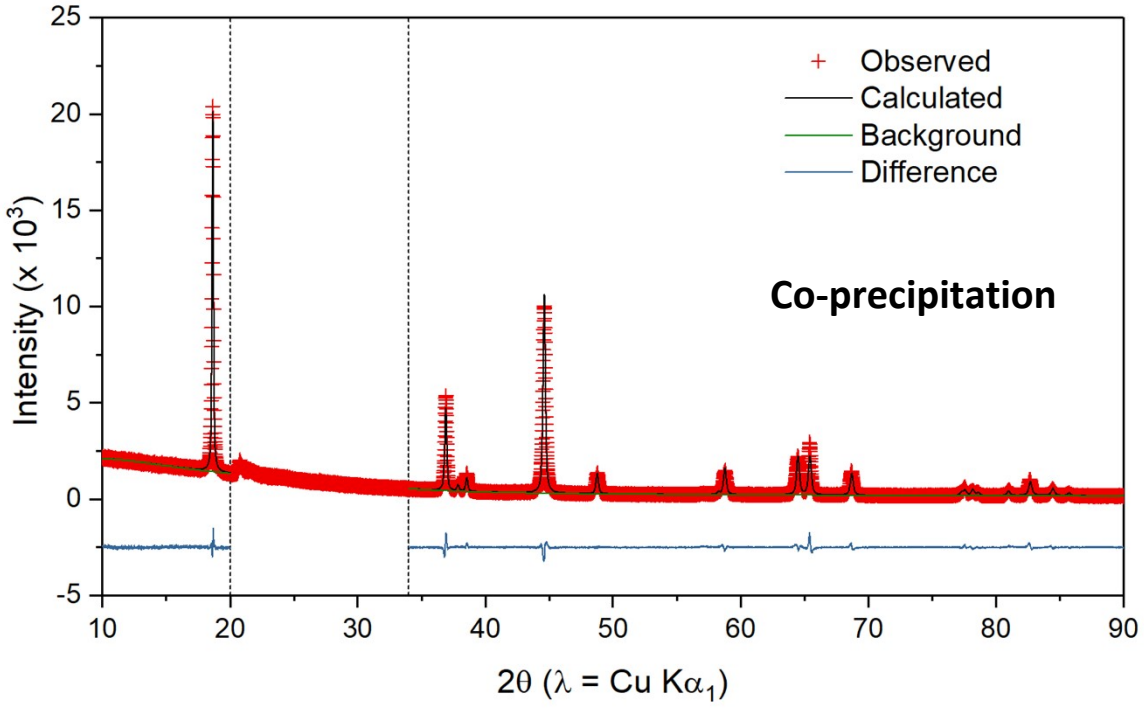
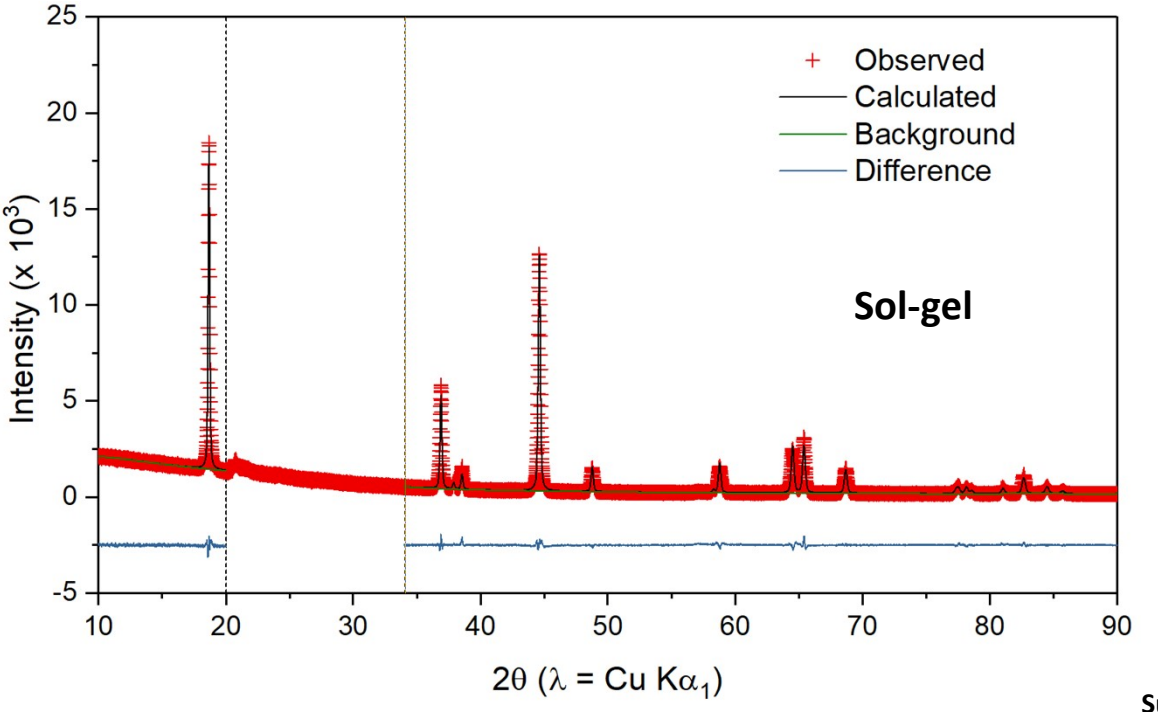
Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Detection of trapped molecular O_2 in a charged Li-rich cathode by Neutron PDF

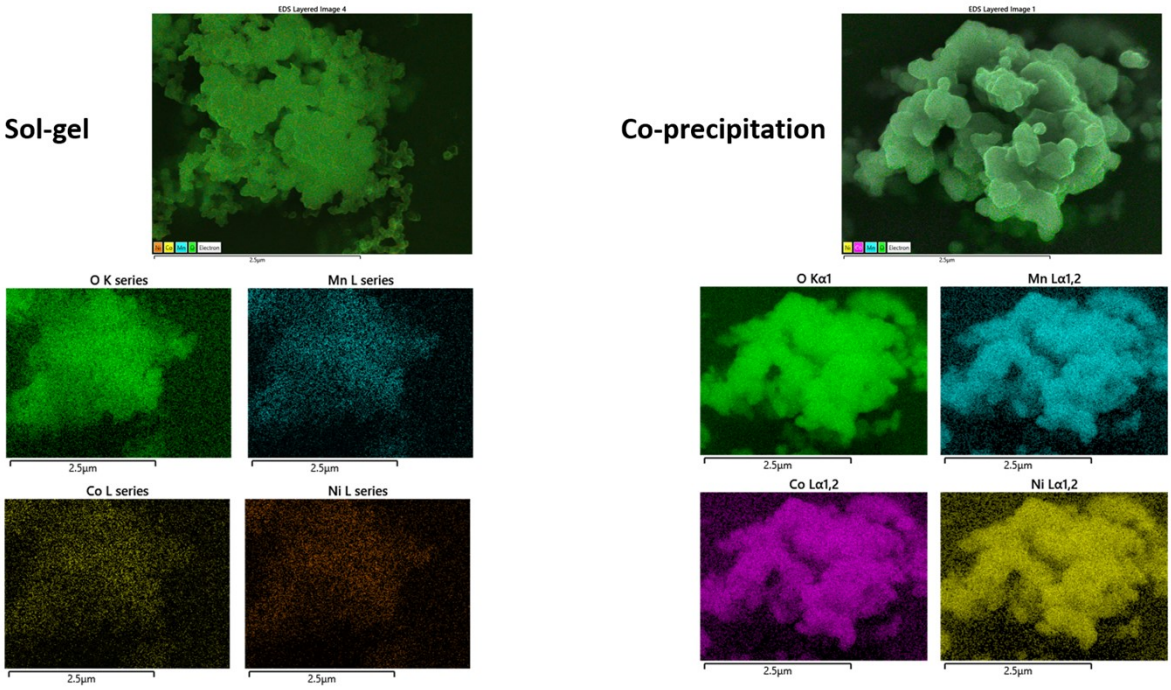
Robert A. House, Helen Y. Playford, Ronald I. Smith, Jennifer Holter, Ian Griffiths, Ke-Jin Zhou, Peter G. Bruce



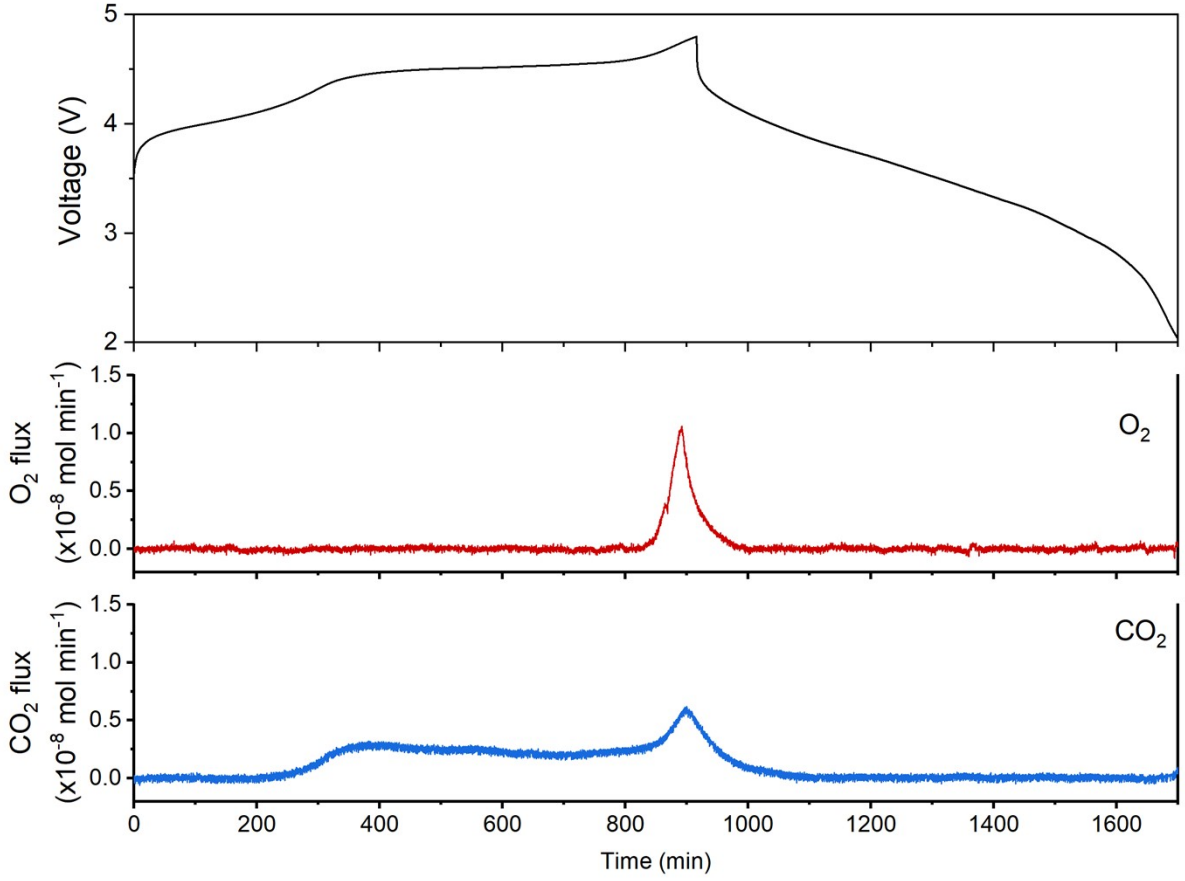


Sup

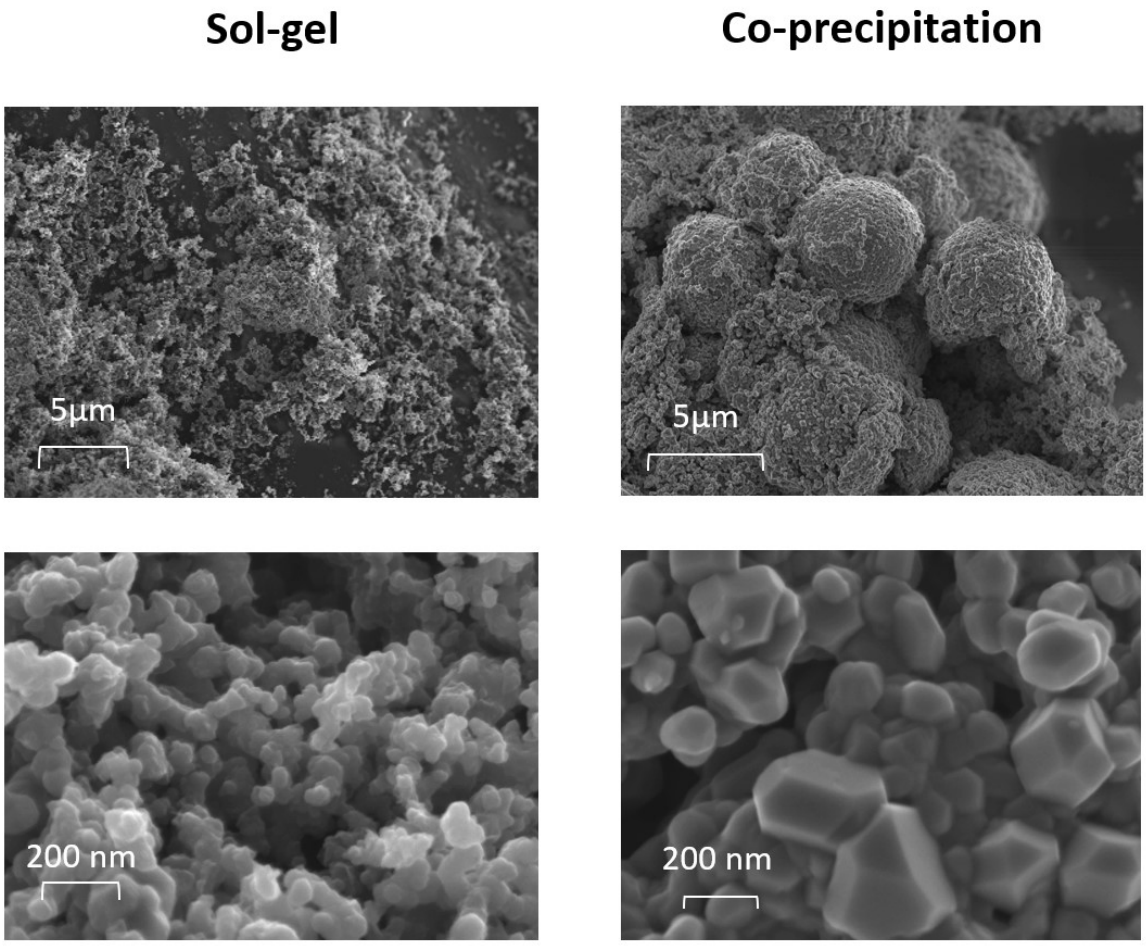
p. Fig. 1. Fitted PXRD data following Rietveld refinement for pristine $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ prepared by carbonate co-precipitation (upper panel) and sol-gel (lower panel).



Supp. Fig. 2. EDX images. Homogeneous mixing of transition metals within and between primary particles for pristine $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ prepared by sol-gel and carbonate co-precipitation.



Supp. Fig. 3. OEMS data. Evolved O_2 and CO_2 gases detected by mass spec for co-precipitation derived $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ charged at a rate of 20 mA g^{-1} between 2 and 4.8 V. 0.0041 moles of O_2 and 0.0159 moles of CO_2 were evolved per mole of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ during the first cycle. The electrode active material mass for the experiment was 10.32 mg.



Supp. Fig. 4. SEM images Primary and secondary particle morphology for pristine $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ prepared by sol-gel and carbonate co-precipitation.

Supp. Tab. 1. X-ray diffraction refinement parameters for **a** pristine $^{7}Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ prepared by co-precipitation for the neutron study and **b** $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ prepared by sol-gel.

a

Atom	Wycoff	x	y	z	Occupancy	U_{iso}
^{7}Li	3a	0	0	0	1	0.0137(2)
Li/Ni/Co/Mn	3b	0	0	0.5	0.2/0.13/0.13/0.54	0.0140(4)
O	6c	0	0	0.2405(1)	1	0.0243(5)
S.G. = R-3m R_w = 0.0555 G.O.F. = 1.6			a = 2.849(1) Å c = 14.226(1) Å		α = 90 β = 90 γ = 120	

b

Atom	Wycoff	x	y	z	Occupancy	U_{iso}
^{7}Li	3a	0	0	0	1	0.0135(2)
Li/Ni/Co/Mn	3b	0	0	0.5	0.2/0.13/0.13/0.54	0.0126(3)
O	6c	0	0	0.2416(1)	1	0.0201(4)
S.G. = R-3m R_w = 0.0516 G.O.F. = 1.5			a = 2.850(1) Å c = 14.221(1) Å		α = 90 β = 90 γ = 120	

Supp. Tab. 2. Neutron PDF refinement parameters for pristine $^{7}Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$

Atom	Wycoff	x	y	z	Occupancy
^{7}Li	4h	0	0.3328(7)	0.5	1
^{7}Li	2c	0	0	0.5	1
^{7}Li/Ni	2b	0	0.5	0	0.6/0.4
Co/Mn	4g	0	0.1617(8)	0	0.2/0.8
O	8j	0.2511(6)	0.3222(2)	0.2231(3)	1
O	4i	0.2184(7)	0	0.2256(5)	1
S.G. = C2/m, R_w = 0.092, Q_{max} = 30 Å, r = 0.5 – 40 Å		a = 4.942(1) Å b = 8.547(2) Å c = 5.031(1) Å		α = 90 β = 109.33(2) γ = 90	

Supp. Tab. 3. X-ray refinement parameters for 4.8V charged $^{7}Li_{0.1}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$

Atom	Wycoff	x	y	z	Occupancy	U_{iso}
^{7}Li/Ni	4h	0	0.333	0.5	0.1/0.03	0.0094(7)
^{7}Li/Ni	2c	0	0	0.5	0.1/0.03	0.0094(7)
Ni/Co/Mn	2b	0	0.5	0	0.10/0.13/0.54	0.0094(7)
Ni/Co/Mn	4g	0	0.167	0	0.10/0.13/0.54	0.0094(7)
O	8j	0.251(5)	0.335(2)	0.235(6)	1	0.0094(7)
O	4i	0.235(1)	0	0.246(1)	1	0.0094(7)
S.G. = C2/m			a = 4.912(2) Å		α = 90	
R_w = 0.0252			b = 8.493(1) Å		β = 108.94(1)	
G.O.F. = 1.2			c = 4.948(2) Å		γ = 90	

Supp. Tab. 4. Neutron PDF refinement parameters for 4.8V charged $^{7}Li_{0.1}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$

Atom	Wycoff	x	y	z	Occupancy
^{7}Li	4h	0	0.333	0.5	0.1
^{7}Li	2c	0	0	0.5	0.1
Ni/Co/Mn	2b	0	0.5	0	0.13/0.13/0.54
Ni/Co/Mn	4g	0	0.167	0	0.13/0.13/0.54
O	8j	0.246(2)	0.337(1)	0.227(1)	1
O	4i	0.237(1)	0	0.200(2)	1
S.G. = C2/m, R_w = 0.193, Q_{max} = 26 Å, r = 0.5 – 40 Å		a = 4.919(4) Å b = 8.486(8) Å c = 4.975(3) Å		α = 90 β = 109.97(6) γ = 90	

Supp. Tab. 5. Neutron PDF refinement parameters for 4.8V charged $^{7}Li_{0.1}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ **a** without and **b** with Ni migration.

a

Atom	Wycoff	x	y	z	Occupancy
^{7}Li	4h	0	0.333	0.5	0.1
^{7}Li	2c	0	0	0.5	0.1
Ni/Co/Mn	2b	0	0.5	0	0.13/0.13/0.54
Ni/Co/Mn	4g	0	0.167	0	0.13/0.13/0.54
O	8j	0.250(2)	0.330(3)	0.214(5)	1
O	4i	0.256(3)	0	0.201(9)	1
S.G. = C2/m R_w = 0.193, Q_{max} = 26 Å r = 0.5 – 4 Å		a = 5.02(3) Å b = 8.28 (4) Å c = 5.04(3) Å		α = 90 β = 111.9(4) γ = 90	

b

Atom	Wycoff	x	y	z	Occupancy
^{7}Li/Ni	4h	0	0.333	0.5	0.1/0.031(7)
^{7}Li/Ni	2c	0	0	0.5	0.1/0.031(7)
Ni/Co/Mn	2b	0	0.5	0	0.099(7)/0.13/0.54
Ni/Co/Mn	4g	0	0.167	0	0.099(7)/0.13/0.54
O	8j	0.250(2)	0.329(2)	0.214(4)	1
O	4i	0.256(3)	0	0.200(8)	1
S.G. = C2/m R_w = 0.166, Q_{max} = 26 Å r = 0.5 – 4 Å		a = 5.01(5) Å b = 8.28 (7) Å c = 5.04(3) Å		α = 90 β = 111.7(5) γ = 90	

Supp. Tab. 6. Neutron PDF refinement parameters for 4.8V charged $^{7}Li_{0.1}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ with Ni migration and solid beta-O_2 phase.

$^{7}Li_{0.1}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ phase fraction = 0.34

Atom	Wycoff	x	y	z	Occupancy
^{7}Li/Ni	4h	0	0.333	0.5	0.1/0.031
^{7}Li/Ni	2c	0	0	0.5	0.1/0.031
Ni/Co/Mn	2b	0	0.5	0	0.099/0.13/0.54
Ni/Co/Mn	4g	0	0.167	0	0.099/0.13/0.54
O	8j	0.250	0.329	0.214	1
O	4i	0.256	0	0.200	1
S.G. = C2/m R_w = 0.138, Q_{max} = 26 Å r = 0.5 – 4 Å		a = 5.01 Å b = 8.28 Å c = 5.04 Å			α = 90 β = 111.7 γ = 90

Beta-O_2 phase fraction = 0.66

Atom	Wycoff	x	y	z	Occupancy
O	6c	0	0	0.0536	1
S.G. = R-3m R_w = 0.138, Q_{max} = 26 Å r = 0.5 – 4 Å		a = 3.307 Å b = 3.307 Å c = 11.26 Å			α = 90 β = 90 γ = 120

Spherical particle diameter (spdiameter = 3.6(8) Å) was also refined to reduce the contribution of intermolecular correlations to the PDF.