Electronic Supplementary Information (ESI)

From Li$_2$NiO$_3$ to High-Performance LiNiO$_2$ Cathodes for Application in Li-Ion and All-Solid-State Batteries

Leonhard Karger[‡a], Philip Henkel[‡a], Saravanakumar Murugan[a], Ruizhuo Zhang[a], Aleksandr Kondrakov[*ab] and Torsten Brezesinski[*a]

[a]Battery and Electrochemistry Laboratory, Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany.

E-mail: torsten.brezesinski@kit.edu

[b]BASF SE, Carl-Bosch-Str. 38, Ludwigshafen 67056, Germany.

E-mail: aleksandr.kondrakov@basf.com

[‡]These authors contributed equally.

Synthesis

Reference LiNiO$_2$ (LNO)

The Ni(OH)$_2$ (d_{50} = 14 μm, BASF SE) and LiOH·H$_2$O (10–20 μm, BASF SE) precursors were dry mixed in a blender (Kinematica) in stoichiometric amounts with some excess of lithium (1:1.01). The reactants were heated in an alumina crucible under O$_2$ flow in a tube furnace (Nabertherm P330) at 400 °C for 4 h, followed by calcination at 700 °C. The heating and cooling rates were set to 3 °C/min. The obtained powder was sieved using a 32 μm stainless steel mesh and stored under Ar atmosphere.

Li$_{1+x}$Ni$_{1-x}$O$_2$ (x = 0, 0.1, 0.2, and 0.33)

The materials were synthesized according to a procedure adapted from Bianchini *et al.*[1] Specifically, Ni(OH)$_2$ and LiOH·H$_2$O were blended in stoichiometric amounts [(1−x)/(1+x)] and then heated at 550 °C for 12 h under O$_2$ flow. The resulting mixture was blended for 10 min using the Kinematica and again heated at 550 °C for 12 h. The obtained powders were sieved and stored under Ar atmosphere.

Decomposition synthesis

The Li$_{1+x}$Ni$_{1-x}$O$_2$ (x = 0, 0.1, 0.2, and 0.33) samples were calcined at 725, 750, 800, 850, or 900 °C for 12 h, followed by sieving and storing under Ar atmosphere.

Cobalt-based coating

Ni(OH)$_2$ and 5 mol% Co(NO$_3$)$_2$, relative to Ni(OH)$_2$, were mixed in the Kinematica for 10 min and then heated at 500 °C for 6 h under O$_2$ flow. LiOH·H$_2$O (1.05 eq.) was added to the mixture, followed by blending in the Kinematica for 10 min prior to heating again at 550 °C for 12 h. The resulting material was finally calcined at 750 °C for 12 h. The heating and cooling rates were set to 3 °C/min. The obtained powder was sieved and stored under Ar atmosphere.

Washing

The samples were dispersed into 0.025 M aqueous LiOH with a ratio of 1:10 CAM to washing solution, followed by shaking by hand for 5 min before centrifuging at 100g for 3 min. The obtained solids were washed using isopropanol and acetone and then dried in a vacuum. Finally, they were calcined at 700 °C for 3 h under O$_2$ flow.

Electrochemical testing

Li-ion battery cells

Electrodes were prepared by casting an N-methyl-pyrrolidone (NMP) based slurry with 94 wt.% CAM, 3 wt.% Super C65 carbon, and 3 wt.% polyvinylidene difluoride binder (Solef 5130 PVDF, Solvay) onto an Al foil current collector. The slurry was prepared by combining all constituents with an additional 20 wt.% NMP in a planetary centrifuge mixer (ARE250, Thinky). The stirring process followed a two-step program with 3 min at 2000 rpm and then 3 min at 400 rpm. The slurry was spread onto the current collector using an Erichsen Coatmaster 510 film applicator at a rate of 5 mm/s. The cathodes were dried overnight under vacuum at 120 °C and calendared at 14 N/mm (Sumet

Messtechnik). Electrodes of 13 mm diameter and 7–10 mg_{CAM}/cm^2 loading were punched out, and half-cells with LP57 electrolyte (1 M $LiPF_6$ in a 3:7 weight ratio mixture of ethylene and ethyl methyl carbonates), GF/D separator, and Li metal counter electrode assembled in an Ar glovebox. Electrochemical testing was performed at 25 °C in the potential range between 3.0 and 4.3 V vs. Li^+/Li. C-rate testing was done at 0.05C, 0.1C, 0.33C, 1C, 2C, and 5C, with 1C = 190 mA/g_{CAM}.

Solid-state battery cells

Cathodes were prepared by combining 70 wt.% CAM, 30 wt.% Li_6PS_5Cl (LPSCl) solid electrolyte, and 1 wt. % Super C65 carbon in a ball-milling jar (FRITSCH planetary mill) using ZrO_2 balls of diameter 10 mm under Ar atmosphere for 30 min at 140 rpm. For the anode preparation, In (99.95% purity) and Li foils of diameter 9 mm and 6 mm, respectively, were punched out. A customized cell setup with a PEEK ring of inner diameter 10 mm and two stainless steel dies as current collectors was used. 100 mg of solid electrolyte was put into the PEEK ring and compressed at 62 MPa. Next, 12 mg of cathode composite was spread onto one side of the separator and compressed at 435 MPa for 3 min. Finally, the anode was attached to the other side, starting with the In foil and followed by the Li foil. The assembled cells were sealed in pouch bags under Ar atmosphere. The electrochemical performance was tested at different C-rates (0.1C, 0.2C, 0.5C, 1C, and 2C, with 1C = 190 mA/g_{CAM}) at 45 °C and at 81 MPa using a MACCOR battery cycler. The potential range was set to 2.3–3.7 V vs. In/InLi (approx. 2.9–4.3 V vs. Li^+/Li).

Characterization

Scanning electron microscopy (SEM)

SEM images were acquired using a LEO-1530 microscope (Carl Zeiss AG) with a field emission source.

Powder X-ray diffraction (XRD)

XRD patterns were collected from the samples on a STADI P (STOE) diffractometer in Debye-Scherrer geometry with monochromatic Mo-$K_{\alpha 1}$ radiation (λ = 0.7093 Å, 50 kV, 40 mA) and a Mythen 1K detector (DECTRIS AG). The diffraction data were analyzed using TOPAS Academic v7 and GSAS-II. Le Bail fitting was performed first, with background correction done by applying a set of Chebyshev polynomials (10 terms). Lattice parameters, zero-shift, and crystallite size (Gaussian and Lorentzian contributions) were refined. In the Rietveld analysis, the parameters from Le Bail fitting were first fixed. Oxygen coordinate, site occupancies, and Debye-Waller factors were refined while applying an absorption correction. For the samples obtained by decomposition synthesis, two occupancy models were tested, featuring substitutional defects with either only nickel in the lithium site or both nickel in the lithium site and lithium in the nickel site. For CAM synthesized at temperatures < 750 °C, the latter model was applied, while for those produced at ≥ 750 °C, the lithium in nickel site substitution converged to zero. Lastly, all parameters were refined in parallel until convergence was achieved. The confidence intervals were three times the estimated standard deviations as obtained from TOPAS Academic v7.

In situ XRD

In situ heating experiments were performed using a customized laboratory spectrometer following a procedure adapted from Geßwein *et al.*[2] and Karger *et al.*[3] Specifically, samples were filled into sapphire capillaries and heated under O_2 flow at 1 K/min from 500 to 800 °C. Each pattern has been acquired over a time of 10 min.
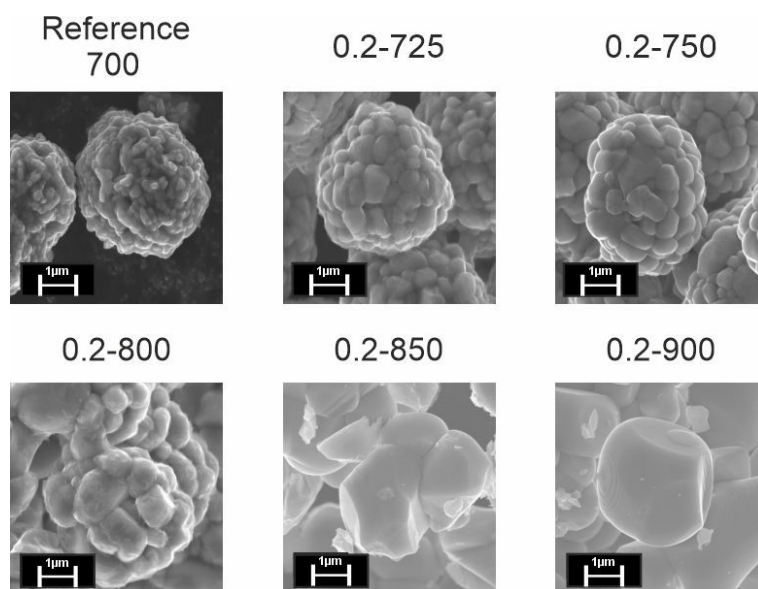

Fig. S1 SEM images of the reference LNO and LRLNO 0.2-725–0.2-900 samples before washing.
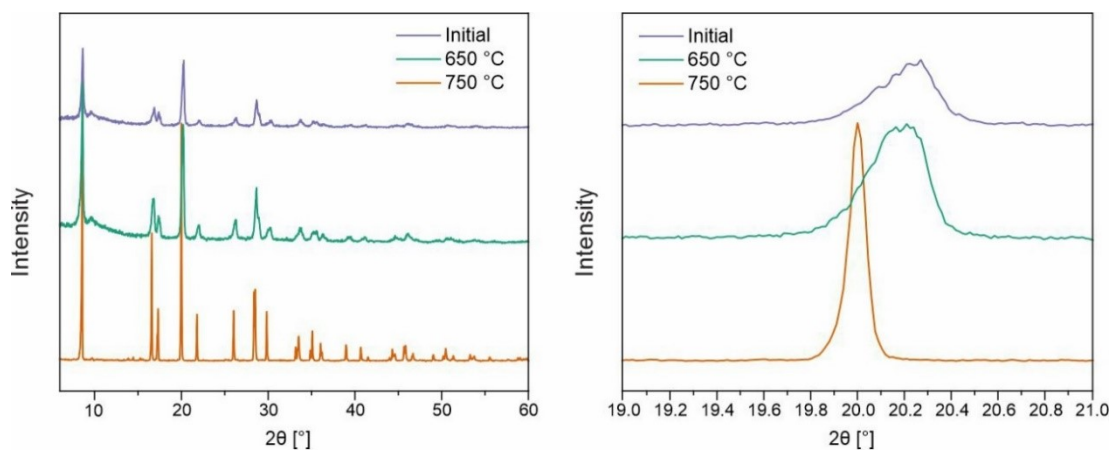

Fig. S2 XRD patterns of $Li_{1.2}Ni_{0.8}O_2$ before and after thermal decomposition. Left: The peak at 8.5° vanishes upon increasing the calcination temperature to 750 °C. Right: The peak at 20.2° belonging to the monoclinic structure is lacking at 750 °C, with the reflection centered at 20.0° being characteristic of hexagonal LNO.
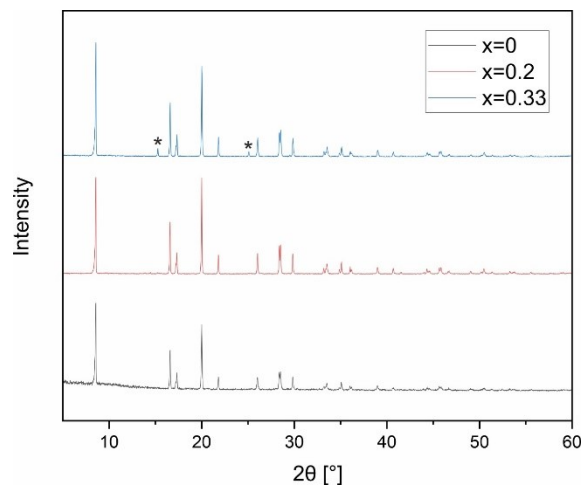
Fig. S3 XRD patterns of the LRLNO samples (*x* = 0, 0.2, 0.33) after thermal decomposition. Reflections representing cubic Li_2O (*Fm−3m* [225]) are denoted by asterisks.
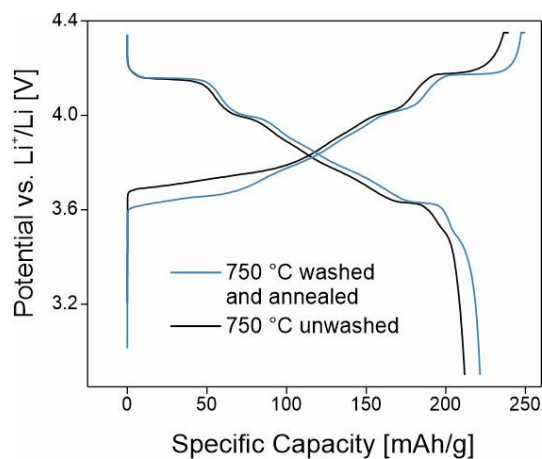

Fig. S4 Initial voltage profiles of LIB half-cells using unwashed and washed/re-annealed LRLNO 0.2-750 cathodes.
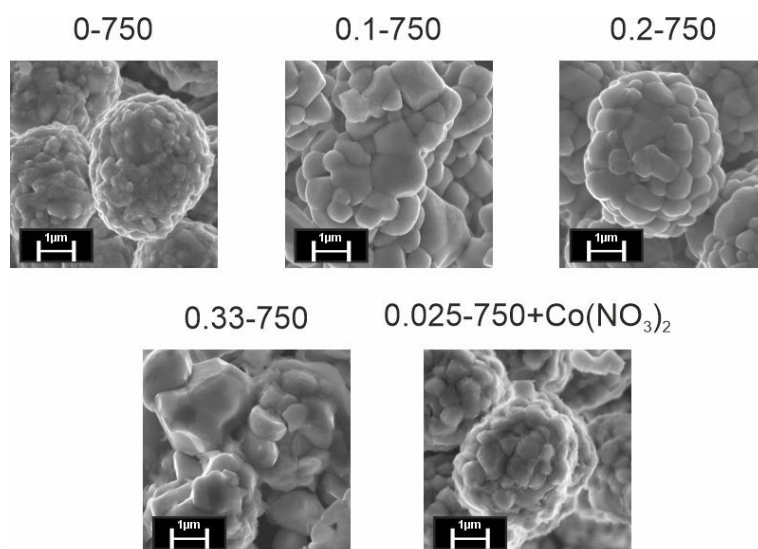
Fig. S5 SEM images of the Co-modified LNO and LRLNO 0-750–0.33-750 samples before washing.
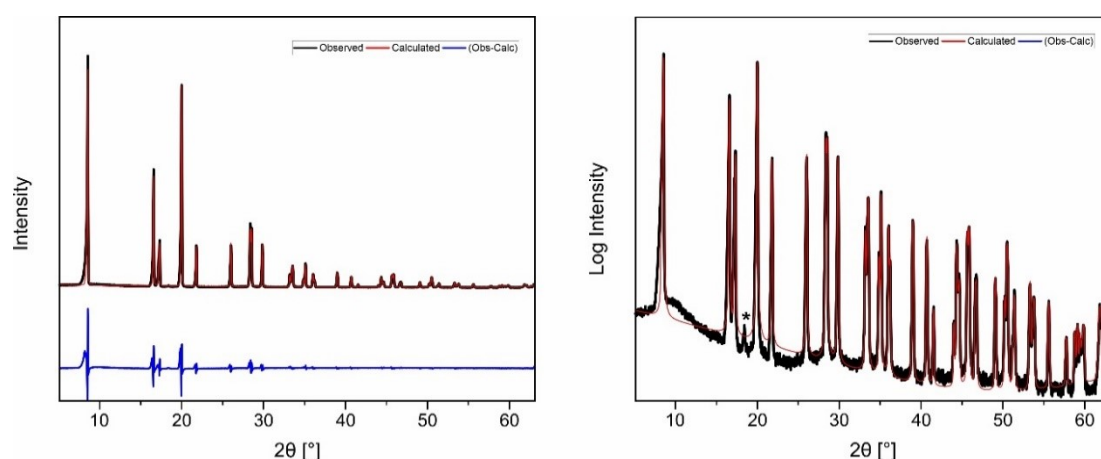

Fig. S6 Rietveld analysis of XRD data collected from the Co-modified LNO with (left) linear and (right) logarithmic scaling of the *y*-axis. The asterisk at 18.3° denotes the presence of an unknown impurity phase.

Tab. S1 Parameters from structural refinement of the reference LNO and LRLNO 0.2-725–0.2-900 samples.

	725 °C	750 °C	800 °C	850 °C	900 °C	Reference
a / Å	2.8707(3)	2.8750(2)	2.8763(3)	2.8800(3)	2.8813(3)	2.8733(1)
c / Å	14.1865(9)	14.1982(12)	14.1983(12)	14.1938(21)	14.1950(24)	14.1853(6)
c/*a*	4.942	4.939	4.936	4.928	4.927	4.937
V / Å³	101.247(20)	101.635(12)	101.726(24)	101.953(27)	102.060(30)	101.420(8)
Ni$_{Li}$ / %	1.0(5)	1.3(3)	1.6(4)	7.4(3)	9.6(3)	1.6(2)
Li$_{Ni}$ / %	2.4(23)	-	-	-	-	-

R_{Bragg}	15.8	13.6	16.9	22.9	21.3	11.0

Tab. S2 Parameters from structural refinement of the Co-modified LNO and LRLNO 0-750–0.33-750 samples.

	x = 0	x = 0.1	x = 0.2	x = 0.33	x = 0.025 + 5 mol% Co(NO₃)₂
a / Å	2.8772(4)	2.8751(3)	2.8750(2)	2.8751(12)	2.8716(9)
c / Å	14.1991(18)	14.1906(15)	14.1982(12)	14.1907(34)	14.1732(18)
c/a	4.9350	4.9357	4.939	4.9357	4.9355
V / Å³	101.792(18)	101.584(15)	101.635(12)	101.589(36)	101.219(20)
Ni_{Li} / %	2.4(3)	1.7(3)	1.3(3)	1.6(2)	1.4(2)
R_{Bragg}	15.8	15.7	13.6	18.7	20.0

[1] Bianchini, M.; Schiele, A.; Schweidler, S.; Sicolo, S.; Fauth, F.; Suard, E.; Indris, S.; Mazilkin, A.; Nagel, P.; Shuppler, S.; Merz, M.; Hartmann, P.; Brezesinski, T.; Janek, J. *Chem. Mater.* **2020**, *32*, 9211.

[2] Geßwein, H.; Stüble, P.; Weber, D.; Binder, J. R.; Mönig, R. *J. Appl. Crystallogr.* **2022**, *55*, 503.

[3] Karger, L.; Weber, D.; Goonetilleke, D.; Mazilikin, A.; Li, H.; Zhang, R.; Ma, Y.; Indris, S.; Kondrakov, A.; Janek, J.; Brezesinski, T. *Chem. Mater.* **2023**, *35*, 648.