Optimising the synthesis of $LiNiO_2$: coprecipitation versus solid-state, and the effect of molybdenum doping

Supporting Information

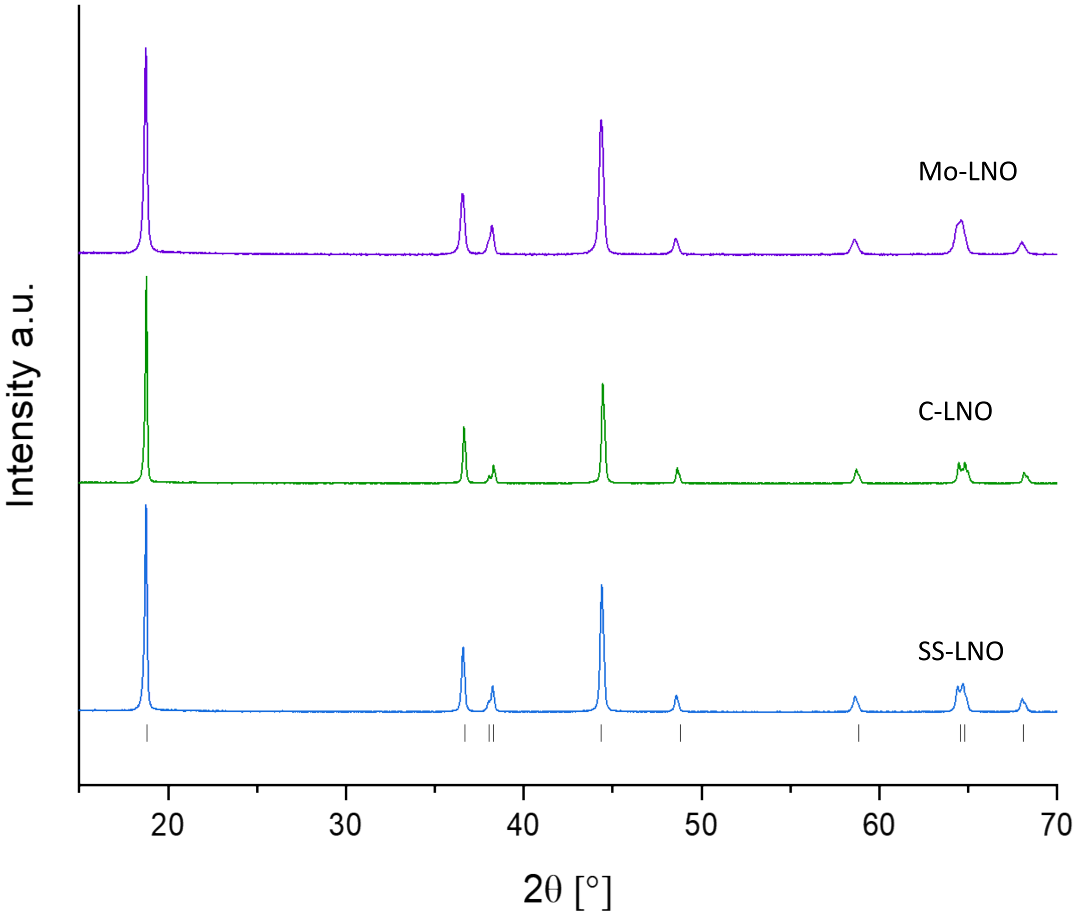


Figure S1-XRD pattern of SS $LiNiO_2$ synthesised at 700 °C for 12 hours in O_2 (black), coprecipitation $LiNiO_2$ synthesised at 800 °C for 1 hour in O_2 (red) and SS Mo-LNO synthesised at 800 °C for 12 hours in O_2 (blue).

Table S1- Rietveld refinements for LNO synthesised materials

Sample	***c* (Å)**	***a* (Å)**	***c/a***	**Volume ($Å^3$)**	**$I_{(003)}/I_{(104)}$**
SS-LNO	14.1948(5)	2.8782(1)	4.932	101.84(1)	1.66
C-LNO	14.2021(4)	2.8795(3)	4.932	101.98(1)	2.12
Mo-LNO	14.1938(7)	2.8788(4)	4.930	101.87(2)	1.53

The $I_{(003)}/I_{(104)}$ ratio for C-LNO, SS-LNO and Mo-LNO are 2.12, 1.63 and 1.53 respectively, showing the materials made via the optimised synthesis have a good layered order. It is worth noting that Mo is a much heavier atom with more electrons and so will more strongly scatter the X-rays. This will affect the intensity of the peaks and therefore also affect the $I_{(003)}/I_{(104)}$ intensity ratio.

The *c/a* ratio for Mo-LNO is 4.930, above the 4.9 accepted value in literature, indicating that this material along with the SS-LNO and C-LNO has a well-defined layered hexagonal structure.

Table S2- Refined site occupancies of synthesised solid-state materials

Sample	*Ni* (3a)	*Li* (3a)	*Ni* (3b)	*Li* (3b)
SS LNO 950 °C/ 12h in air	1	0	0.228	0.772
SS LNO 900 °C/ 12h in O_2	1	0	0.129	0.871
SS LNO 700 °C/ 12h in O_2	1	0	0.016	0.984

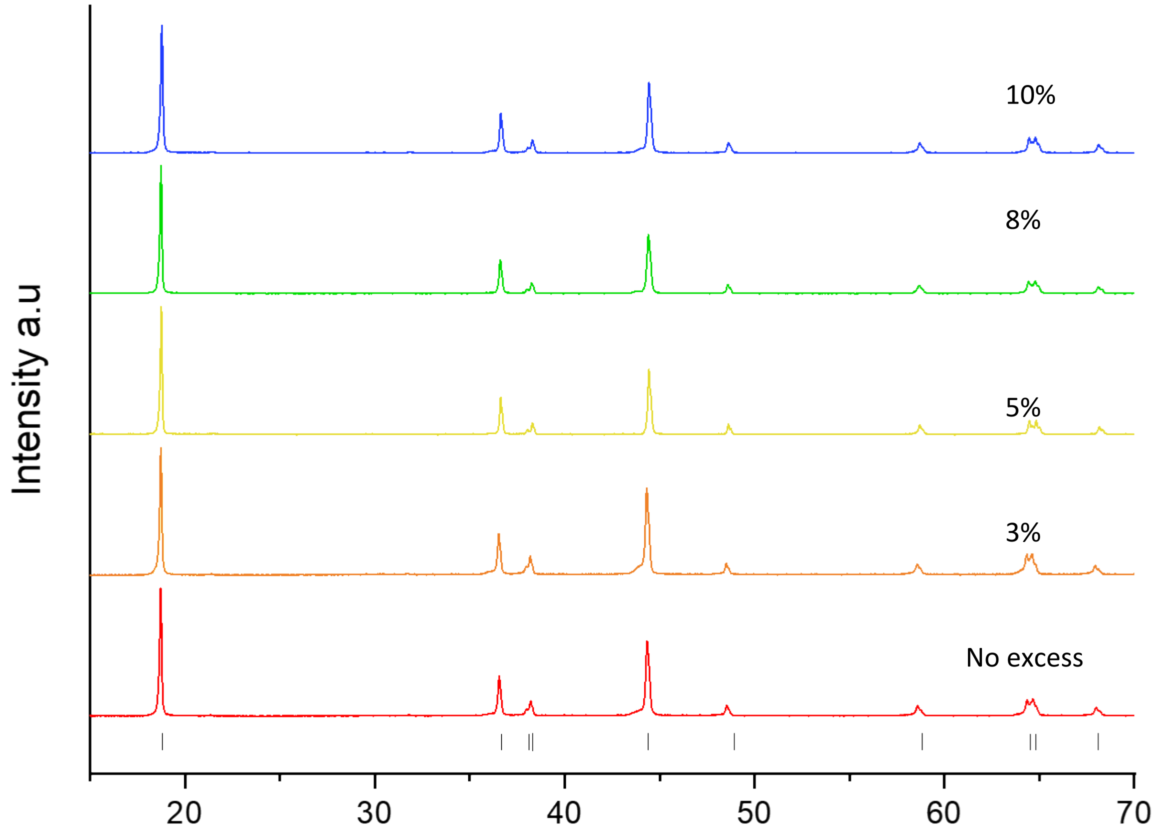


Figure S2- Overlay of XRD patterns for $LiNiO_2$ synthesised via coprecipitation at 700 °C for 12 hours under O_2 flow. Caption for each pattern outlines amount of Li excess used.

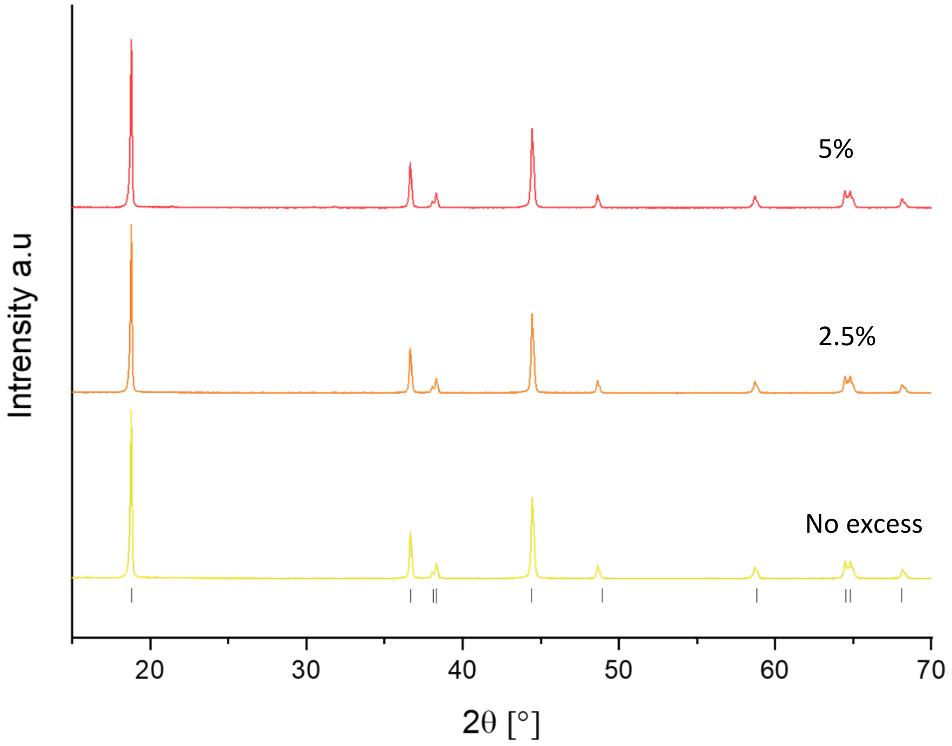
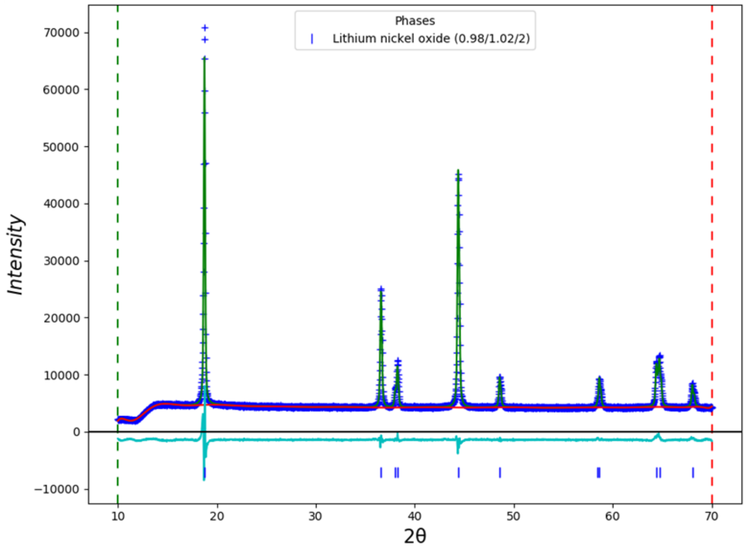


Figure S3-Overlay of XRD patterns for $LiNiO_2$ synthesised via coprecipitation at 800 °C for 1 hour. Caption for each

Table S3- synthesis tests performed on coprecipitation LNO

C-LNO sample number	***Li Source***	***Li* Excess/ %**	***Sintering temperature/ °C***	***Sintering time/ h***	***Sintering Atmosphere***	***PXRD phase pure***
1	Li_2CO_3	5%	700	12	O_2	No
2	$LiOH.H_2O$	0%	700	12	O_2	No
3	$LiOH.H_2O$	3%	700	12	O_2	No
4	$LiOH.H_2O$	5%	700	12	O_2	No
5	$LiOH.H_2O$	8%	700	12	O_2	No
6	$LiOH.H_2O$	10%	700	12	O_2	No
7	$LiOH.H_2O$	0%	800	12	O_2	No
8	$LiOH.H_2O$	5%	800	1	O_2	No
9	$LiOH.H_2O$	2.5%	800	1	O_2	No
10	$LiOH.H_2O$	0%	800	1	O_2	Yes



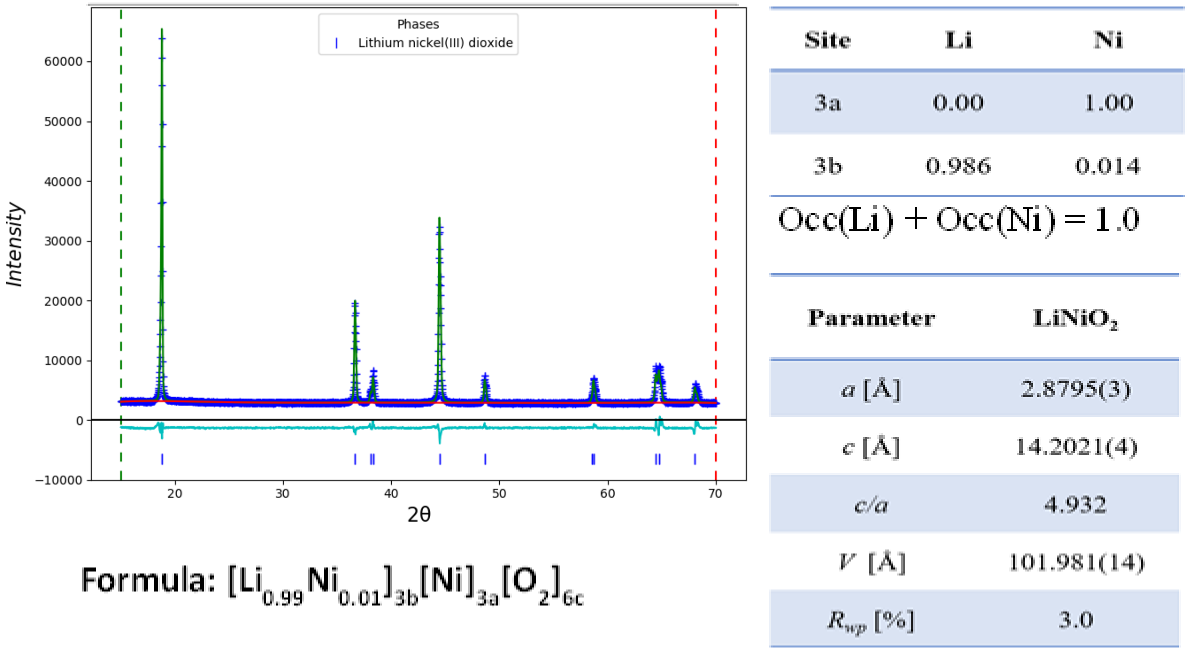
Formula: $[Li_{0.98}Ni_{0.02}]_{3b}[Ni]_{3a}[O_2]_{6c}$

Site	**Li**	**Ni**
3a	0	1
3b	0.984(8)	0.016(8)

$$Occ(Li) + Occ(Ni) = 1.0$$

Parameter	**$Li_{0.98}Ni_{1.02}O_2$**
a [Å]	2.8782(1)
c [Å]	14.1948(5)
c/a	4.932
V [Å]	101.837(6)
R_{wp} [%]	4.1

Figure S4- Observed, calculated and difference plots for $LiNiO_2$ sample synthesised at 700 °C for 12 hours under O_2 flow, along with cell parameters and site occupancy data.



Formula: $[Li_{0.99}Ni_{0.01}]_{3b}[Ni]_{3a}[O_2]_{6c}$

Site	Li	Ni
3a	0.00	1.00
3b	0.986	0.014

$$Occ(Li) + Occ(Ni) = 1.0$$

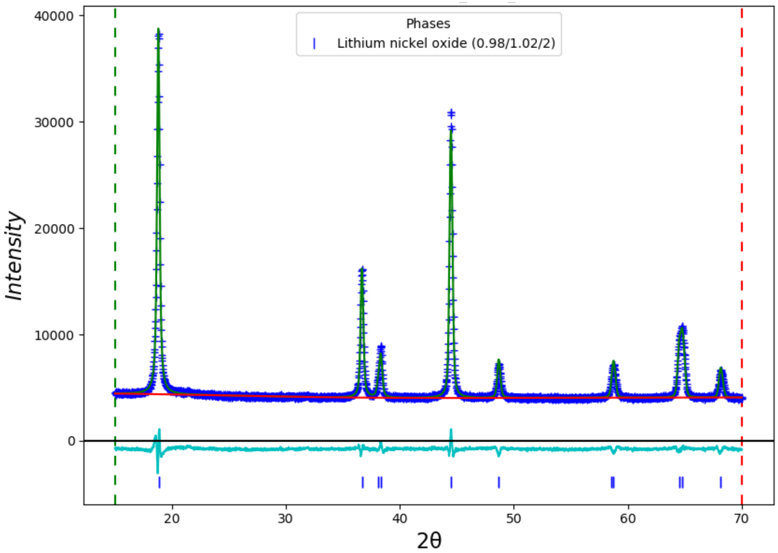
Parameter	$LiNiO_2$
a [Å]	2.8795(3)
c [Å]	14.2021(4)
c/a	4.932
V [Å]	101.981(14)
R_{wp} [%]	3.0

Figure S5- Observed, calculated and difference plots for Coprecipitation $LiNiO_2$ sample synthesised at 800 °C for 1 hour under O_2 flow, along with cell parameters and site occupancy data.

Site occupancies were refined for the LNO materials and these are given in table S2. SS-LNO has 2% Ni/Li exchange compared to 1% for C-LNO, highlighting the lower degree of cation mixing in C-LNO. It is accepted in literature that the degree of cation mixing (6% and above) will influence the structure and hence hinder the electrochemical performance.[2,43,44] Low level cation mixing means that the material behaves like an ideal layered oxide LNO and the correct phase transitions can occur. If Ni/Li mixing is high, then the formation of the monoclinic phase is supressed and so the hexagonal structure will be maintained throughout the charging process.[43]

Table S4- Refined site occupancies of synthesised materials

Sample	***Ni* (3a)**	***Li* (3a)**	***Ni* (3b)**	***Li* (3b)**
SS $LiNiO_2$	1	0	0.016	0.984
Coprecipitation $LiNiO_2$	1	0	0.012	0.988



Parameter	$Li_{1.03}Mo_{0.02}Ni_{0.95}O_2$
a [Å]	2.8788(4)
c [Å]	14.1938(7)
c/a	4.930
V [Å]	101.872(21)
R_{wp} [%]	2.6

Figure S6- Observed, calculated and difference plots for SS $Li_{1.03}Mo_{0.02}Ni_{0.95}O_2$ sample synthesised at 800 °C for 12 hours under O_2 flow, along with cell parameters and site occupancy data.

Long term cycling and rate tests for SS-LNO

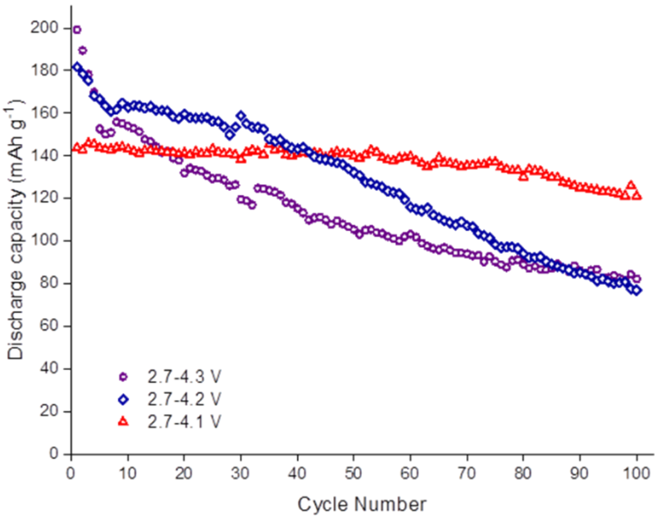


Figure S7- Long term cycling performance of SS-LNO at 10 mA g^{-1} between: 2.7-4.3 V (purple circle) 2.7-4.2 V (blue diamond) and 2.7-4.1 V (red triangle)

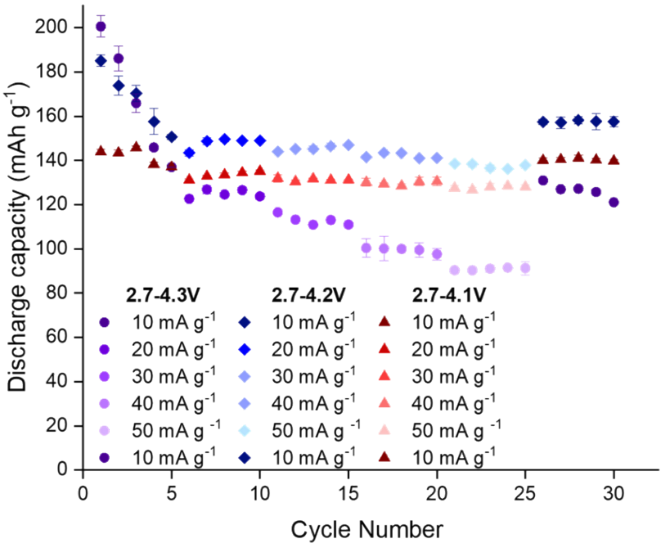


Figure S8- Rate performance of SS-LNO/ Li half-cells between: 2.7-4.3 V (purple circle) 2.7-4.2 V (blue diamond) and 2.7-4.1 V (red triangle)

Long term cycling and rate tests for C-LNO

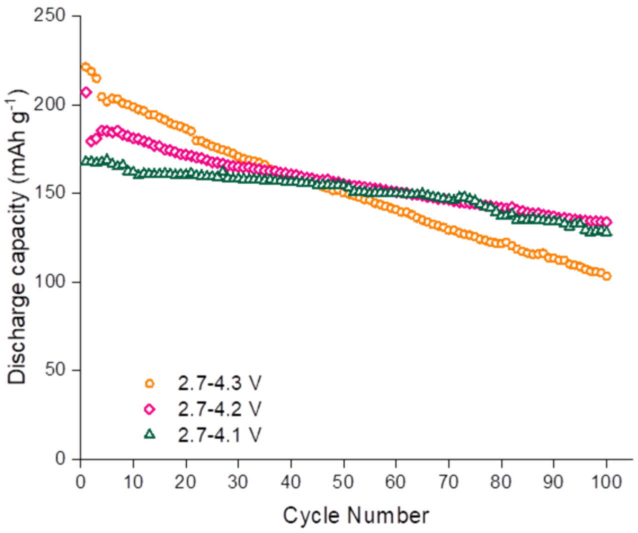


Figure S9- Long term cycling performance of C-LNO at 10 mA g^{-1} between: 2.7-4.3 V (orange circle), 2.7-4.2 V (pink diamond) and 2.7-4.1 V (green triangle)

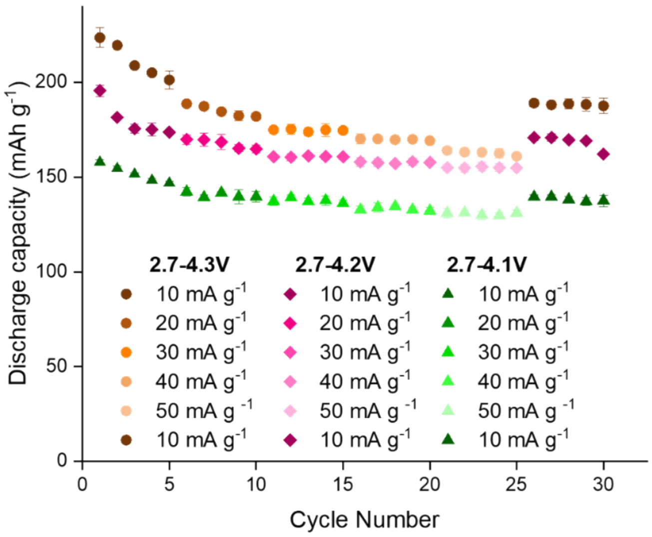


Figure S10- Rate performance of C-LNO/ Li half-cells between: 2.7-4.3 V (orange circle), 2.7-4.2 V (pink diamond) and 2.7-4.1 V (green triangle)

Long term cycling and rate tests for Mo-LNO

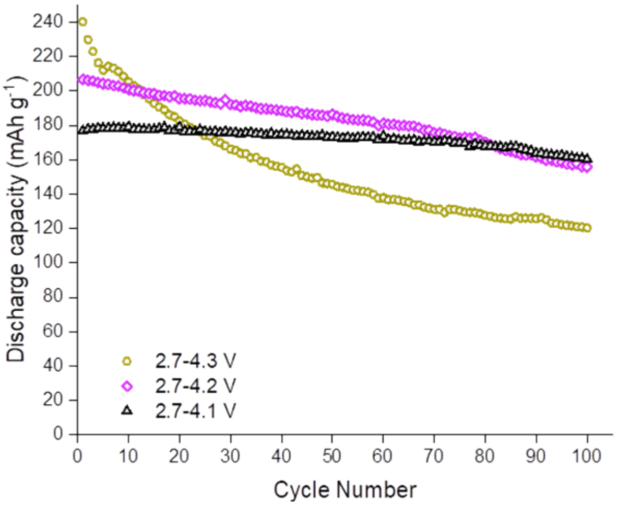


Figure S11- Long term cycling performance of Mo-LNO at 10 mA g^{-1} between: 2.7-4.3 V (yellow circle), 2.7-4.2 V (purple diamond) and 2.7-4.1 V (black triangle)

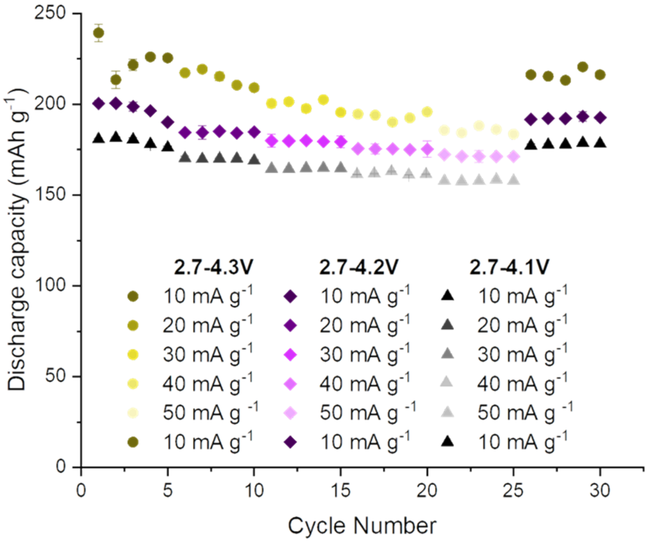


Figure S12- Rate performance of Mo-LNO/ Li half-cells between 2.7-4.3 V (yellow circle), 2.7-4.2 V (purple diamond) and 2.7-4.1 V (black triangle)

Comparison of first cycle voltage profiles for SS-LNO, C-LNO and Mo-LNO:

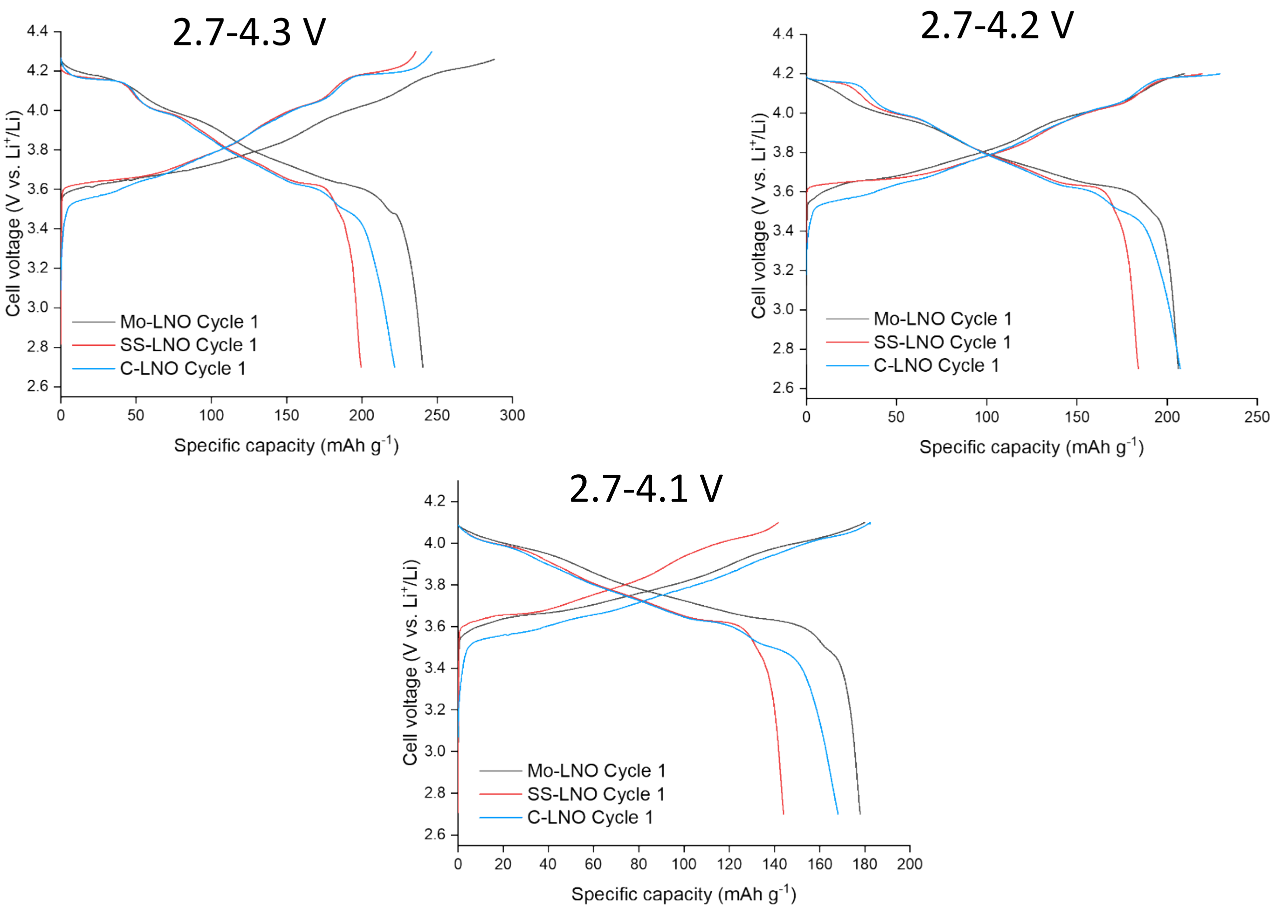
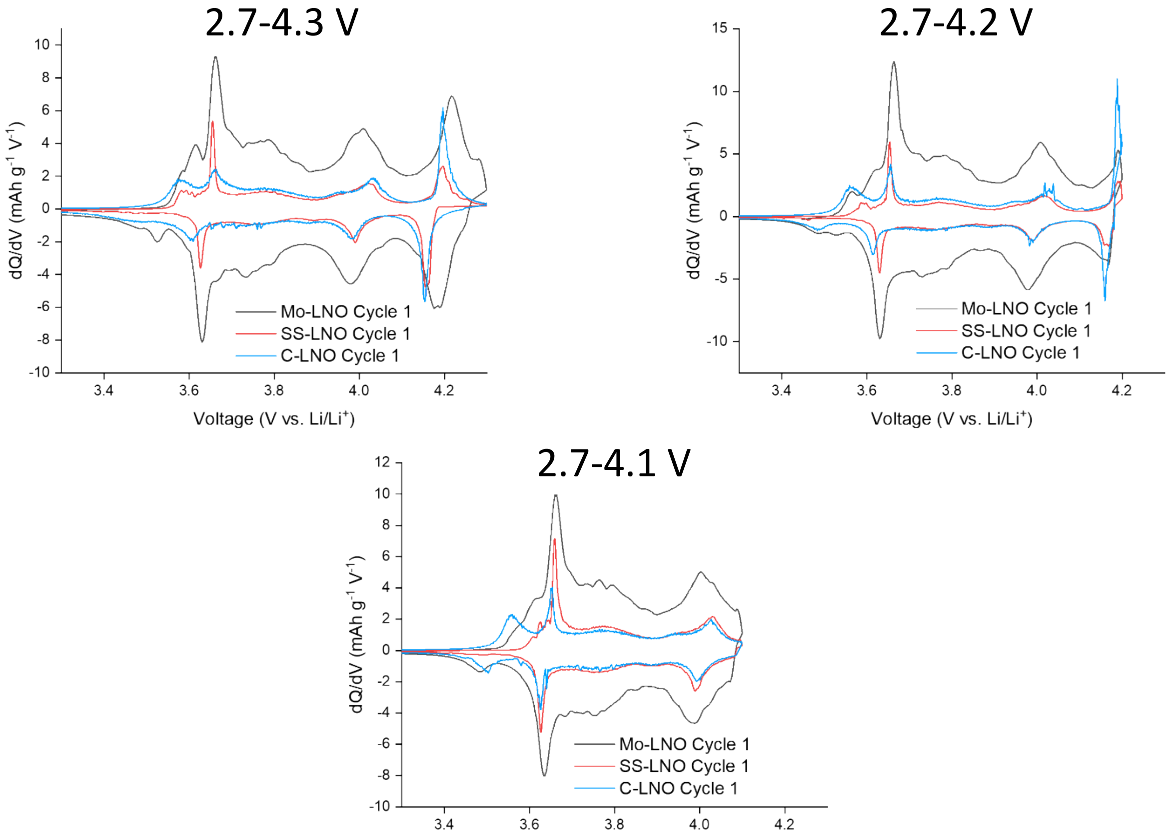


Figure S13- Comparison of first cycle voltage profiles for Mo-LNO, SS-LNO and C-LNO in the voltage windows 2.7-4.3 V, 2.7-4.2 V and 2.7-4.1 V.

Comparison of first cycle dQ/dV profiles for SS-LNO, C-LNO and Mo-LNO:



Increasing the Mo concentration in SS Mo-LNO:

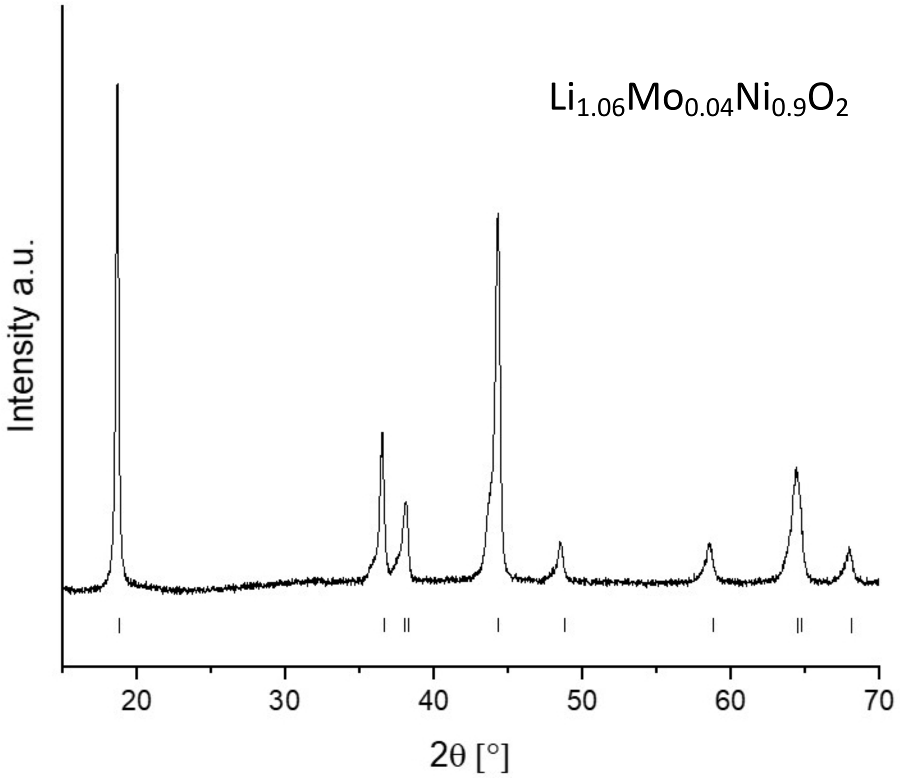


Figure S15 – XRD pattern of $Li_{1.06}Mo_{0.04}Ni_{0.9}O_2$ synthesised at 800 °C for 12 hours in O_2

We attempted to synthesise a material via solid state with double the amount of molybdenum compared to the material discussed in the main body of the paper. However, when the concentration of Mo was increased, the XRD pattern was no longer phase pure. There appears to be a disordered rock salt impurity - evidenced by the shoulders present on some of the peaks in the XRD pattern.