

Supporting Information

The Effect of Gallium Doping on the Structure and Electrochemical Performance of LiNiO_2 in Lithium-Ion Batteries

David Kitsche,^a Simon Schweidler,^a Andrey Mazilkin,^{a,b,c} Holger Geßwein,^{d,e} Francois Fauth,^f Emmanuelle Suard,^g Pascal Hartmann,^{a,h} Torsten Brezesinski,^a Jürgen Janek^{*a,i} and Matteo Bianchini^{*a,h}

^a Battery and Electrochemistry Laboratory, Institute of Nanotechnology, Karlsruhe Institute for Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^b Institute of Nanotechnology, Karlsruhe Institute for Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^c Institute of Solid State Physics, Russian Academy of Sciences, Ac. Ossipyan str. 2, 142432 Chernogolovka, Russia.

^d Institute for Applied Materials, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^e Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081 Ulm, Germany.

^f CELLS - ALBA Synchrotron, 08290 Cerdanyola del Vallès, Barcelona, Spain.

^g Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France.

^h BASF SE, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany.

ⁱ Institute of Physical Chemistry & Center for Materials Science (ZfM/LaMa), Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany.

* Corresponding authors: matteo.bianchini@kit.edu, Juergen.Janek@phys.Chemie.uni-giessen.de

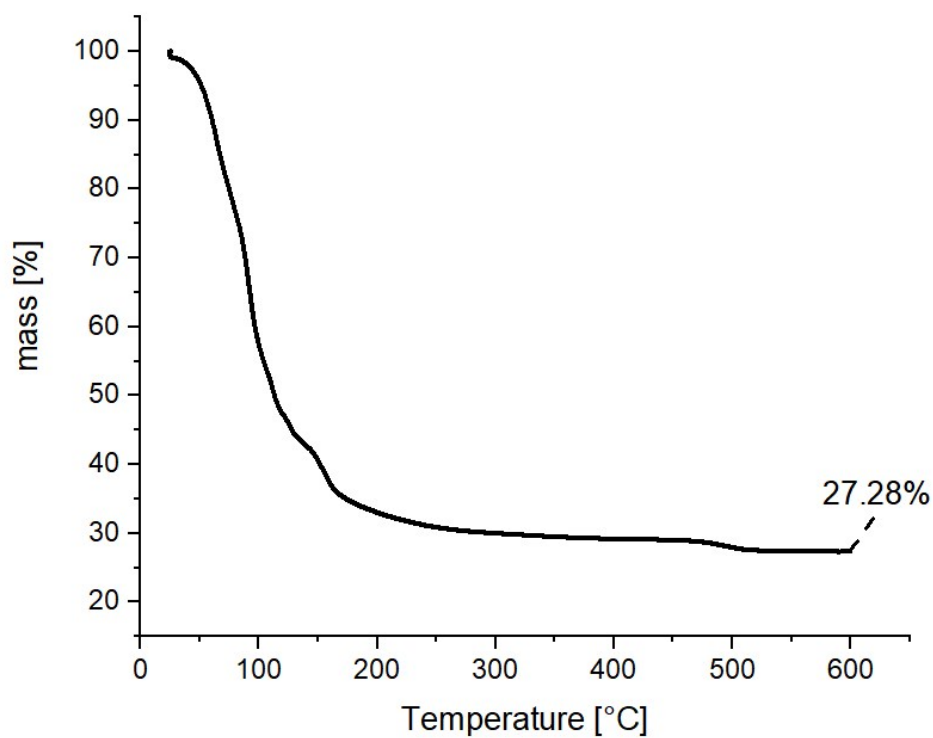


Figure S1. TGA curve of Ga(NO₃)₃·xH₂O precursor. Assuming full conversion to Ga₂O₃, the measured mass loss corresponds to $x \approx 4.9$.

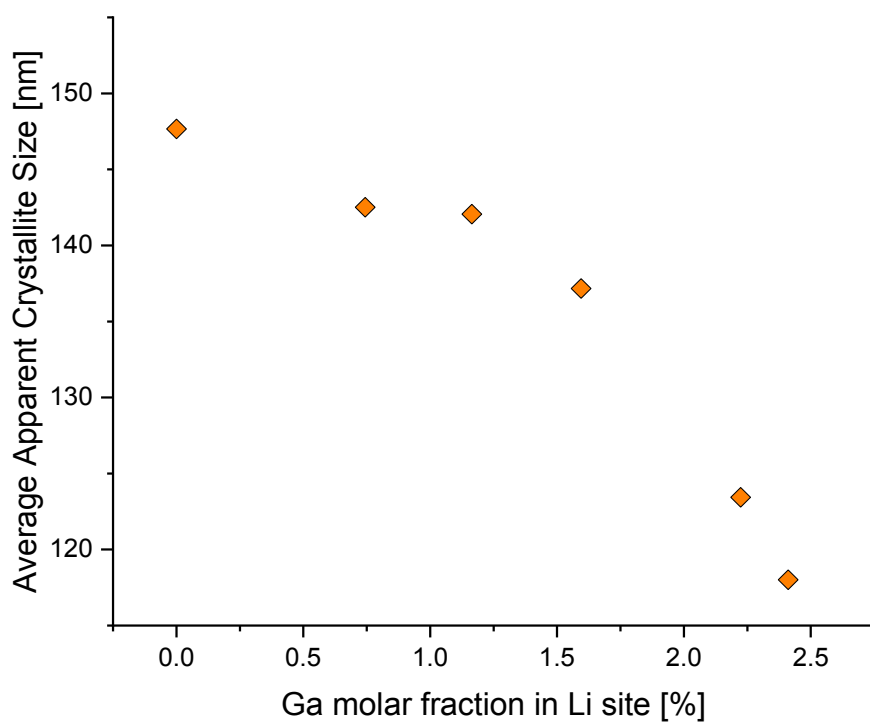


Figure S2: Average Apparent Crystallite Size as function of the Ga molar fraction in the Li site.

Table S1. ICP-OES data and Rietveld refinement results for XRD experiments on calcination products.

Nominal molar fraction of Ga (mol%)	Molar equivalents from ICP-OES (mol)			Molar fraction of Ga in Li layer (mol%)	a (Å)	c (Å)	V (Å ³)	c/a	z_{Ox}
	Ga	Li	Ni						
0	-	1.03 (2)	1.00	0	2.87548 (1)	14.1999 (1)	101.6805 (9)	4.93826 (5)	0.2585 (2)
1	0.010 (0)	1.04 (2)	0.99 (2)	0.7 (2)	2.87565 (1)	14.2017 (1)	101.7054 (9)	4.93864 (5)	0.2586 (2)
2	0.018 (0)	1.03 (2)	0.98 (2)	1.2 (2)	2.87694 (1)	14.2082 (1)	101.843 (1)	4.93867 (5)	0.2585 (2)
3	0.026 (0)	1.03 (2)	0.97 (2)	1.6 (2)	2.87787 (1)	14.2119 (1)	101.936 (1)	4.93836 (5)	0.2584 (2)
4	0.035 (0)	1.02 (2)	0.96 (1)	2.2 (3)	2.87884 (1)	14.2159 (1)	102.032 (1)	4.93807 (5)	0.2583 (2)
5	0.039 (0)	1.02 (2)	0.96 (2)	2.4 (3)	2.87903 (1)	14.2170 (1)	102.054 (1)	4.93816 (5)	0.2583 (2)

Nominal molar fraction of Ga (mol%)	S (Å)	I (Å)	$B_{iso}(Ni)$	$B_{iso}(O)$	R_{Bragg} (%)	χ^2	Molar fraction of Li_5GaO_4 (mol%)
0	2.123 (3)	2.610 (3)	0.30 (1)	0.70 (4)	2.05	9.8	-
1	2.122 (3)	2.612 (3)	0.27 (1)	0.69 (4)	2.14	10.4	-
2	2.124 (3)	2.612 (3)	0.33 (1)	0.76 (5)	2.17	10.5	-
3	2.129 (3)	2.608 (3)	0.36 (1)	0.80 (5)	2.28	11.2	0.5 (1)
4	2.132 (3)	2.607 (3)	0.35 (1)	0.82 (5)	2.37	12.6	0.8 (1)
5	2.132 (3)	2.607 (3)	0.36 (1)	0.82 (5)	2.44	10.1	0.9 (1)

Table S2. Refinement result for test of hypothesis involving placement of Ga in the Ni layer of _____ LNO.

LiNi _{1-y} Ga _y O ₂ (4% nominal doping)						
<i>R</i> -3 <i>m</i> , <i>Z</i> = 2			<i>R</i> _{Bragg} = 2.31%			
<i>a</i> = 2.878836 (5) Å			<i>R</i> _{wp} = 7.21%			
<i>c</i> = 14.21591(4) Å			χ^2 = 12.7			
<i>V</i> = 102.0327(4) Å ³						
Atom	Wyckoff position	Atomic position			Occ	<i>B</i> _{iso}
		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>		
O	6c	0	0	0.2582	2	1.02(2)
Ni	3a	0	0	0	1.22(2)	0.372(6)
Ga	3a	0	0	0	-0.22(2)	0.372(6)
Li	3b	0	0	0.5	0.9754(9)	0.86(6)
Ni	3b	0	0	0.5	0.0246(9)	0.86(6)