich compounds in a broader range of transition metal systems.



Fig. S18 ⁷Li (top) and ⁶Li (bottom) MAS-NMR spectra of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$. The spinning sidebands are only detected in the ⁷Li spectrum, and are indicated by a *. The short relaxation delay (50 ms) used in the ⁶Li MAS NMR experiment leads to an underestimation of the diamagnetic component stemming from Li_4MoO_5 . The comparison of the experiments allowed us to rule out the presence of lithium in the paramagnetic phase with small negative chemical shifts.

Supplementary note I. Calculation of the size Li₄MoO₅-rich domain.

To infer the size of Li₄MoO₅ domains, we computed the ratio between the area of the bulk signal of Li₄MoO₅ (around 0 ppm) and the interface signal (the LiNi_xMo_{1-x} peaks, which are expected to have at least one Ni³⁺ as second neighbor, and have shifts between 80 and 350 ppm). Spherical clusters of Li₄MoO₅ with a radius of *R* Å (computed with CrystalMaker derived from the XRD structure of Li₄MoO₅) usually contain 0.4944*R*^{2.9627} atoms. Assuming that the interface is a layer with a thickness of 4.25Å (corresponding to the Li-O-M distance), the ratio between the bulk and interface signals varies linearly, with *R* = 13.6 A(bulk)/A(interface) + 6.5. As the ratios were measured at 0.7, 1.02, 1.74 and 2.21 for Li_{1.03}Ni_{0.95}Mo_{0.02}O₂, Li_{1.06}Ni_{0.9}Mo_{0.04}O₂, Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ and Li_{1.12}Ni_{0.8}Mo_{0.8}O₂, respectively, our simple model would imply the existence of Li₄MoO₅ domains of diameters roughly equal to 3.2, 4.1, 6.0 and 7.3 nm approximatively.

Supplementary note II. Discussion of the CO₂ release by OEMS.

The amount of CO_2 release is in similar (even less) amount compared with that of previously reported Li-rich compounds charged to 4.8V, both using same amount (150µl) of LP30 electrolyte (see Table R1 below). Note that as we did the OEMS of LiNiMoO in the voltage range of 2.0-4.8V and the "compound" is Li-rich, it makes sense to compare both together. This demonstrates that most of the extra Li added should enter in the LiNiO₂ domain rather than forming Li₂CO₃, as otherwise the amount of CO₂ release should be much higher than expected.

Compound	electrolyte	Voltage range	1 st cycle CO ₂	Reference
			release	
Li1.09Ni0.85Mo0.06O2	150µl LP30	2.0-4.8V	547.9 μmol·g ⁻¹	This work
Li _{1.2} Ti _{0.6} Ni _{0.2} O ₂	150µl LP30	2.0-4.8V	739(17) µmol·g⁻¹	Ref.1
$Li_{1.17}Ti_{0.58}Ni_{0.25}O_2$	150µl LP30	2.0-4.8V	739(35) µmol·g ⁻¹	Ref.1
Li _{1.09} Ti _{0.55} Ni _{0.36} O ₂	150µl LP30	2.0-4.8V	580(16) μmol·g ⁻¹	Ref.1
Li _{1.17} Ti _{0.33} Fe _{0.5} O ₂	150µl LP30	2.0-4.8V	1070(45) µmol·g ⁻¹	Ref.4

Table S-note1. Comparison of the amount of CO₂ release in different cathode materials.

Nominal composition	ICP determined atomic ratio				
-	Li	Ni	Мо		
LiNiO ₂	0.991181	1	0		
$Li_{1.03}Ni_{0.95}Mo_{0.02}O_2$	1.04	0.95	0.00984		
$Li_{1.06}Ni_{0.90}Mo_{0.04}O_2$	1.05	0.90	0.01935		
$Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$	1.10	0.85	0.033633		
Li _{1.12} Ni _{0.80} Mo _{0.08} O ₂	1.11	0.80	0.045802		

Li-Ni-Mo-O compounds.

Table S2. Ni/Mo ratios determined from SEM-EDX method.

	Li _{1.03} Ni _{0.95} Mo _{0.02} O ₂	Li1.06Ni0.9Mo0.04O2	Li1.09Ni0.85Mo0.06O2	Li _{1.12} Ni _{0.8} Mo _{0.08} O ₂
Nominal	Ni _{0.95} Mo _{0.02}	Ni _{0.9} Mo _{0.04}	Ni _{0.85} Mo _{0.06}	Ni _{0.8} Mo _{0.08}
EDX	Ni _{0.95} Mo _{0.023}	Ni _{0.90} Mo _{0.039}	Ni _{0.85} Mo _{0.063}	Ni _{0.80} Mo _{0.076}

Table S3 Crystallographic data of Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ (pristine, charged, and discharged) determined from combined Rietveld refinement of SXRD and NPD patterns.

$Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ (Pristine) $\chi^2 = 4.14$, Bragg R-factor = 5.01 % (weighted average)							
Phase 1 : Li _{1.0}	Phase 1 : $\text{Li}_{1.04}\text{Ni}_{0.93}\text{Mo}_{0.03}\text{O}_2$ (95.2(7) mol%) Space group: $R^{\overline{3}}m$ $a = 2.88097(5)$ Å, c=14.19145(58),						
α=β=90°, γ=1	$\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}, V = 102.008(5) \text{ Å}^3$						
Atom	Site	x/a	y/b	z/c	Occupancy	B_{iso} (Å ²)	
01	6 <i>c</i>	0	0	0.25998(6)	1.000	0.693(16)	
Lil	3 <i>b</i>	0	0	0.5	0.953(1)	1.138(54)	
Ni2	3 <i>b</i>	0	0	0.5	0.047(1)	1.138(54)	
Ni1	3 <i>a</i>	0	0	0	0.883(1)	0.196(4)	
Mol	3 <i>a</i>	0	0	0	0.03	0.196(4)	
Li2	3 <i>a</i>	0	0	0	0.087(1)	0.196(4)	
Phase 2 : Li_4MoO_5 (4.8(3) mol%) S		Space gro	oup: <i>Fm</i> ³ <i>m</i>	<i>a</i> = 4.09378(51) Å,	$\alpha = \beta = \gamma = 90^{\circ}, V =$	68.608(15)Å ³	
Lil	4a	0	0	0	0.800	1.000	
Mol	4a	0	0	0	0.200	1.000	
01	4b	0.5	0.5	0.5	1.000	1.000	

Note: Ni^{2+} can form and intermix with Mo^{6+} in the Li_4MoO_5 -rich rock-salt phase. This can be partially inferred from NMR where there are some intermediate signals in between $LiNiO_2$ and Li_4MoO_5 signal that might originate from these kinds of species. However, the amount of Ni^{2+} is not significant as observed from XAS (Fig.S16b). Therefore, we neglected the Ni^{2+} in Li_4MoO_5 in a purpose of simplifying the model of refinement to deliver a general idea of what kind of the structure it is, otherwise too many uncertainties, including phase separation, Ni/Mo ratio in each phase, as well as Li/Ni disorder etc., may cause over-fitting of the data and over-interpretation.

Table S4 Crystallographic data of Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ (charged) determined from combined Rietveld refinement of SXRD and NPD patterns.

Li_{0.28}Ni_{0.85}Mo_{0.06}O₂ (Charged) $\chi^2 = 3.02$, Bragg R-factor = 8.64 % (weighted average)

Atom	Site	x/a	y/b	z/c	Occupancy	B _{iso} (Å ²)
01	6 <i>c</i>	0	0	0.26362(1)	1.000	1.432(22)
Lil	3 <i>b</i>	0	0	0.5	0.116(1)	0.640(141)
Ni2	3 <i>b</i>	0	0	0.5	0.044(1)	0.467(141)
Ni1	3 <i>a</i>	0	0	0	0.886(1)	0.588(5)
Mo1	3 <i>a</i>	0	0	0	0.03	0.588(5)
Li2	3 <i>a</i>	0	0	0	0.084(1)	0.588(5)
Phase 2 : Li ₄ N	40O ₅ (1.8(2) mol	1%) Space gr	oup: <i>Fm</i> ³ <i>m</i>	$a = 4.01753(23)$ Å, $\alpha = \beta = \gamma = 90^{\circ}$, $V = 64.845($		
Å ³						
Lil	4a	0	0	0	0.800	1.000
Mol	4a	0	0	0	0.200	1.000
01	4b	0.5	0.5	0.5	1.000	1.000

Phase 1 : $\text{Li}_{0.2}\text{Ni}_{0.93}\text{Mo}_{0.03}\text{O}_2$ (98.2(8) mol%) Space group: R^3m a = 2.81997(11) Å, c = 13.9771(23), $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, V = 96.258(17) Å³

Table S5 Crystallographic data of Li_{1.09}Ni_{0.85}Mo_{0.06}O₂ (discharged) determined from combined Rietveld refinement of SXRD and NPD patterns.

$Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ (Discharged) $\chi^2 = 1.69$, Bragg R-factor = 2.62 % (weighted average)							
Phase $1 : Li_{1.0}$	₄ Ni _{0.93} Mo _{0.03} O ₂ (96	5.8(8) mol%)	Space group	a = 2	.88256(3) Å, <i>c</i> =1	4.20854(25),	
α=β=90°, γ=1	20°, V = 102.439(2) Å ³					
Atom	Site	x/a	y/b	z/c	Occupancy	B_{iso} (Å ²)	
01	6 <i>c</i>	0	0	0.25896(7)	1.000	0.830(17)	
Lil	3 <i>b</i>	0	0	0.5	0.943(1)	0.919(51)	
Ni2	3 <i>b</i>	0	0	0.5	0.057(1)	1.091(51)	
Nil	3 <i>a</i>	0	0	0	0.873(1)	0.122(5)	
Mo1	3 <i>a</i>	0	0	0	0.030	0.122(5)	
Li2	3 <i>a</i>	0	0	0	0.97(1)	0.122(5)	
Phase 2 : Li ₄ N	40O ₅ (3.2(3) mol%	b) Space gro	oup: <i>Fm</i> 3 _m	<i>a</i> = 4.10247(94)	Å, α=β=γ=90°, <i>V</i>	/=68.534(3)	
Å ³							
Lil	4a	0	0	0	0.800	1.000	
Mo1	4a	0	0	0	0.200	1.000	
O1	4b	0.5	0.5	0.5	1.000	1.000	

Table S6 Crystallographic data of $Li_{1.09}Ni_{0.85}Mo_{0.06}O_2$ (50th cycle discharged) determined from Rietveld refinement of SXRD patterns.

$Li_{1.09}Ni_{0.85}Mo_{0.06}O_2 (50 \text{ th cycle-discharged}) \qquad \chi^2 = 1.63, \text{ Bragg R-factor} = 5.99 \% (\text{weighted average})$								
Phase 1 : Li _{1.0}	Phase 1 : $\text{Li}_{1.04}\text{Ni}_{0.93}\text{Mo}_{0.03}\text{O}_2$ (95.4(7) mol%) Space group: R^3m $a = 2.87731(2)$ Å, $c = 14.19496(16)$,							
$\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}, V = 101.774(1) \text{ Å}^3$								
Atom	Site	x/a	y/b	z/c	Occupancy	B _{iso} (Å ²)		
01	6 <i>c</i>	0	0	0.25888(6)	1.000	1.447(14)		
Lil	3 <i>b</i>	0	0	0.5	0.898(1)	0.433(34)		
Ni2	3 <i>b</i>	0	0	0.5	0.042(1)	0.433(34)		
Ni1	3 <i>a</i>	0	0	0	0.888(1)	0.567(4)		
Mol	3 <i>a</i>	0	0	0	0.03	0.567(4)		
Li2	3 <i>a</i>	0	0	0	0.082(1)	0.567(4)		
Phase 2 : Li ₄ N	40O5 (4.6(2) mol%	6) Space g	roup: <i>Fm</i> ³ m	<i>a</i> = 4.08789(9) Å	, α=β=γ=90°, V	= 68.312(3)		
Å ³								
Lil	4a	0	0	0	0.800	1.000		
Mol	4a	0	0	0	0.200	1.000		
O1	4b	0.5	0.5	0.5	1.000	1.000		

Table S7. Determination of Li_4MoO_5 phase from ⁷Li NMR fitting.

Com	positio	n	LiNiO ₂	Li in	Mo in	Li/Mo in	mol%	of ⁷ Li in
				Li ₄ MoO ₅				
Li	Ni	Mo					expected	experimental
1.03	0.95	0.02	0.95	0.08	0.02	4.0	7.8%	7.1%
1.06	0.9	0.04	0.90	0.16	0.04	4.0	15.1%	12.6%
1.09	0.85	0.06	0.85	0.24	0.06	4.0	22.0%	21.1%
1.12	0.8	0.08	0.80	0.32	0.08	4.0	28.6%	24.1%

Table S8. Detailed fitting parameters and results for ⁷Li NMR.

Phase	Peak	Shift (ppm)	Width (ppm)	G/L ratio	Weight
	А	681	101	0.46	75.8%
	В	774	129	1	13.4%
LiNiO ₂	С	441	138	1	2.9%
	D1	1	15	1	3.4%
	D2	-14	176	1	4.5%
	А	678	96	0.57	53.5%
	В	766	116	1	8.5%
	E	621	138	1	9.4%
	С	435	199	1	11.4%
	LiNi _x Mo _{1-x}	296	83	1	0.7%
	LiNi _x Mo _{1-x}	216	154	1	2.7%
	LiNi _x Mo _{1-x}	35	205	1	6.7%
	D2	8	39	1	2%
	D3	3	13	1	1.8%
	D1	1	11	0.2	3.3%
	А	680	103	0.53	49.7%
	В	781	103	1	5.3%
	E	607	152	1	8.8%
Li _{1.06} Ni _{0.9} Mo _{0.04} O ₂	С	432	189	1	11.3%
	LiNi _x Mo _{1-x}	284	132	1	3.8%
	LiNi _x Mo _{1-x}	185	119	1	2.3%
	LiNi _x Mo _{1-x}	60	163	1	6.2%

	D2	11	43	1	1.8%
	D3	4	13	0.15	5.8%
	D1	0	7	0.2	5.0%
	А	681	112	0.51	45.2%
	В	781	103	1	5.8%
	E	607	152	1	6.1%
	С	432	189	1	9.6%
	LiNi _x Mo _{1-x}	285	132	1	3.5%
$L1_{1.09}$ $1_{0.85}$ $1_{0.06}$ O_2	LiNi _x Mo _{1-x}	186	119	1	2.3%
	LiNi _x Mo _{1-x}	60	164	1	6.4%
	D2	1	47	1	3.7%
	D3	1	11	1	8.1%
	D1	-1	7	0.2	9.3%
	А	670	105	0.66	47.0%
	В	781	83	1	3.9%
	E	573	95	1	2.8%
	С	424	219	1	11.3%
	LiNi _x Mo _{1-x}	282	112	1	2.0%
$L_{1,12} = 10.8 = 100.08 = 0$	LiNi _x Mo _{1-x}	181	131	1	3.1%
	LiNi _x Mo _{1-x}	55	147	1	5.8%
	D2	-1	39	1	5.9%
	D3	1	12	1	5.7%
	D1	-1	6	0.1	12.5%

Supplementary References

1. Li, B., Kumar, K., Roy, I., Morozov, A.V., Emelyanova, O.V., Zhang, L., Koc, T., Belin, S., Cabana, J., Dedryvere, R., et al. (2022). Capturing dynamic ligand-to-metal charge transfer with a long-lived cationic intermediate for anionic redox. Nature Materials 21, 1165-1174.

2. Matsuhara, T., Tsuchiya, Y., Yamanaka, K., Mitsuhara, K., Ohta, T., and Yabuuchi, N. (2016). Synthesis and Electrode Performance of Li₄MoO₅-LiFeO₂ Binary System as Positive Electrode Materials for Rechargeable Lithium Batteries. Electrochemistry 84, 797-801.

3. Yabuuchi, N., Tahara, Y., Komaba, S., Kitada, S., and Kajiya, Y. (2016). Synthesis and Electrochemical Properties of Li_4MoO_5 -NiO Binary System as Positive Electrode Materials for Rechargeable Lithium Batteries. Chemistry of Materials 28, 416-419.

4. Li, B., Sougrati, M.T., Rousse, G., Morozov, A.V., Dedryvere, R., Iadecola, A., Senyshyn, A., Zhang, L., Abakumov, A.M., Doublet, M.L., and Tarascon, J.M. (2021). Correlating ligand-tometal charge transfer with voltage hysteresis in a Li-rich rock-salt compound exhibiting anionic redox. Nature Chemistry 13, 1070-1080.