

Developing a high-performance, cobalt-free, 3V battery cell

based on high-voltage spinel (LNMO) cathode and mixed niobium oxide (XNO) anode

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Lithium-ion batteries are widely accepted as the energy-storage norm, and are expected to become the primary energy source for a more diverse range of mobile and stationary applications over the next decade. However, current Li-ion technology cannot satisfy the charge-speed and cycle-life requirements needed to achieve widespread acceptance in markets like rail, micro-transport, and e-ferris.

A Li-ion cell's performance is the result of careful interplay between its various components, guided by active materials, cell design, and voltage limits. With these factors in mind, Haldor Topsoe and Echion Technologies have developed a cobalt-free 3 V system designed for fast charging, optimal safety, and maximum cycle life by combining a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) spinel cathode and an Nb-based XNO anode.

The use of the higher-voltage anode material, XNO, allows for faster charging compared to graphite anodes, and higher-capacity retention at fast charging rates compared to LTO. The high-voltage LNMO spinel material increases the average cell voltage of systems using XNO anodes from 2.2 V to 3 V, compared to NMC-type materials. The system does not allow lithium plating or overcharging, making it inherently safer than cells whose chemistries include graphite or NMC-type materials.

The LNMO-XNO cell's 3 V nominal voltage unlocks a range of use cases, and allows for easy integration without requiring an expensive redesign of existing power electronics. Topsoe's collaboration with Echion focuses on applying new innovations that enable high-powered, long cycle-life cell systems to push boundaries in terms of application-specific requirements for safety, power, energy density, and temperature-based performance.

LNMO and XNO electrochemical properties

When designing the LNMO-XNO system, it was important to consider the electrochemical behaviour of the two individual materials compared to that of Li/Li⁺ in half-cells with lithium-negative electrodes. This allowed for an investigation of material properties like voltage profiles, first-cycle efficiencies, specific capacity values, and charge/discharge rates.

Figure 1(A) shows the first-formation cycle for the XNO anode, with initial lithiation to 1.1 V vs. Li/Li⁺, followed by delithiation to 3.0 V vs. Li/Li⁺. The material exhibits a high first-cycle efficiency of 98.5%, due to a very low degree of Li-ion trapping within the crystal structure upon delithiation.

This is due to the open nature of Nb-containing, Wadsley-Roth block structures, which facilitates extremely fast Li-ion diffusion. The Nb^{5+/3+} redox couple also enables a high voltage capacity above 1 V, thereby preventing SEI formation.

Figure 1(B) shows an XNO delithiation-rate test at room temperature, corresponding to discharge of a full cell containing XNO anode material. The lithiation rate is low at 0.1 C, and XNO retains almost full capacity at 10 C delithiation.

Figure 1(C) shows a first-formation cycle for the LNMO cathode, with initial delithiation to 5 V vs. Li/Li⁺,

followed by lithiation to 3.5 V vs. Li/Li⁺. Delithiation of LNMO comprises three electrochemical reactions: Mn³⁺ oxidizing to Mn⁴⁺ at around 4 V; Ni²⁺ oxidizing to Ni³⁺ at 4.7 V; and Ni³⁺ oxidizing to Ni⁴⁺ at 4.75 V. The exact shape of the voltage profile depends on the composition and crystal structure of the LNMO, explained in greater detail in previous work from Haldor Topsoe¹.

Figure 1(D) shows a lithiation-rate test of LNMO at room temperature, corresponding to discharge of a full cell containing LNMO cathode material. The delithiation rate is low at 0.5 C, and LNMO retains capacity of around 80% at 10 C lithiation.

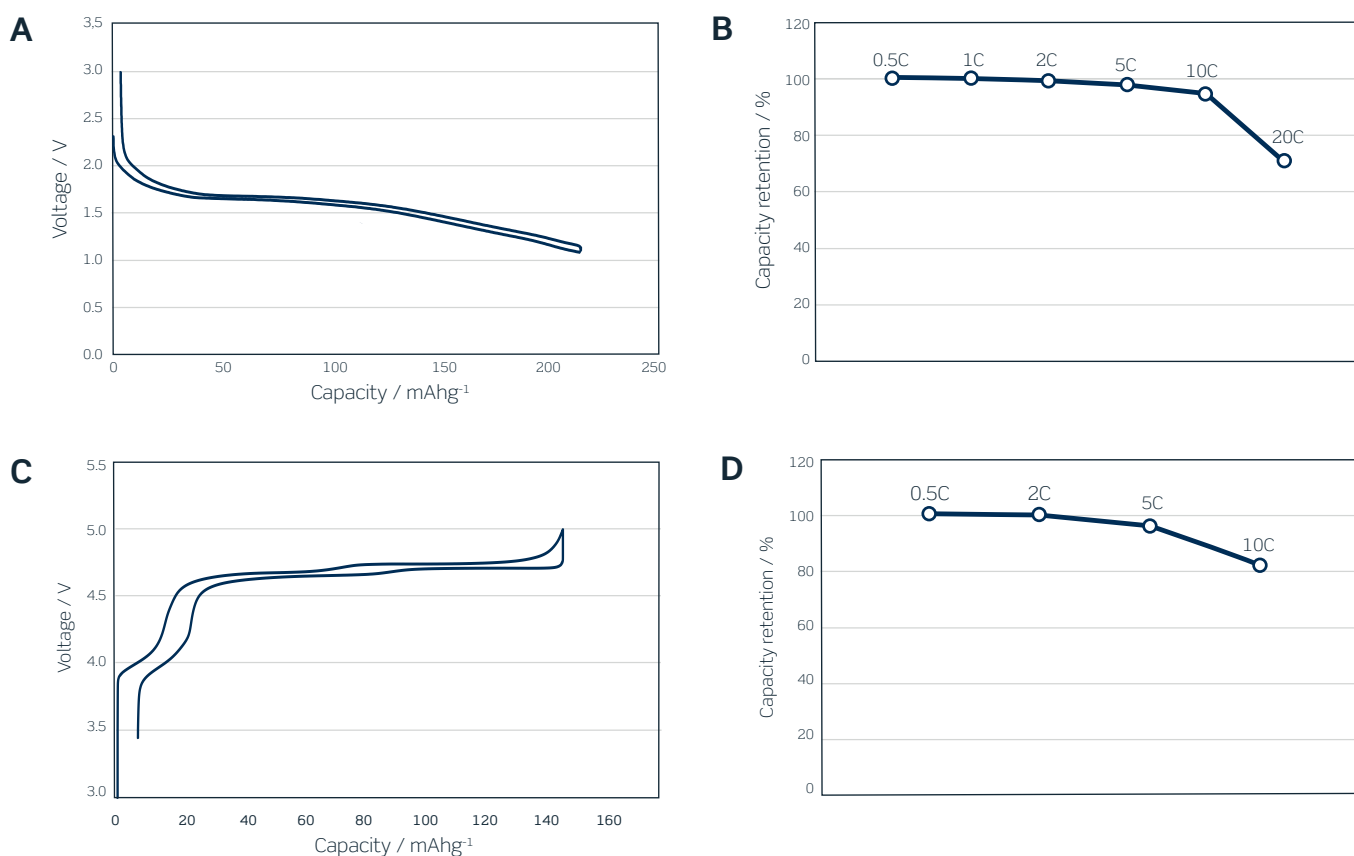


Figure 1. (A) First-formation cycle of XNO-anode material in a half-cell, demonstrating reversible capacity of 215 mAhg⁻¹ and 98.5% first-cycle efficiency. (B) Delithiation-rate test of XNO-anode material in a half-cell, demonstrating 95% capacity retention (vs 0.5 C) at 10 C and 70% at 20 C. Tests were conducted in coin cells, with an electrode composite loading of 1.4 mAhcm⁻². (C) First-formation cycle of LNMO-cathode material in a half-cell, demonstrating reversible capacity of 137 mAhg⁻¹ and 95% first-cycle efficiency. (D) Lithiation-rate test of LNMO-cathode material in a half-cell, demonstrating 80% capacity retention (vs 0.5C) at 10 C. Tests were conducted in coin cells at 25°C, with electrode composite loadings of 1.1 mAhcm⁻².

¹[Characterization of high-voltage Li_{1.0}Ni_{0.5}Mn_{1.5}O₄ and correspondence between Ni content in spinel, lattice size, and 4 V capacity. <https://www.topsoe.com/industries/batteries>].

LNMO-XNO full cell

Figure 2(A) shows the first-formation cycle of an LNMO-XNO battery recorded in a 3-electrode cell, with an Li reference used to follow the individual potentials of the cathode and anode during charge and discharge. An extended voltage interval of 1.5–3.8 V was used to explore the full voltage window. To

optimize cycle life, however, cathode voltage should not exceed 5 V while maintaining a high usable capacity; an upper cut-off of around 3.5 V is optimal for this specific N/P ratio.

Figure 2(B) shows the charge- and discharge-rate performance of the LNMO-XNO coin cell. As expected

from the half-cell results, discharge performance was excellent: when discharging at 10 C, 86% of capacity was retained. Charge-rate performance is lower than the discharge rate, but the LNMO/XNO system still demonstrates up to 80% retention at 5 C, and 68% retention at 10 C.

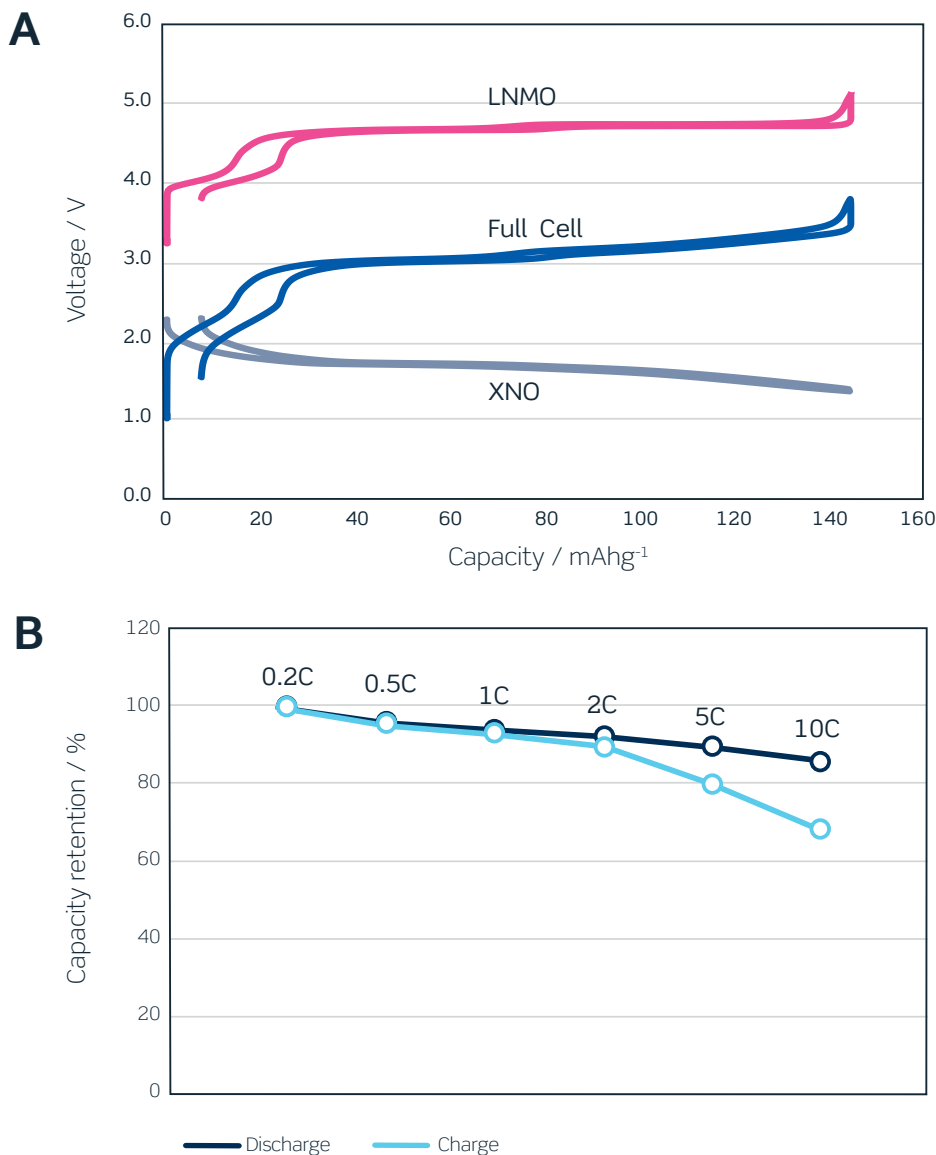


Figure 2. (A) First-formation charge-discharge voltage curve of LNMO-XNO full cell and the individual cathode and anode voltages, displaying a full cell nominal voltage of 3 V. (B) Charge and discharge rate performance of LNMO-XNO full coin cell. All tests conducted at 25°C.

In addition to excellent rate performance, the LNMO-XNO system exhibits very good cycling stability. Figure 3 shows the development in 0.1 C-discharge capacity (measured every 50 cycles), over 1000 cycles,

when cycling between 2.5 V and 3.5 V at 1 C. Under these conditions, the system retains 93% of its initial capacity after 1000 cycles. This result was achieved through use of a standard electrolyte without any

additives, and further improvement to overall cycle life can be expected with additional optimization of the electrolyte formula.

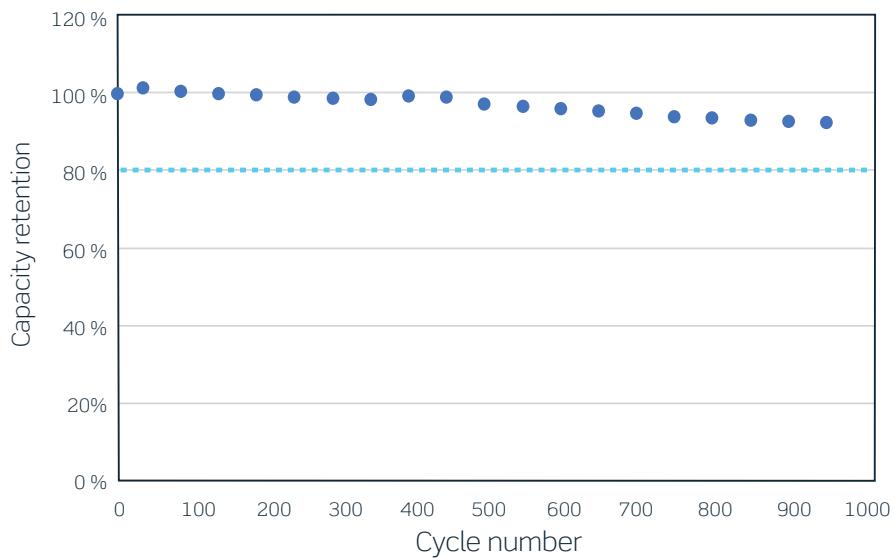


Figure 3. Cycle life of LNMO-XNO full coin cell at 25°C. The plot shows reference capacity checks at 0.1 C measured every 50 cycles.

Commercial-format cell modelling

Echion used a model wherein LNMO/XNO performance was compared to three other systems: NMC/LTO, NMC/XNO, and LNMO/LTO.

Figure 4 shows various cell designs capable of fast charging at above 5 C. Substituting LTO with XNO, and NMC with LNMO, demonstrates an increase in energy density for a total of almost 130 WhL⁻¹ at 10 C charge. The model also shows volumetric LNMO/XNO energy density of up to 420 WhL⁻¹ at charge rates up to 5 C (not included in Figure 4). The modelling suggests that, compared

to LTO, the higher gravimetric energy density and crystal density of XNO, in conjunction with the higher potential of LNMO compared to NMC622, increases the cell's energy density by 55%. In addition, the cheaper raw-material costs of LNMO, compared to NMC622, reduce the cell cost of an LNMO/XNO system by 21% compared to the NMC/LTO system. When comparing these new systems to graphite-based, high-power Li-ion cells, it is important to note that while the latter are certainly capable of high-discharge power, they are severely limited in lifetime and charge

power because of safety issues stemming from lithium-dendrite formation. This is not an issue for the LNMO/XNO system, which opens up new performance potential for high-power Li-ion cells at significantly higher energy densities.

Based on the performance and improved energy density achieved by the LNMO/XNO cell system, it becomes clear that cell manufacturers have an excellent opportunity to develop differentiated, higher-value cell designs.

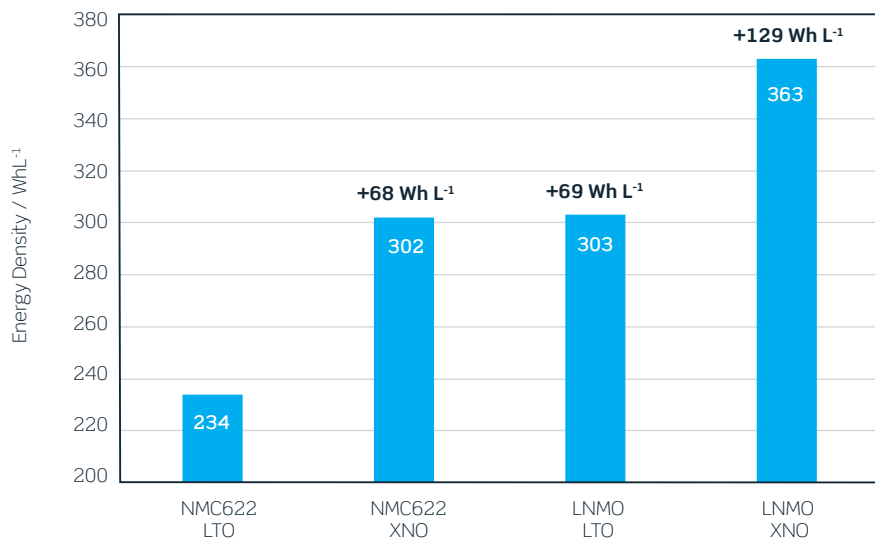


Figure 4. Modelled output data comparing the energy density of different cathode/anode pairings that can achieve 80% retention in charge/discharge at 10 C.

Application outlook

Today's battery research and innovations primarily target passenger electric vehicles (EVs), but such efforts don't address the user-acceptance criteria for high-duty-cycle mission profiles (high-duty-cycle vehicles) across the areas of cost, performance, safety, and sustainability. A key battery-performance requirement for high-duty-cycle vehicles is super-fast charging (e.g., a 6-minute charge, or a 10 C charge rate), which is typically limited by the anode.

Next-gen EV-battery systems, based on silicon/graphite (Si/Gr)

anodes and NMC/NCA cathodes, are not expected to support safe fast-charging at a rate greater than 3-4 C while maintaining high (>5000) cycle life. This is due to the low voltage of the anode and the high strain placed on the silicon anode-conversion material. Systems with LTO (lithium titanate oxide) anode material fulfill these criteria, but with low volumetric and gravimetric energy densities.

The 3 V LNMO/XNO system provides advantages similar to those of NMC/LTO, NCA/LTO systems, but with up to 55% higher volumetric-

energy density (Figure 4). This superior performance facilitates a wide range of applications for high-duty-cycle missions - including those relevant for NMC/LTO, NCA/LTO systems - offering greater financial benefits in terms of total cost of ownership and lifecycle costs, and supporting new applications where other systems' low energy density fails to address the user-acceptance criteria, including electric ferries, railway rolling stock, automated guided vehicles (AGVs), and mining or construction vehicles.

Final message

Haldor Topsoe and Echion welcome opportunities for collaboration with cell manufacturers and OEMs interested in the LNMO-XNO cell system presented in this whitepaper.

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Methods

Modelling

A fully parameterized geometric model was implemented in order to describe the LNMO/XNO system and compare its chemistry with that of other systems. Values were generated by considering the

separate anode and cathode half-cell capacities, along with electrode loadings, optimized porosity, and N/P ratios from experimental test data in half- and full-cells from above. For direct comparisons (i.e.,

LNMO/XNO vs. LNMO/LTO), the anode-mass loading, N/P ratio, porosity, and cell volume have all been fixed.

Electrochemical testing

The XNO anode material was cast on an aluminum current collector, with a loading of 7 mg/cm² and an active material:carbon:binder ratio of 92:5:3. The electrodes were calendared to densities between 2.6–2.8 g/cm³, corresponding to 31–35% porosity, and then dried under a vacuum at 120°C for 12 hours. They were tested in CR2032-type coin cells, with pre-cut lithium disks serving as counter electrodes. The formation protocol consisted of 2x0.1 C cycles between 1.1–3.0 V.

LNMO cathode material was cast on a carbon-coated aluminum current collector, with a loading of 8–11 mg/cm² and an active material:carbon:binder ratio of 92:4:4. The electrodes were

calendared to densities between 2.6–2.7 g/cm³, corresponding to 31–35% porosity, and then dried under a vacuum at 120°C for 12 hours. Half-cells were assembled in CR2032-type coin cells with a Celgard separator, 1M LiPF₆ in an EC:DEC 1:1 electrolyte, and a pre-cut Li metal anode. Tests were performed at room temperature, with a formation protocol of 2x0.1 C cycles between 3.5–5.0 V.

To investigate the individual voltages of both the anode and cathode while cycling in a full-cell configuration, 3-electrode cell tests were performed in an EL-cell PAT cell, using lithium as a reference electrode. For the 3-electrode cell test, an NP ratio between 1.1–1.2

was used for balancing the cell, calculated from the 1 C reversible half-cell capacities of LNMO and XNO (135 mAhg⁻¹ and 200 mAhg⁻¹, respectively). The loading was kept at a relatively low range in order to facilitate high-rate charge/discharge capability.

Long-term cycling tests were performed under the following conditions: CR2032 cells, Celgard H2010 separator, 1M LiPF₆ in EC:DEC; temperature at a constant 25°C; cells cycled at 1 C in charge, with a CV step and a 1 C discharge. Every 50 cycles, the cells were checked via a reference cycle of low C-rate at 0.1C

Haldor Topsoe

Haldor Topsoe is a global leader in 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 rechargeable-battery materials 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 next-generation 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.

Echion Technologies

Spun-out from the University of Cambridge in 2017, Echion is a world-leading developer of advanced lithium-ion battery anode materials, whose products enable cell manufacturers to deliver cost-effective, fast-charging, high-energy density, and long-life power cells for a wide range of markets including automotive, premium consumer electronics, and grid-storage applications. Echion provides materials and battery-cell manufacturers with packages of protected intellectual property, customization options, materials synthesis, and cell-integration know-how for different end-user markets.