



20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
20 - 24 September 2026
BLED - SLOVENIA

THE THERMAL BEHAVIOR OF THE Li-ION BATTERIE CATHODE MATERIAL $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$

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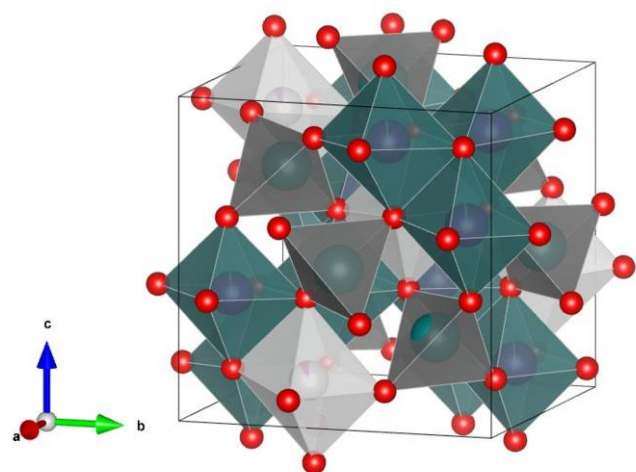


What is LNMO?

- **LNMO** stands for **L**ithium**n**ickel**m**angane**s**e**o**xide
- So called stoichiometric LNMO is $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$
- LNMO exists in the range $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$, $0 \leq x \leq 0.5$
- LNMO has a classic cubic spinel crystal structure
- It shows a phase transformation from an ordered LT-modification to a disordered HT-modification whereby ordering refers to the transition metal atomic position(s). The transition temperature is approx. 650 °C for stoichiometric LNMO and varies with Ni/Mn ratio.
- LNMO is derived from LiMn_2O_4 , LMO, which is isostructural with disordered LNMO.

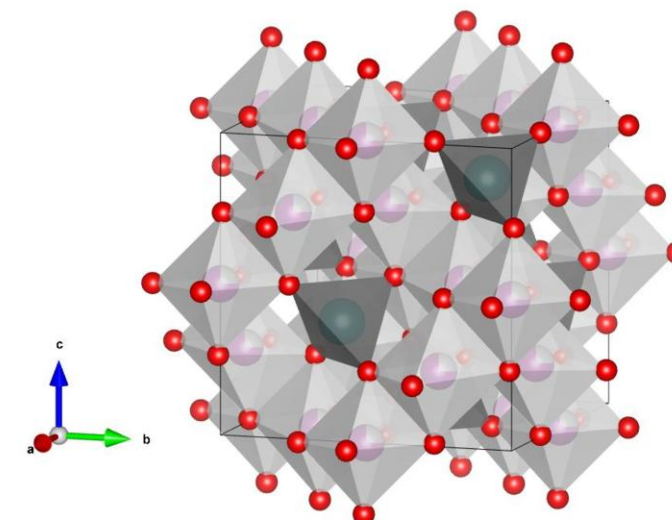


Structure and modifications of LNMO



Ordered LNMO, $P3_32$
stable up to approx. 650 °C

$a: 817.52 \text{ pm} \rightarrow 817.99 \text{ pm}$

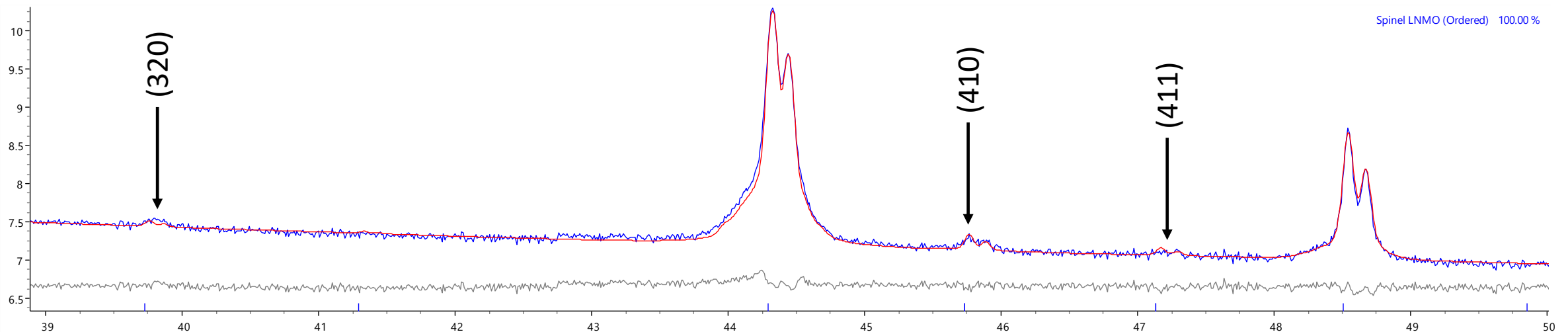


Disordered LNMO, $Fd\bar{3}m$
stable from approx. 700 °C



Where from we got the LNMO for our investigations?

- Disordered LNMO was provided by Topsoe, Denmark
- It was synthesized involving spray drying processes and exhibits a secondary particle structure
- By heat treatment we transformed it at least partly to ordered LNMO





How Li-ion batteries work?

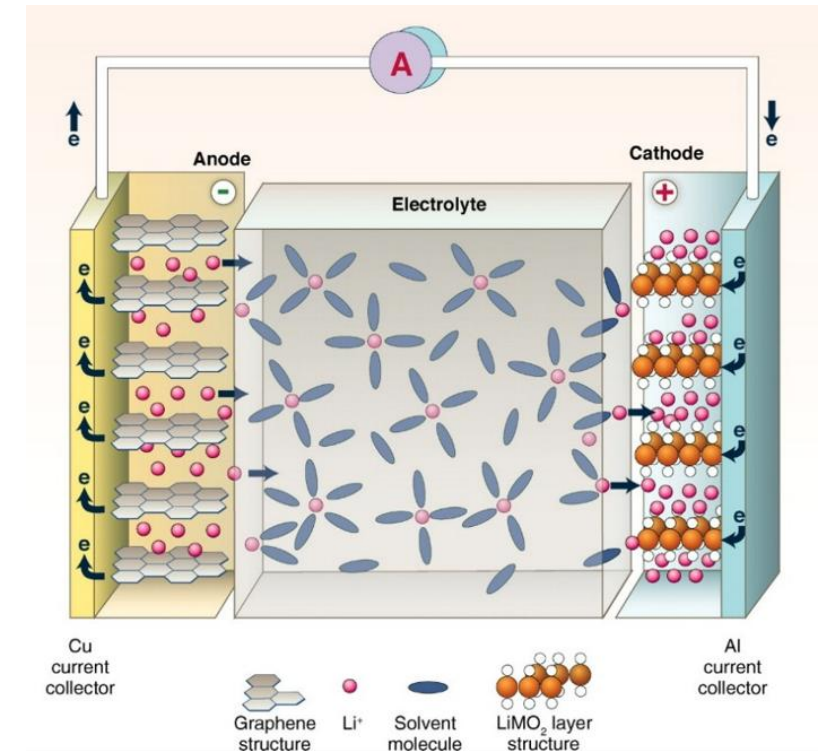
Main components:

- Anode Material (Graphite in most cases)
- Cathode Material (see next slide)
- Electrolyte (e.g. LiPF_6 diss. in EC, DEC)
- Separator (PE, PP) or Borsilicate glass fibers

Li-ions are transferred from one host structure to another.

Driving force on discharge: $\mu_{\text{Li}}(\text{Anode}) > \mu_{\text{Li}}(\text{Cathode})$

If the battery is functioning properly, there will never be any lithium metal present.

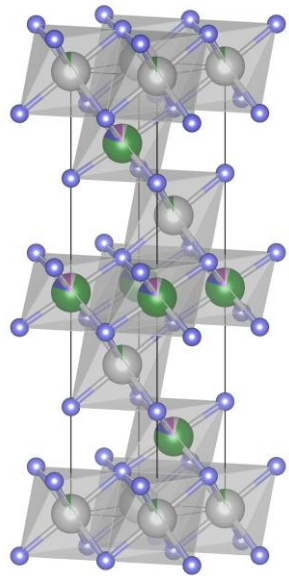


Farag, Mohammed. (2013). Lithium-Ion Batteries: Modelling and State of Charge Estimation.



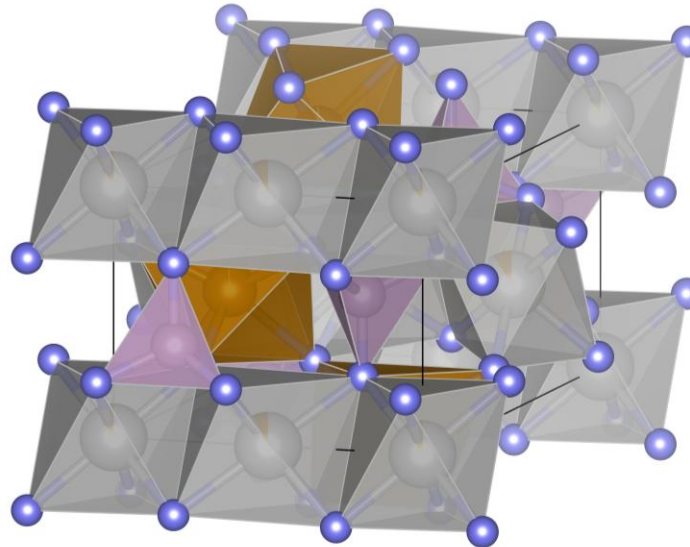
Types of Cathode materials for Li-ion batteries

Layered metal oxide type, e.g. NMC811



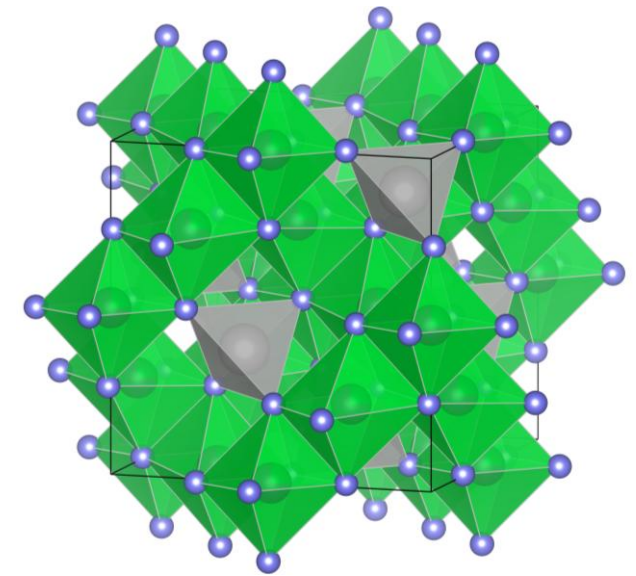
High Voltage
High Cost

Olivine type, e.g. LFP



Low Voltage
Low Cost

Spinel type, e.g. LNMO



High Voltage
Low Cost



The pros and cons of LNMO as a cathode material

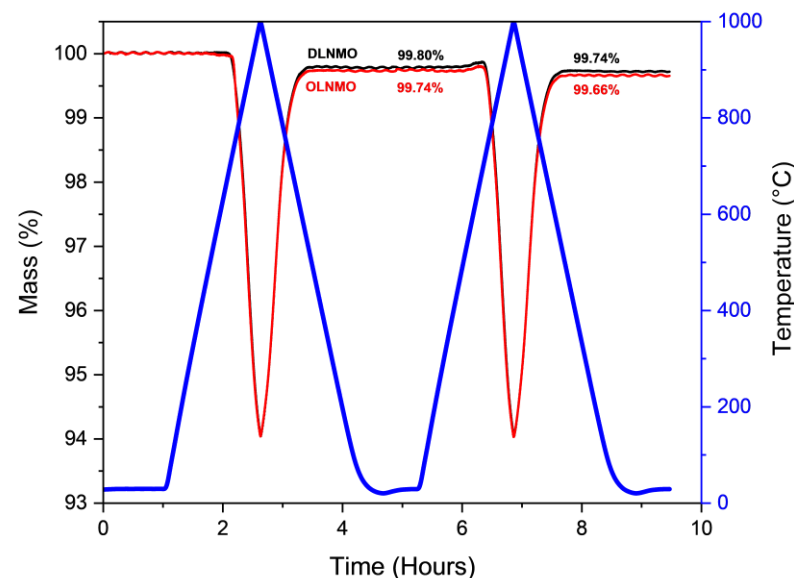
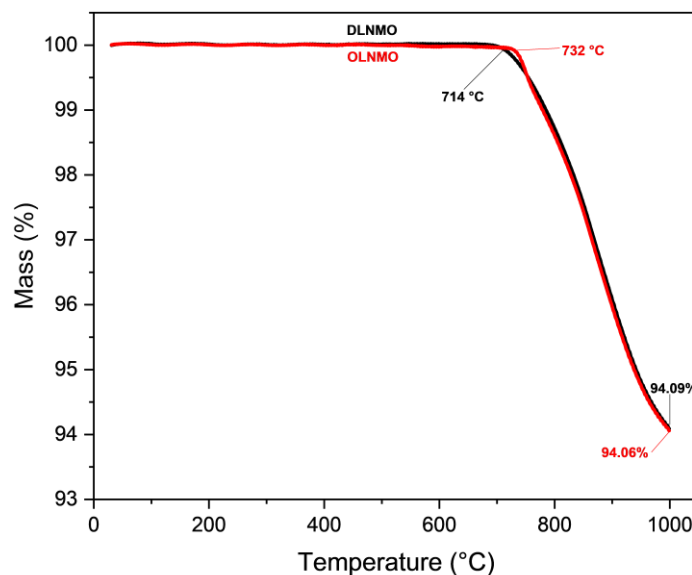
- | | |
|---|--|
| <ul style="list-style-type: none">• High Specific Energy• Cobalt-free• Cost effective• Excellent Rate Capability• Enhanced Safety | <ul style="list-style-type: none">• Electrolyte Degradation (High Voltage)• Manganese Dissolution and Capacity Fade• Lower Power Density• Complex Synthesis |
|---|--|

For several reasons, it is important to understand the thermal behavior of battery materials. Heat dissipation, phase transitions, and decomposition products are of great relevance in terms of operational safety and battery heat management.



The thermal decomposition of LNMO under air

Disordered as well as ordered LNMO was heated and cooled twice with 10 K/min in a TGA-DSC under air



Mass loss: 6 wt.%

T_{in} -ordered: 732 °C

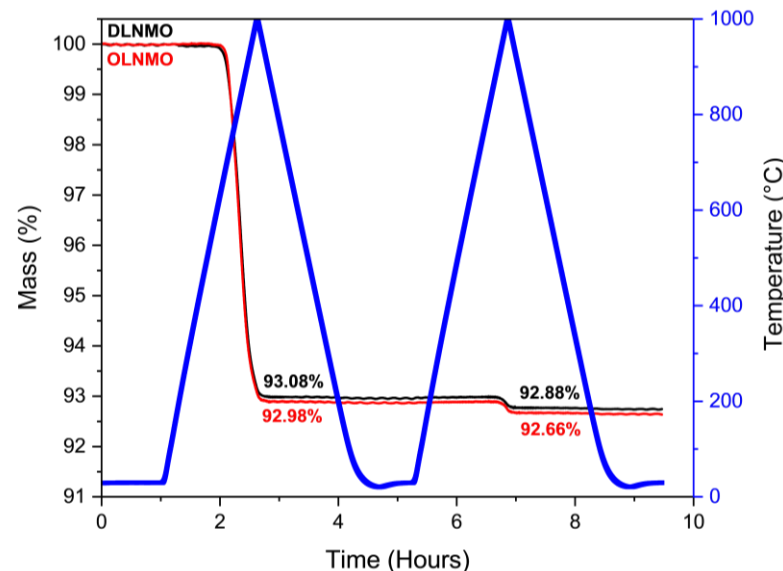
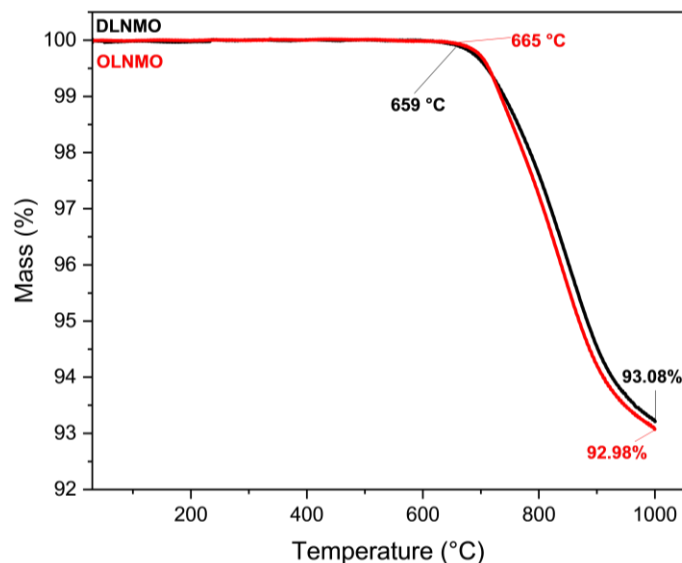
T_{in} -disordered: 714 °C

Almost totally reversible on cooling. Disorder promotes decomposition!



The thermal decomposition of LNMO under Ar

Disordered as well as ordered LNMO was heated and cooled twice with 10 K/min from RT – 1000 °C in a TGA-DSC under Ar



Mass loss: 7 wt.%

T_{in} -ordered: 665 °C

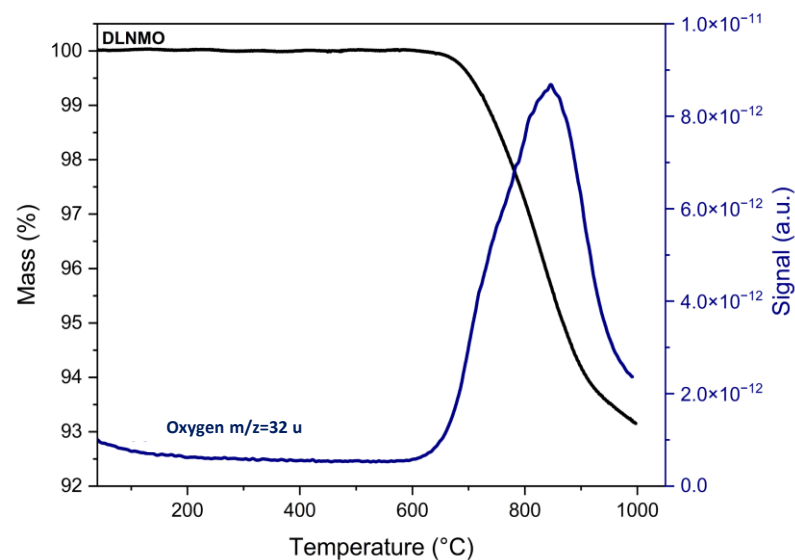
T_{in} -disordered: 659 °C

Mass loss irreversible on cooling. Mass loss by $O_2 \uparrow$?



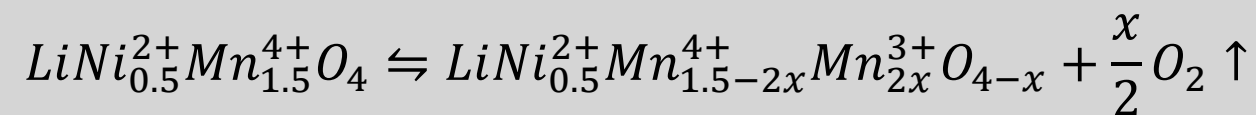
The thermal decomposition of LNMO

Disordered LNMO was heated with 10 K/min in a TGA-DSC-MS under Ar



Mass loss corresponds to a release of oxygen!

This was initially interpreted as follows:

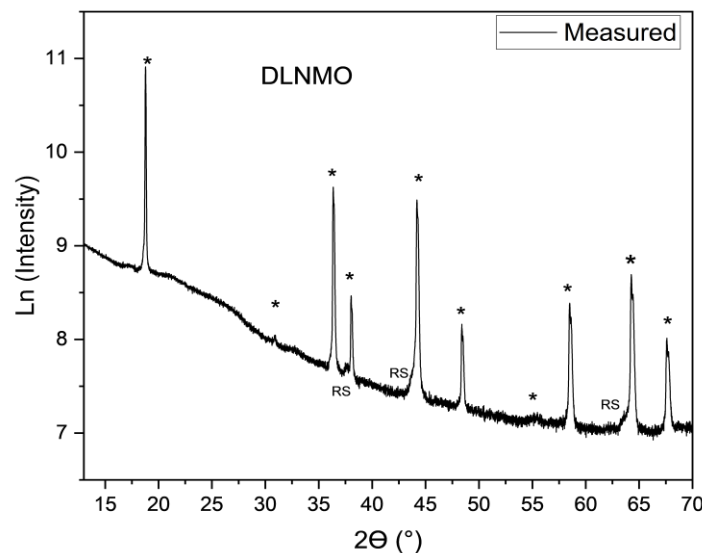




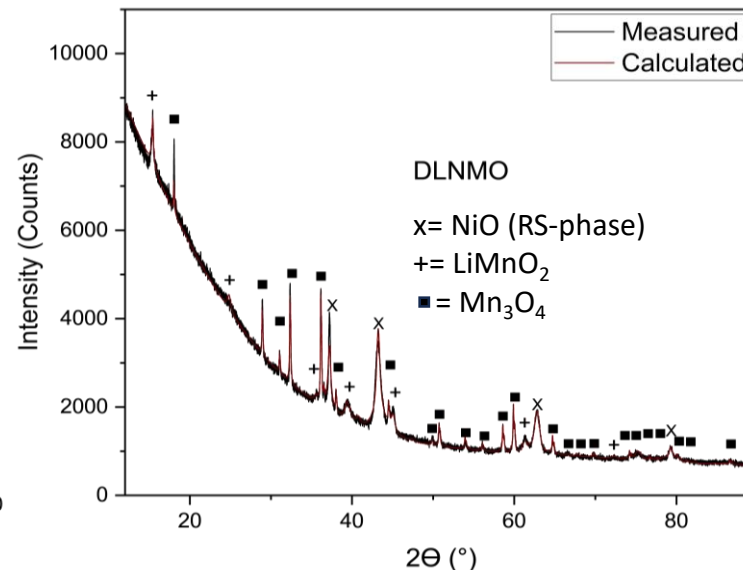
The thermal decomposition of LNMO under Ar

Powder-XRD after decomposition of DLNMO under Air and Ar

Air



Ar



Air Small amounts of a rock salt structured phase (RS-phase), here described as NiO, remained after reuptake of oxygen.

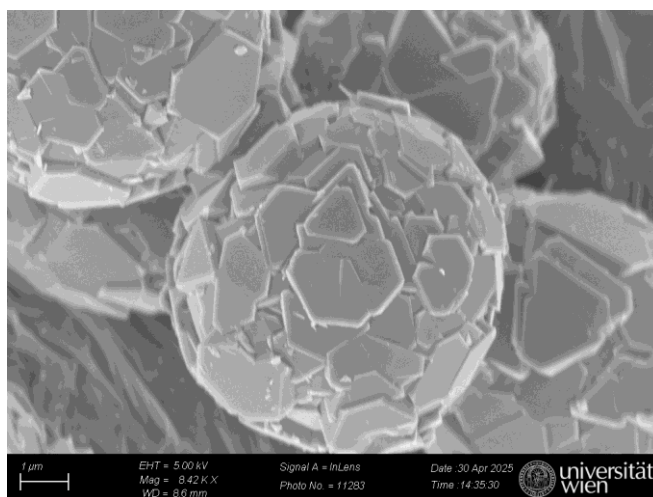
Ar LNMO completely vanished, the decomposition products are the RS-phase, refined as NiO, LiMnO₂, a layered MnO₂ structure with Li intercalated and Mn₃O₄, a spinel.



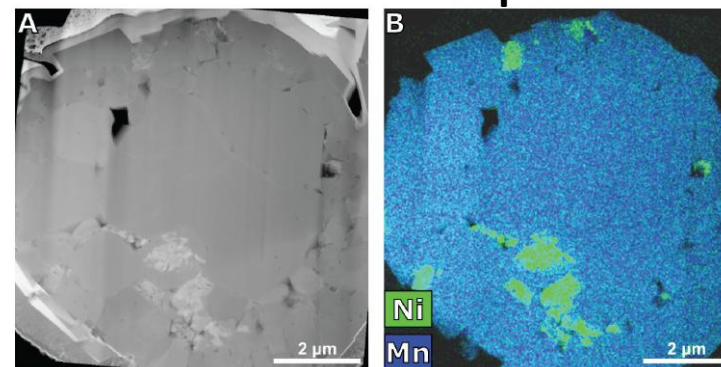
The thermal decomposition of LNMO – reversibility!

How the decomposition to LNMO and RS-phase on air can be almost fully reversible?

DLNMO after TGA in air



DLNMO after heat treatment in air:
STEM and elemental map



C. Fink, L.F. Lundegaard, J.W. Høj, J. Højberg,
C. Fink Elkjaer, Haldor topsoe white www.topsoe.com.

- **The RS-phase** is rather formed in smaller domains within the LNMO crystallites.
- No bulk phase separation occurs.
- This allows for rapid and complete reintegration during cooling in air.

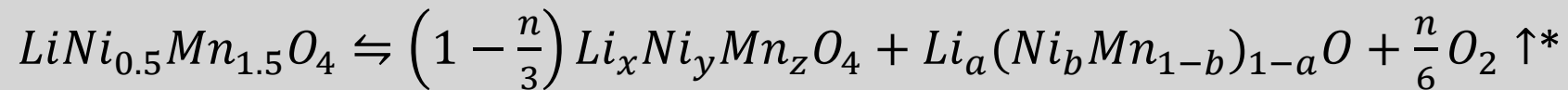


The thermal decomposition of LNMO – valid interpretation

LNMO has a metal/oxygen ratio of 3:4.

The formation of the RS-phase with a metal/oxygen ratio of 1:1 requires the release of oxygen!

Mass loss and release of oxygen by formation of RS-phase



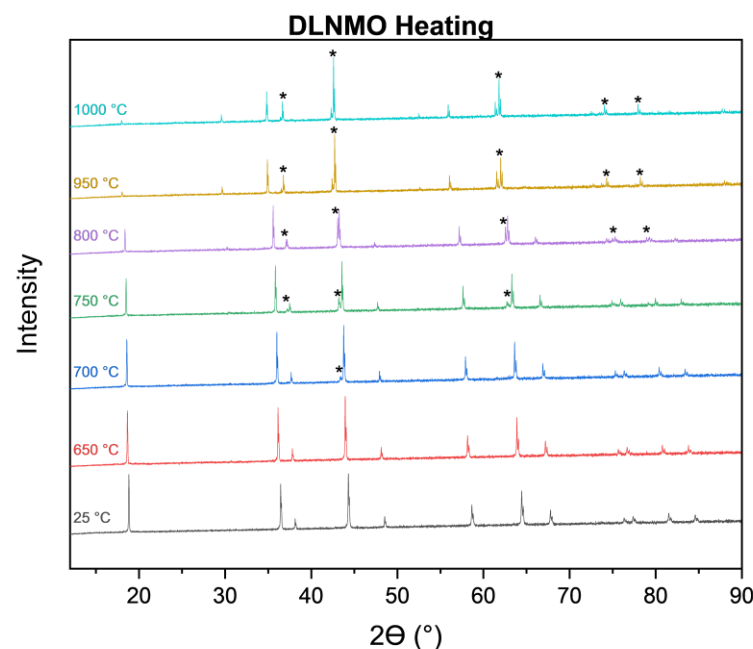
Neutron diffraction investigations: No prove for an oxygen defect LNMO structure under air!

*P. Stüble, V. Mereacre, H. Geßwein, J.R. Binder, On the composition of $LiNi_{0.5}Mn_{1.5}O_4$ cathode active materials, Adv. Energy Mater. 13 (2023)

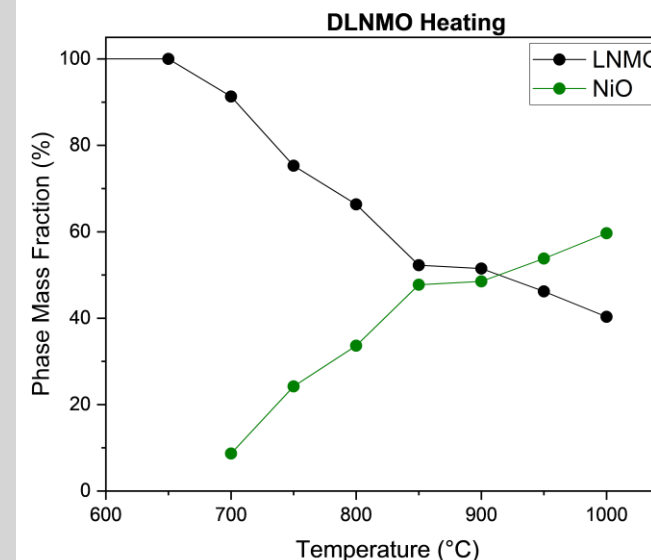


The thermal decomposition of LNMO – HT-XRD investigations under air

DLNMO was heated stepwise from RT to 1000 °C in 50 K increments



The RS-phase (*) is formed upon 700 °C and becomes dominant upon 900 °C. From 800 °C, there is a significant decrease in the intensity of (1 1 1) peaks and an increase in the intensities of (2 2 0) and (4 2 2) peaks which are indications of partial occupation of the 8b tetrahedral positions (usually occupied by Li only) with transition metal ions.





The thermal decomposition of LNMO – HT-XRD investigations under air

The mass fractions of RS-phase and remaining LNMO derived from Rietveld refinement of HT-XRD patterns were used to calculate the oxygen mass loss versus temperature.

The formula* used is

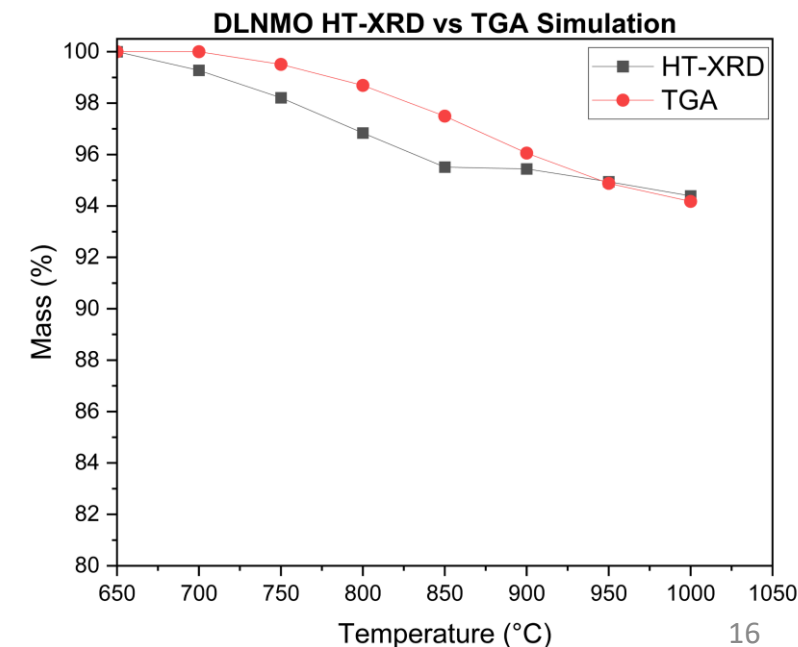
$$m(O_2) = m(RS) \times \frac{M(O_2)}{6M(RS)}$$

The composition of LNMO was considered to be constant. The composition of RS was assumed to be NiO up to 750 °C and $\text{Li}_{0.33}\text{Ni}_{0.44}\text{Mn}_{0.22}\text{O}$ for temperatures ≥ 800 °C.♦

*P. Stüble, V. Mereacre, H. Geßwein, J.R. Binder, On the composition of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode active materials, Adv. Energy Mater. 13 (2023)

♦ L. Cai, Z. Liu, K. An, C. Liang, Unraveling structural evolution of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by in situ neutron diffraction, J. Mater. Chem. A Mater 1 (2013) 6908–6914

DLNMO was subjected to the same temperature program in a TGA-DSC as in the HT-XRD.





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Ceramics International 52 (2026) 27736–27749



Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Insights into the thermal decomposition of LNMO

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ARTICLE INFO

Keywords:
LNMO
Cobalt-free cathodes
XRD
Thermal stability
TGA
HT-XRD
Cathodes

ABSTRACT

LNMO ($\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$) is a promising cathode material for Lithium-ion batteries, which crystallizes in two structures (ordered and disordered) depending on synthesis temperature and post-synthesis annealing. In this work, the thermal stabilities of both ordered and disordered LNMO were investigated under air and argon, and the decomposition products were analyzed with XRD. The decomposition under air was also investigated by high-temperature XRD. Above approx. 700 °C, a Ni-rich rock-salt phase ($\text{Ni}_{1-x}\text{Li}_x\text{Mn}_2\text{O}_4$) is formed, and oxygen is released. We observed that ordered LNMO has a higher onset temperature of decomposition than disordered LNMO when heated in air. This was also reflected in the high-temperature XRD experiments, which confirmed that a higher fraction of the rock-salt phase was found in the disordered LNMO at 700 °C compared to ordered LNMO. The results indicate that disordering could facilitate the formation of ($\text{Ni}_{1-x}\text{Li}_x\text{Mn}_2$)O, driven by Ni^{2+} clusters that can act as crystallization seeds. When the heat treatments are performed in air, the decomposition of both ordered and disordered LNMO is accompanied by the formation of Mn-rich LNMO, where the TM-ions can occupy the lithium position. Upon cooling, the particle morphology is maintained, but only the disordered LNMO is re-formed with a small amount of ($\text{Ni}_{1-x}\text{Li}_x\text{Mn}_2$)O. This implies that the rock-salt structure forms within domains of the crystallites and does not precipitate as a bulk phase.

Under argon, both LNMO structures showed lower decomposition onset temperatures and higher total mass losses compared to when the heat treatments were performed in air. In addition to the rock-salt phase, a further irreversible decomposition occurs at higher temperatures, where the Mn-rich LNMO decomposes into Mn_2O_3 and LiMnO_2 . In this case, however, although the secondary particle morphology is still maintained, the primary particles change significantly. They lost their regular shape and the crystallite size diminished.

Journal of Thermal Analysis and Calorimetry (2026) 151:6397–6407

<https://doi.org/10.1007/s10973-026-15452-0>



Heat capacities of selected battery materials and components

Mahmoud Reda^{1,2} · Hans Flandorfer¹

Received: 30 October 2025 / Accepted: 11 March 2026 / Published online: 29 March 2026

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Abstract

The specific heat capacities of solid battery materials like active electrode materials and separators were measured from approx. 300–550 K in this study. First, the method was validated by measuring the heat capacities of active anode materials silicon and tin disulfide, which could then be compared to data from literature. The second set of measurements were done on two separator materials (Celgard 2500 and Whatman GF/C), and the results were compared to the heat capacity measurements of pure polypropylene and borosilicate glass from literature. The C_p of Celgard 2500 was between of 1.79 and 2.16 J.g⁻¹K⁻¹ and the C_p of Whatman GF/C was between 0.83 and 0.96 J.g⁻¹K⁻¹. In addition, heat capacity values of both types of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), disordered LNMO (DLNMO) and ordered LNMO (OLNMO), are reported for the first time, ranging between 0.72–0.90 J.g⁻¹K⁻¹ and 0.73–0.86 J.g⁻¹K⁻¹ for DLNMO and OLNMO, respectively. Compared to each other, both DLNMO and OLNMO have similar heat capacities at lower temperatures. However, with increasing temperature, DLNMO starts to have higher heat capacities. Both heat capacities were compared to a heat capacity calculation according to Neumann–Kopp based on the heat capacities of the binary oxides. When compared to the “Parent” material LiMn_2O_4 (LMO), both DLNMO and OLNMO had lower heat capacities. The data are highly relevant for battery thermal management and for thermal modeling and simulation of lithium-ion batteries.

Keywords Battery materials · LNMO · Heat capacity · Separators · LMO · SnS_2



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**Thank you for your
kind attention!
Questions?**