Batteries - LNMO material
Technical status
Version 1.0, Jan. 2021

Technical status for **Haldor Topsoe LNMO material**

TBM-129 high-voltage LNMO spinel material

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This technical summary report describes the current status for battery cells based on high-voltage LNMO spinel material ($LiNi_xMn_{2-x}O_4$) produced by Haldor Topsoe.

HALDOR TOPSØE

Summary

The high-voltage $LiNi_xMn_{2-x}O_4$ (LNMO) spinel material from Topsoe (TBM-129) is developed to secure high electrode density, easy slurry processing and reduced degradation reactions on the surface during cycling. The current production capacity is 4 ton/year, and we plan to install a 100 ton/year pilot line in 2021.

In this report, stable cycling of LNMO based cells for 500 cycles at 23 °C is demonstrated. At this temperature, the capacity retention is more than 80% for graphite and 90% for LTO ($Li_4Ti_5O_{12}$). At 45 °C, 80% of the initial capacity remains after 130 cycles in LNMO-graphite cells.

Based on our learnings from degradation mechanisms and system stabilization, we expect to increase the cycling stability even in 2021.

Our performance targets are summarized in Table 1.

TABLE 1 We expect to reach the following performance targets in 2021

Performance targets for 2021	Initial capacity	Cycle life (80% capacity retention)
LNMO-graphite at 23 °C	120 mAh/g	1000 cycles
LNMO-graphite at 45 °C	120 mAh/g	200 cycles
LNMO-LTO at 23 °C	130 mAh/g	2000 cycles

Initial capacity at 0.1C. Cycling at 1C discharge and 0.5C and 1C charge for graphite and LTO, respectively.

TABLE 2 Scale-up timeline

Scale-up timeline	Capacity per year
Spring 2020	4 tons
Q4 2021	100 tons (pilot)
202x	1000s tons

A full-scale production will depend on technical readiness of the system and market acceptance.

Please do not hesitate to contact our LNMO expert Jonathan Højberg at jhoj@topsoe.com

Optimized
LNMO material - TBM-129

Topsoe is world leading within heterogenous catalysis. Our business is based on the core value of scientifically based development. We have used this approach to optimize the synthesis of LNMO high-voltage spinel to obtain a cheap and energy dense material with a long cycle life.

The result is TBM-129.

We are currently able to produce 4 tons TBM-129 per year with high reproducibility, and we plan to install a 100 ton/year pilot line in 2021.

The material is based on dense spherical particles with a tunable average particle size between 5 µm and 20 µm. Figure 1:a shows a SEM image of TBM-129 in low Magnification displaying the uniformity of the material.

Figure 1:b shows cross sections of TBM-129 measured by SEM and TEM, displaying the dense particles.

Figure 1:c shows particle size distributions of selected samples.

Fig. **1:a**

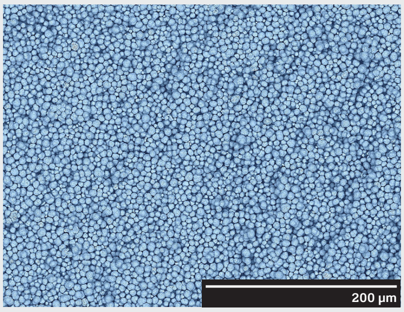


Fig. **1:b**

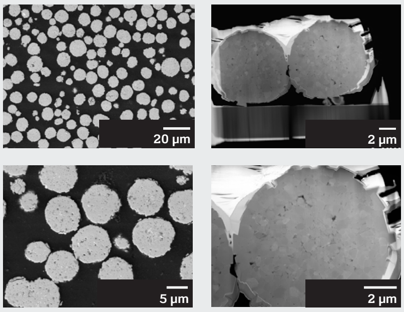


Fig. **1:c**

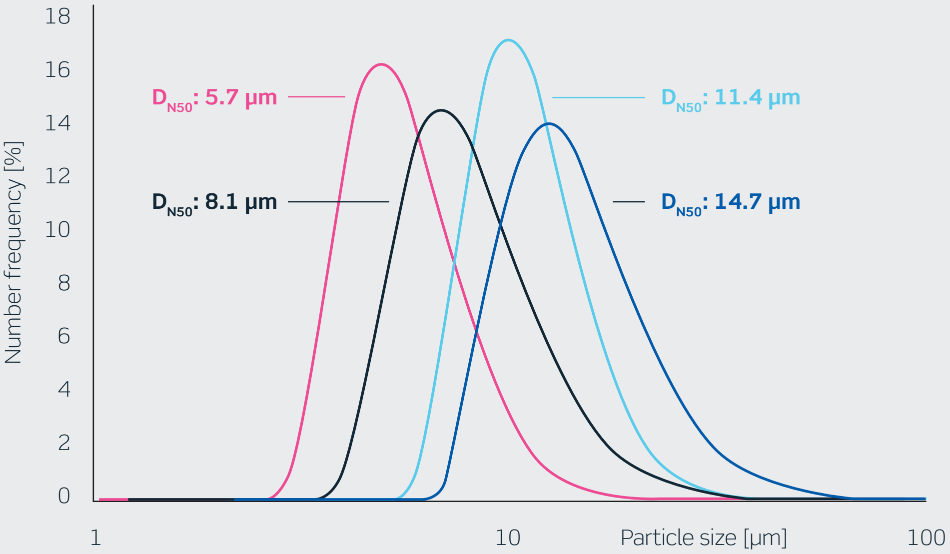


Figure 1:a: SEM image of TBM-129 LNMO particles. b: Cycling curves at 1C of TBM-129 in LNMO-lithium cells at room temperature and 55 °C. Every 20th cycle is performed at 0.2C.

The TBM-129 LNMO particles are multicrystalline. Typically, the size is around 8 µm with primary particles around 500 nm and our calcination procedure ensure that the individual particles do not agglomerate. The spherical morphology gives a low surface area, which limits degradation reactions on the surface and enables easy slurry preparation.

The material has high phase purity. Typically, with around 97 wt% spinel material to ensure a high capacity, and the chemistry is carefully controlled to make it possible to produce customized products for specific applications.

LNMO has several beneficial properties compared to NMC and NCA

1. **Reduced cost and more abundant materials.** LNMO is Co-free and uses less Li and Ni. The cost per kg is reduced by 50% at material level and by 10-20% at cell level.
2. **High operating potential.** Fewer cells are required in series in batteries and single cell applications for 4.5 V systems are possible.
3. **LNMO is stable in water.** It is easy to carry out water-based electrode manufacturing to avoid NMP, and the shelf life of LNMO is much longer than layered materials.
4. **Fully delithiated LNMO is stable.** No oxygen evolution of LNMO when delithiated completely. This increases safety and simplifies battery management.

TBM-129 is very stable during cycling and LNMO-lithium cell tests show very little degradation.

Figure 2:a shows the cycling curve in a LNMO-lithium coin cell at room temperature and at 55 °C.

The capacity is 135-140 mAh/g, and within the first 100 cycles, the capacity fade at room temperature is less than 1% per 100 cycles and only 2% per 100 cycles at 55 °C.

Figure 2:b shows the voltage curve of lithiation and delithiation of LNMO vs. Li/Li$^+$ with the characteristic three plateaus; Mn^{3+}/Mn^{4+} redox at 4V and Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} redox at around 4.7 V vs. Li/Li$^+$.

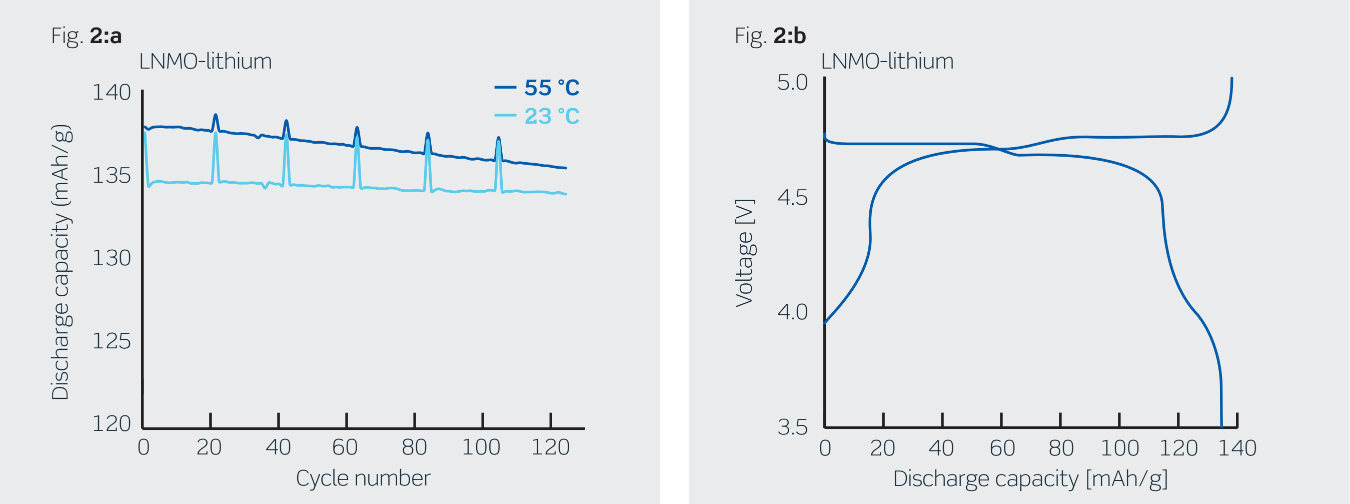


Figure 2: Cycling curves at 1C of TBM-129 in LNMO-lithium cells at room temperature and 55 °C. Every 20th cycle is performed at 0.2C. b: Voltage curve of LNMO-lithium during charge and discharge.

The main issue encountered with LNMO-graphite cells is the fact that lithium gets fixated in the SEI layer on the anode during cycling.[1.a, 1.b, 1.c] In standard carbonate electrolytes like LP30 and LP40, degradation products from the cathode migrate to the anode and enhances this effect in such a way that 40% of the lithium is fixated on the anode after 300 cycles at room temperature in LNMO-graphite cells. This is shown in Figure 3:a as 'Standard electrolyte'.

In 2020 we ran an internal project in Topsoe to improve the cycling of LNMO-graphite and LNMO-LTO cells by optimizing non-LNMO components in the system. By selecting additives to stabilize the surface of both anode and cathode, we have succeeded in improving the cyclability of these cells significantly.

Our best electrolyte so far is based on 1M $LiPF_6$ in EC:DEC (LP40) with 1% tris(trimethylsilyl) phosphite (TMSP)[1.d, 1.e] and 1% lithium bis(oxalato)borate (LiBOB)[1.f], and we recommend this electrolyte as a starting point if you would like to test our LNMO material.

Figure 3:a shows two stages of optimization; 1. Standard electrolyte and 2. Improved electrolyte. The improved electrolyte reduces capacity fade significantly and increases the remaining capacity after 500 cycles from 61% to 82%. The improved electrolyte also significantly affects the performance at 45 °C.

Figure 3:b compares cycle curves based on cells with standard and improved electrolyte at 45 °C. The additives have prolonged the 80% end of life limit from 10 cycles to 130 cycles.

Fig. **3:a**

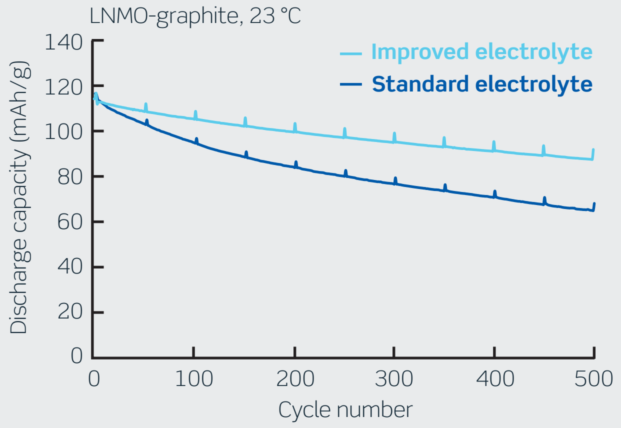


Fig. **3:b**

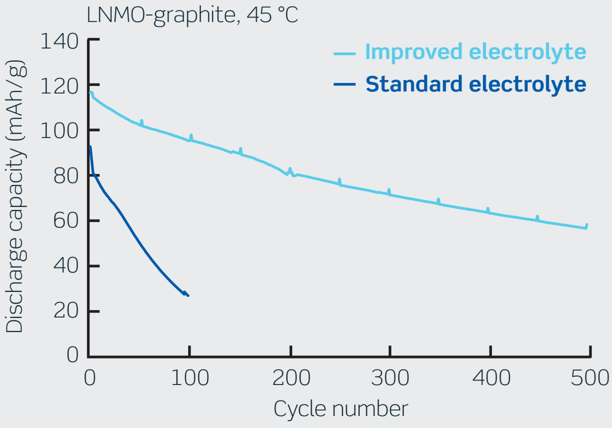


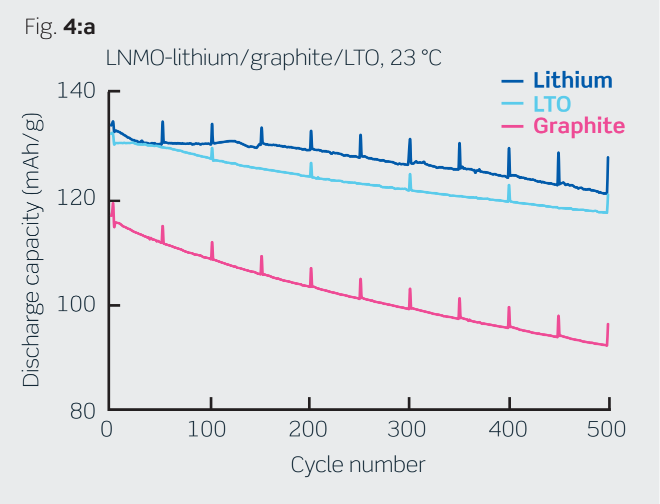
Figure 3: Cycling curves of LNMO-graphite cells at 1C discharge and 0.5C charge with TBM-129 cathode at a: 23 °C and b: 45 °C with two stages of system optimization

In terms of cycling, LTO is an even better choice of anode compared to graphite.

Figure 4:a shows a comparison of discharge curves of LNMO-lithium, LNMO-graphite and LNMO-LTO cells with TBM-129 cathode. The LTO system shows a high initial capacity of 130 mAh/g and a remaining capacity of 91% after 500 cycles.

Figure 4:b shows the corresponding voltage curves of the third formation cycle and it is clearly seen that the cells with lithium and LTO as anode show similar shapes corresponding to the nickel and the manganese redox activity. As opposed to this, lithium is fixated in the SEI layer on the anode in the graphite-based cell, which means that the manganese redox activity is almost lost.

These significant improvements were achieved in just six months and we still have several system improvements in the pipeline.



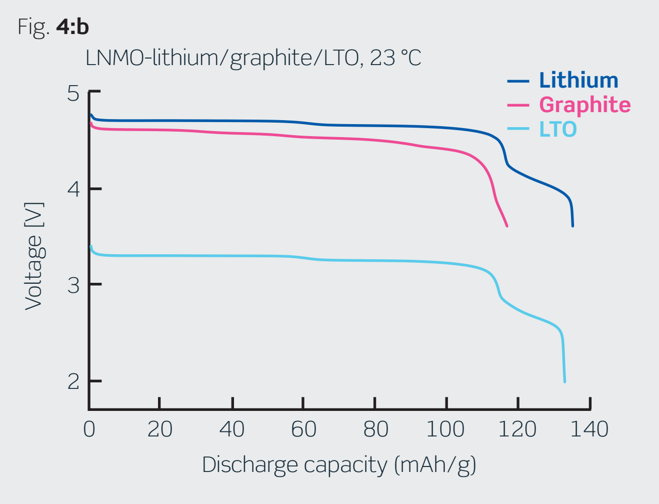


Figure 4: a: Cycling curves and b: voltage curves of LNMO-lithium, LNMO-graphite and LNMO-LTO cells with TBM-129 cathode. Cycling is performed at 1C discharge and 0.5C charge for LNMO-lithium and LNMO-graphite cells and 1C charge and discharge for LNMO-LTO cells. Voltage curves are from the end of formation at 0.1C rate.

Development of LNMO at Topsoe

Using our characterization competencies from catalysis to in-depth understanding of the synthesis, we have obtained full control of the morphology, particle size and chemistry.

We have published some of our findings in the White Paper *'Characterization of high-voltage* $Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$ *and correspondence between Ni content in spinel, lattice size and 4V capacity'* downloadable at www.topsoe.com/batteries.

Although we have developed TBM-129, we are continuously improving the LNMO material to increase cycle life even further. We are, e.g. currently improving the synthesis of single-crystal LNMO and investigating different post-treatments of the LNMO material to improve cycle life of LNMO-graphite cells.

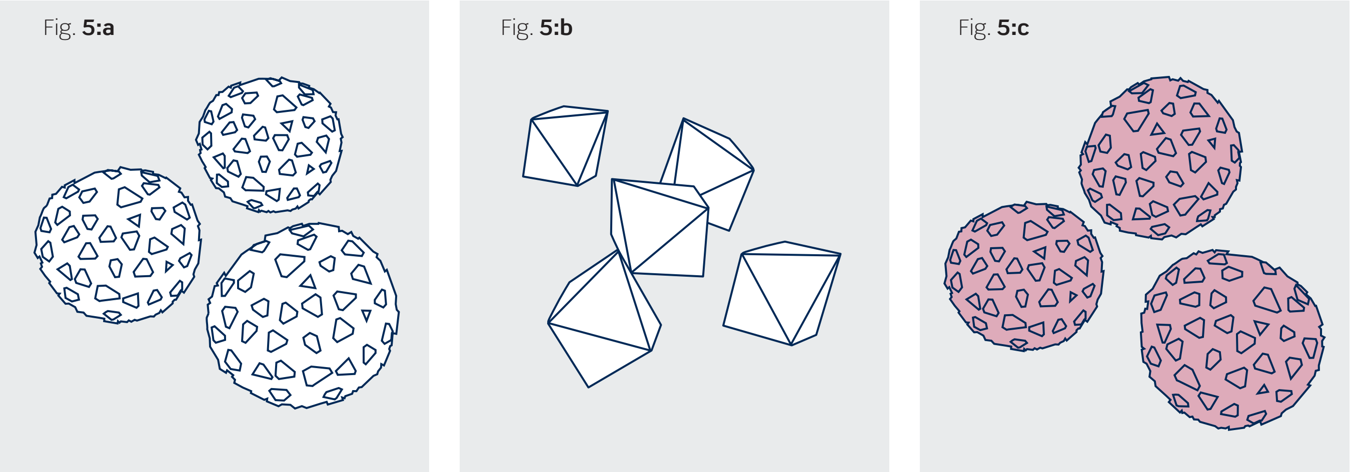


Fig. **5:a**
Fig. **5:b**
Fig. **5:c**

Figure 5: Different strategies pursued at Haldor Topsoe to improve performance of the LNMO material. In addition to TBM-129 (a), Topsoe is developing a single-crystal LNMO material (b) and LNMO materials with coating and doping (c).

Designing the chemistry of LNMO is essential to obtain a good cycle life. The general formula for LNMO is:

$Li_1^{1+}Ni_{0.5-x}^{2+}Mn_{1.5-x}^{4+}Mn_{2x}^{3+}O_4$, where $0<x\leq0.5$.

The theoretical capacity of the material is essentially 147 mAh/g for all values of x, but Ni-redox is substituted by Mn-redox when x is decreased.

As Ni-redox (Ni^{2+}/ Ni^{3+}/Ni^{4+}) occurs around 4.7 V vs. Li/Li^+, and (Mn^{3+}/ Mn^{4+}) occurs around 4.0 V vs. Li/Li^+, this will lower the average voltage and thereby the energy density.

As shown in the White Paper, this is, however a trade-off with cycle life, as LNMO materials with values of x around 0.40-0.45 show much less degradation compared to materials with $x = 0.5$. These findings are summarized in Figure 6:a.

In addition to the chemistry, the morphology is also important to the performance of the LNMO material.

Figure 6:b and Figure 6:c show how the average particle size and the morphology of the particles affect degradation in LNMO-lithium cells at 55 °C.

The LNMO materials used to determine the impact of morphology and particle size were synthesized with identical Ni content to isolate the effects of the morphology from those of the chemistry.

A combination of these findings has led us to the present design of TBM-129.

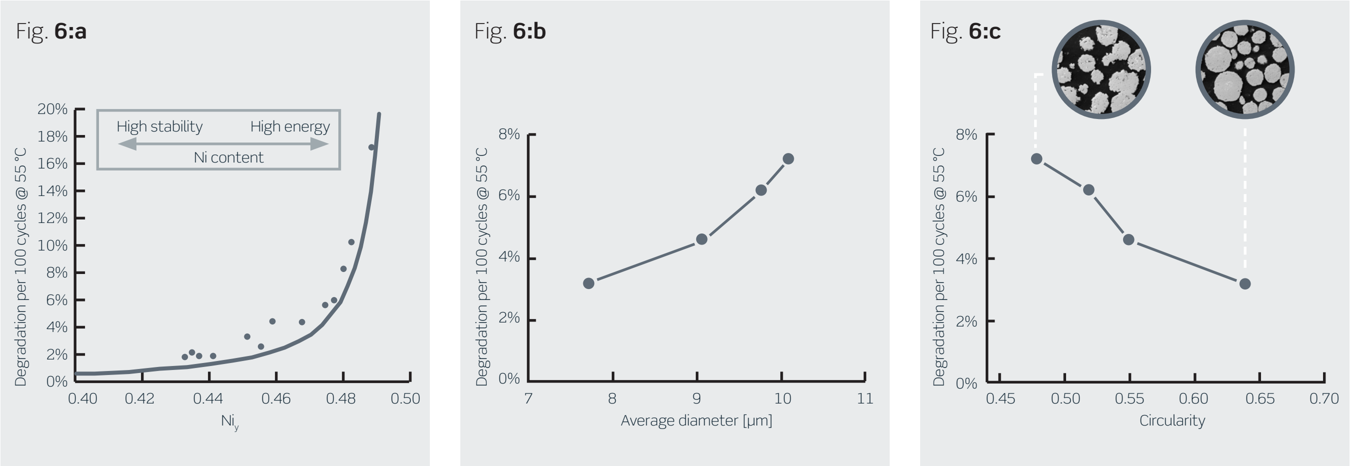


Fig. **6:a**

Fig. **6:b**

Fig. **6:c**

Figure 6: a: Correspondence between the Ni-content in LNMO, b: particle size and c: morphology and the degradation per 100 cycles measured for LNMO-lithium cells at 55 °C. To obtain a low degradation, the spinel should have a low Ni content, a small diameter and a spherical shape.

Business **perspective** of LNMO

One of the key benefits of LNMO compared to NMC and NCA is a raw material cost reduction of 50% per kg. As the production methods and downstream processes are similar this corresponds to 10-20% cost reduction per kWh at cell level.[2.a,2.b]

The low cost relis on three factors;
1. LNMO is cobalt free
2. LNMO transfers 100% more electrons per nickel atom and 25% more electrons per lithium atom compared to NMC622
3. The high operating voltage enables the use of less anode to obtain the same energy.

Cobalt is expensive and with fluctuating prices over the past years this metal constitutes a significant risk factor for price sensitive applications such as, e.g. batteries for the automotive industry. With only a few exceptions, cobalt is a side product from nickel and copper mines, which makes it difficult to scale the supply to satisfy increasing demand from the fast-growing battery industry.

Nickel and lithium are also expensive and should be utilized to their fullest from both a cost and resource perspective. In NMC and NCA, 20-40% of lithium is kept in the material to stabilize the structure. This is not necessary in the LNMO because the three-dimensional lattice allows full delithiation of the material without compromising the structural stability. In NMC and NCA, nickel is oxidized from Ni^{2+} to around Ni^{3+}. In LNMO, nickel is oxidized all the way from Ni^{2+} to Ni^{4+}.

Less anode is required in an LNMO cell compared to a cell with NMC and NCA. This is due to the higher potential of the LNMO cell.

The average discharge potential is 4.55 V for LNMO-graphite and 3.6 V for NMC622-graphite, and the (anode) capacity needed for a 1 kWh battery is 220 Ah and 278 Ah, respectively.

LNMO is compatible with water-based electrode manufacturing.[3a,3b,3c] The reason is the strong binding of lithium in the LNMO crystal lattice (hence the high operating potential) so proton ion exchange is very limited. The avoidance of NMP improves the economy and environmental impact of the electrode production.

As part of the commercialization of TBM-129, we plan to install a 100 t/year pilot line in 2021. A large-scale production is foreseen when the LNMO system has been validated by end users of, e.g., automotive or other main stream applications.

Fig. **7**

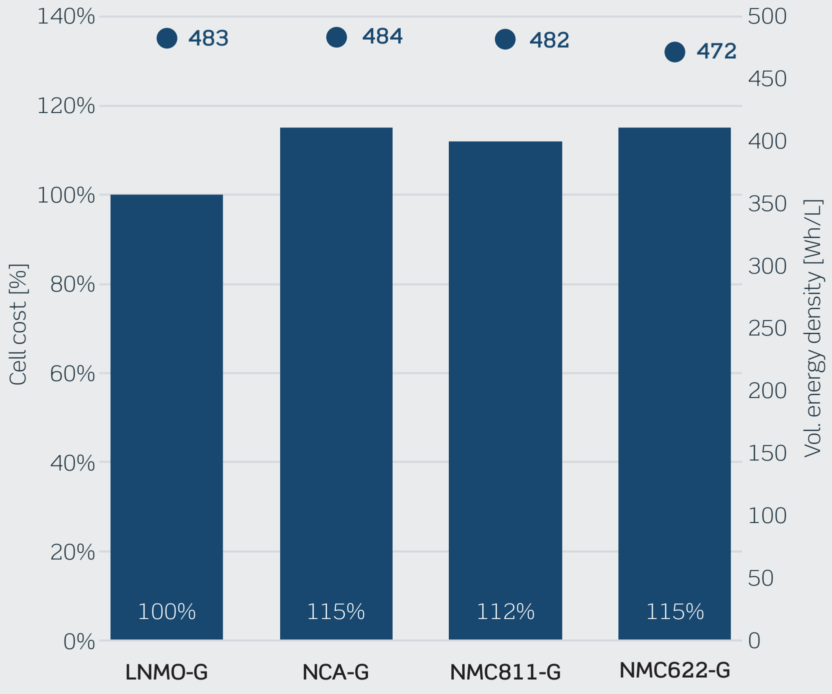


Figure 7: Comparison of cell cost per kWh for large format cells in 4 kWh battery module with LNMO, NCA and NMC cathodes and graphite anode. Cell calculations are performed using BatPac 3.0.

Collaboration

Improving cycle life of an LNMO-based cell requires a system approach, and an important part of our commercialization strategy is to collaborate with companies and research institutions that are experts in other parts of the cell.

We collaborate with cell producers, electrolyte manufacturers, OEMs and participate in two large projects funded by the European Commission with the target to demonstrate the ability of LNMO-based battery packs to decrease the cost and dependence on cobalt, nickel, and lithium.

The two projects are CoFBAT (GA-875126) and 3beLiEVe (GA-875033).

We are always interested in engaging in a collaboration. If you are interested, please reach out to our LNMO battery expert Jonathan Højberg (jhoj@topsoe.com).

Recommended readings **on LNMO**

1. High voltage electrolyte stability and cycling in LNMO-graphite cells

a. W Li et al., Journal of Power Sources 2020, 473, 228579. *Enabling high areal capacity for Co-free high voltage spinel materials in next-generation Li-ion batteries.* doi.org
Brief: Test of non-LNMO components for LNMO-graphite cells.

b. R Jung et al., J. Phys. Chem. Lett. 2017, 8, 4820-4825. *Chemical versus Electrochemical Electrolyte Oxidation on NMC111, NMC622, NMC811, LNMO, and Conductive Carbon.* doi.org
Brief: Difference in high voltage degradation of carbonates in NMC and LNMO systems.

c. B Michalak et al., Journal of Physical Chemistry C 2017, 121, 211–216. *Electrochemical cross-talk leading to gas evolution and capacity fade in* $LiNi_{0.5}Mn_{1.5}O_4$*/graphite full-cells.* doi.org
Brief: Characterization of gassing from SEI layer during cycling in LNMO-graphite cells.

d. Y-M Song et. al., J. Mat. Chem. A 2014, 2, 9506. *A multifunctional phosphite-containing electrolyte for 5 V-class* $LiNi_{0.5}Mn_{1.5}O_4$ *cathodes with superior electrochemical performance.* doi.org
Brief: Introduction of TMSP additive.

e. G Xu et. al., Advanced Energy Materials 2018, 8, 1701398. *Prescribing Functional Additives for Treating the Poor Performances of High-Voltage (5 V-class)* $LiNi_{0.5}Mn_{1.5}O_4$*/MCMB Li-Ion Batteries.* doi.org
Brief: 500 cycles with LNMO-graphite cell using TMSP and PCS additives.

f. A Hofmann et al., ChemElectroChem 2019, 6, 5255–5263. *Additives for Cycle Life Improvement of High-Voltage LNMO-Based Li-Ion Cells.* doi.org
Brief: LiBOB and LIDFOB electrolyte additives. 820 cycles in LNMO-graphite cell.

2. Comparison of energy density and cost of batteries based on LNMO and competing cathode materials

a. M Wentker et al., Energies 2019, 12, 1–18. *A bottom-up approach to lithium-ion battery cost modeling with a focus on cathode active materials.* doi.org
Brief: Comparison of cost and energy density between NMCxyz, NCA, LNMO and LFP.

b. Argonne National Laboratory. BatPaC 3.0: *A Lithium-Ion Battery Performance and Cost Model for Electric-Drive Vehicles*. 2020. Available online: https://www.anl.gov/cse/batpac-model-software (accessed on 28 September 2020).
Brief: Calculation of energy density and price of cells based on material specific inputs.

3. LNMO stability in water

a. NPW Pieczonka et al., Adv. Energy Mater. 2015, 5, 1501008. *Lithium Polyacrylate (LiPAA) as an Advanced Binder and a Passivating Agent for High-Voltage Li-Ion Batteries.* doi.org
Brief: Use of LiPAA as aqueous binder system for LNMO electrodes.

b. M Kuenzel et al., ChemSusChem 2018, 11, 562-573. *Co-Crosslinked Water-Soluble Biopolymers as a Binder for High-Voltage* $LiNi_{0.5}Mn_{1.5}O_4$*|Graphite Lithium-Ion Full Cells.* doi.org
Brief: 1000 cycles in LNMO-graphite cell using water based binder system.

c. D Bresser et al., Energy Environ. Sci. 2018, 11, 3096-3127. *Alternative binders for sustainable electrochemical energy storage-the transition to aqueous electrode processing and bio-derived polymers.* doi.org
Brief: Review of aqueous cathode electrode processing.

About
Haldor Topsoe A/S

Haldor Topsoe wants to be the global leader within carbon emission reduction technologies for the chemical and refining industries. By perfecting chemistry for a better world, we enable our customers to succeed in the transition towards renewable energy.

The development of better battery materials for rechargeable batteries is key to the future of many industries. Utilizing our long history within catalysis and surface science; from product development at the nanoscale to fully industrialized manufacturing at ton-scale we are developing the next generation battery materials for rechargeable batteries that will be safer, lighter, more durable, faster to charge, more powerful and cost-efficient.

Topsoe is headquartered in Denmark and serves customers around the globe.

Get in touch today:
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