ECHION TECHNOLOGIES

XNO whitepaper

The world's leading niobium active anode materials for lithium-ion batteries

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Graphite and graphite-silicon-based active anode materials are the dominant active anode materials in today's lithium-ion (Li-ion) batteries. They enable the highest energy densities and lowest costs (in $/kWh) for Li-ion cells. That's ideal for passenger electric vehicles (EVs), the biggest current and future Li-ion battery market.

But EV-optimised batteries aren't as well-suited for industrial and commercial applications, which have higher operational duty cycles and service lifetimes. Industrial and commercial vehicles need batteries which can safely and repeatedly fast charge across more charge-discharge cycles.

Graphite and graphite-silicon-based anodes offer the lowest price per kWh for Li-ion batteries. But their limited cycle life makes them prohibitively costly on a $/kWh/cycle basis, especially under fast charge conditions.

Lithium-titanate (LTO) active anodes address the fast charge and cycle life limitations of graphite and graphite-silicon. However, energy density limitations make them challenging to package in mobile industrial and commercial applications.

Using niobium, we developed our proprietary mixed niobium oxide (XNO) active anode materials. XNO enables fast charging, long-life, high-density Li-ion batteries that let cell manufacturers move beyond graphite, graphite-silicon, or LTO materials.

This whitepaper explores the scientific rationale for XNO's performance edge over other chemistries. For cell manufacturers, it's a case for adopting a new battery chemistry for future product development.

Today's active anode materials for Li-ion batteries

Graphite-based anodes

Graphite is the dominant anode material, with over 90% market share, due to its high energy density and low cost. But for fast charging, graphite-based cells are typically limited to a maximum charge rate of 4C. They can't be continuously fast charged across the whole state of charge (SoC) range (the full charge cycle.)

Potential Li dendrite growth leads to safety concerns, dramatically shortening cycle life. Much focus has been on reducing this inherent safety risk during fast charging through material, cell, and system-level engineering.

Proposed fixes have included the use of coatings, morphology control, complex battery management systems, and various cooling designs. Regardless, graphite-based cells still can't meet the cycling demands of long-life, high-power, heavy-duty applications at a wide range of temperatures.[i]

Silicon-based anodes

Silicon-based anodes are widely regarded as the next advancement in high-energy Li-ion cell chemistries. This is due to their 10x higher specific capacity (mAh/g), and 3x volumetric capacity (mAh/cm^3) compared to graphite.

However, silicon-based anodes experience extensive volume expansion (up to 300%) during cycling. This significant drawback is hindering widespread adoption. Currently, the most common solutions include nanosizing or mounting onto a carbon framework to reduce cycling stresses.[ii]

But these don't resolve the cycle life impairments caused by expansion, unwanted side reactions, and solid electrolyte interface (SEI) breakdown. Today, cells with silicon-based anodes have a typical lifespan of 500-1000 cycles. That's well below the requirements of heavy industry and commerce. Meanwhile, pure silicon-based materials are yet to reach commercial maturity.

Instead, the commercial use of silicon is restricted to adding small amounts (10-20%) to graphite to increase energy density. But this comes with graphite's limitations; lithium plating concerns at potentials close to 0V, reducing cycle life and safety.

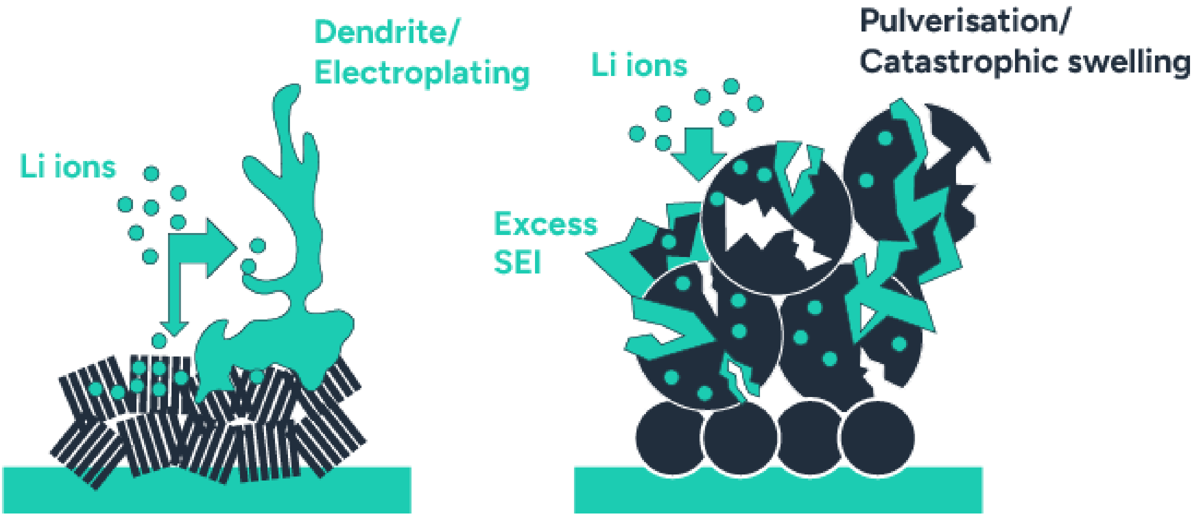


Figure 1: Summary of the main drawbacks for graphite and Silicon based cells.

Lithium-titanate (LTO)

LTO is the incumbent material of choice for high-power, long-life, safety-conscious applications. LTO-based cells typically charge at 4-20C, with a long lifetime of 10,000-20,000 cycles. Compared to graphite, LTO operates and performs better in both low (-30°C) and high (60°C) temperatures.

The relatively high operating voltage of LTO (1.55V vs Li/Li^+) makes it inherently safer than graphite or silicon-based anodes. The conditions leading to lithium dendrite formation are eliminated, and LTO is less likely to have a significant SEI present. The cells' long lifetime stems from its near-zero lattice strain[iii] which eliminates failure modes associated with electrode swelling.

However, to achieve these performance characteristics, LTO materials must be highly engineered due to their low ionic and electrical conductivity. It takes conductive coatings and particle morphology control, as well as nanosizing.

LTO's primary drawback is its low energy density at the cell level. It's up to 230Wh/L, vs up to 600Wh/L for NMC-Graphite and 325Wh/L for LFP-Graphite. The nanosizing required to use LTO as a battery material improves rate performance, but reduces maximum achievable electrode density. This puts further limits on LTO-based cells' energy density.

Finally, LTO-based cells are known to suffer from gas generation and build-up during cycling. This 'gassing' causes cell swelling concerns at high temperatures unless electrolyte additives and protective coatings are used. As a result, cell-level costs increase.[iii]

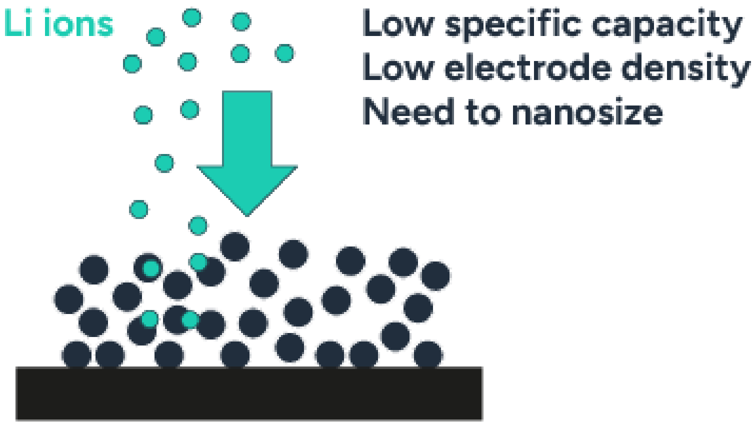


Figure 2: Summary of the main drawbacks for LTO based cells.

Beyond Li-ion

Besides improving current Li-ion anode materials, alternative battery chemistries are also being commercialised to meet decarbonisation and sustainability objectives. If the world is to meet its electrification goals, a range of battery chemistries will be required.

Diverse supply will satisfy a broad range of applications' demands, while minimising supply chain risks. Solid-state and sodium-ion battery technologies are two of the more advanced alternative chemistries. Both have seen support from large manufacturers like Panasonic and CATL[iv].

Solid-state batteries

Solid-state batteries boast a high energy density, up to 2.5x that of other batteries when paired with lithium metal anodes. Removing flammable liquid electrolytes and polymer separators also makes them safer than Li-ion cells.

But there are still challenges to resolve before they can be mass produced with usable battery lifetimes. These include contact issues between the solid interfaces which allow lithium transport, and low Li-ion conductivity at temperatures below 25°C.[v]

Interfaces are also more sensitive to volumetric changes of electrodes during lithiation and delithiation. Challenges in the use of lithium metal as a counter electrode also contribute to lifecycle limitations.[5]

Sodium-ion batteries

Compared to Li-ion systems, sodium-ion battery development is driven by their cost effectiveness and high availability of raw materials. As demand for battery minerals increases, costs fluctuate and alternatives using more readily sourced components become more appealing.

Sodium-ion also has a generally high charge rate and good safety characteristics. The chemistry has seen increased investment and development, leading to commercially available cells targeting low-cost transport and stationary energy storage.

Nevertheless, there have been challenges in finding suitable cathode and anode materials. Achieving a high enough energy density paired with desired cycle life is also complicated. Typically, hard carbon is used as the anode[vi], thanks to its advantages of:

- Low price
- Good conductivity
- High sodium storage capacity
- A lighter environmental footprint

However, research is ongoing to improve upon low first-cycle coulombic efficiency[vii] and improve cycle life to >3000 cycles.

Niobium-based active anode materials

Niobium (Nb) was identified as battery material in the 1980s but not used effectively in a cell until relatively recently. It's seen commercial uptake in cathodes[viii] as a dopant, and as a dominant material in anode active materials.[ix]

It's more common than cobalt, tin, and tungsten in the earth's crust, but has been less exploited for commercial use.[x] Its primary destination today is the steel industry, with an estimated global market of ~110,000 t/y, backed by plentiful reserves.

Large growth is expected for the battery industry. Raw material producers like Companhia Brasileira de Metalurgia e Mineração (CBMM) in Brazil will play a key role. Meanwhile, global interest in available resources is growing.[xi]

Full commercial deployment and end user uptake of Nb anodes in Li-ion cells, particularly in e-mobility, isn't yet realised. But Nb is particularly advantageous in anode active materials:

- It has a two-electron redox process (Nb^{5+} to Nb^{3+}). This enables high specific capacities at moderate operating voltages (~1.6V), avoiding lithium plating safety concerns
- It's abundant, non-toxic, chemically stable, and environmentally sustainable to source
- Supply chain design provides greater price stability than other volatile battery feedstocks like cobalt and nickel

The importance of crystal structure and formulation

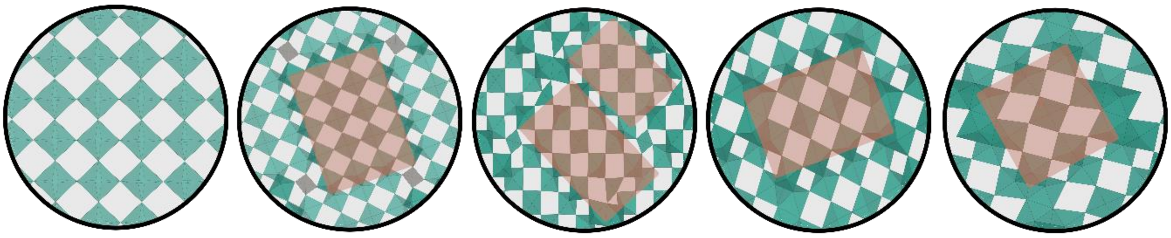
Nb-based crystal structures have been extensively researched as potential battery material candidates for high-power Li-ion batteries. They're stable, with a large number of Li-ion intercalation sites and moderate electrochemical potential (~1.6V vs Li/Li^+). That makes Nb safe (no Li dendrites), with an extended lifespan and exceptional capacity retention at high charge rates.

These materials belong to a family of oxides known as Wadsley-Roth crystal structures, first reported in 1961.[xii] They're oxygen-deficient derivatives of the ReO_3 crystal structure (MO_{3-x}). Oxygen deficiency leads to crystallographic shear planes, caused when some of the corner-sharing (MO_6) polyhedra shift to an edge-sharing coordination.

This creates blocks of corner-sharing octahedra anchored by edge-sharing units, effectively creating Li-ion highways. In some cases, tetrahedral units (MO_4) are generated. As a result, these structures are extremely stable throughout repeated intercalation and de-intercalation of Li ions, with minimal structural changes. This potentially enables a very long cycle life when used in Li-ion cells.

Key electrochemical properties include rate capability, first-cycle coulombic efficiency, structural stability, specific capacity, and voltage. These depend on the Wadsley-Roth block size, shape, and a wide range of other cations used alongside Nb. These materials have been extensively researched, but not typically tested under commercially relevant or comparable conditions.

Within this complex material space, Echion have developed our XNO anode material by optimising composition, structure, manufacturing, and physicochemical properties. XNO's third-generation formulation offers the best commercially available combination of cell characteristics and electrode processability.



$ReO_3\,(\infty\times\infty)_\infty$
A/C=3

$W_5Nb_{16}O_{55}\,(4\times5)_1$
A/C=2.62

H-$Nb_2O_5\,(3\times4)_1(3\times5)_\infty$
A/C=2.5

$AlNb_{11}O_{29}\,(3\times4)_\infty$
A/C=2.42

$TiNb_2O_7\,(3\times3)_\infty$
A/C=2.33

Figure 3: Example of different block structures and their anion/cation ratio

XNO: Key features and benefits

- Stable to air, water, and heat, with a long shelf life
- Compatible with both NMP and aqueous electrode preparation methods
- Compatible with a range of cathode materials (NMC, NCA, LNMO)
- High electrode density (3g/cm), with low porosity achievable (<30%)
- Structural and chemical stability gives a long cycle life
- Low carbon footprint from the material (~2x lower than LTO or graphite)[xiii]
- Recoverable at end of life
- Non-toxic, and not classified as a dangerous good or substance

Third-generation XNO: Typical physical and electrochemical characteristics

BET surface area, N_2 ($m^2\ g^{-1}$)	0.6-0.8
Average particle diameter, laser diffraction (μm)	4-6
Initial Coulombic Efficiency, C/10 CC 1.1-3.0 V vs Li/Li^+	>98%
Specific reversible capacity, C/10 CC 1.1-3.0 V vs Li/Li^+ (mAh/g)	208-218*
Material true density (g cm^{-3})	>4.5

*Higher specific capacities achievable with CV or wider operating voltage windows

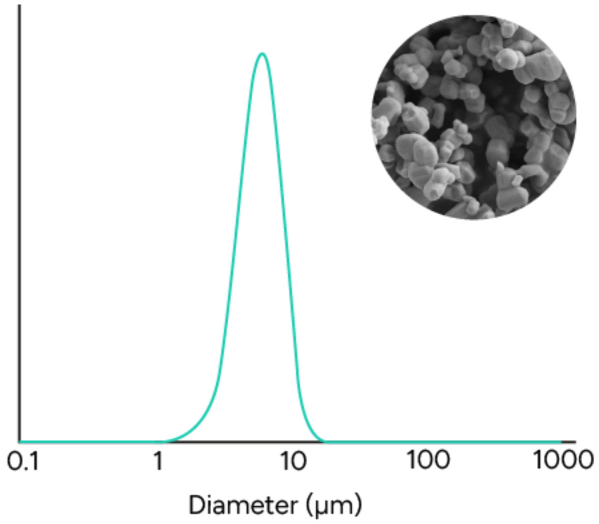


Figure 4: Particle size distribution and SEM of XNO. Narrow distribution, uniform morphology, and low surface area allows easier processing of XNO into high-performance electrodes using standard processing techniques and additives.

XNO's features highlighted above are made possible by carefully selected cations alongside Nb, as well as crystal structure tuning.

Larger Wadsley-Roth blocks generally have higher Li-ion diffusion rates than smaller structures; the path used by Li ions is clearer. Examples of larger block materials include several tungsten niobates like $W_5Nb_{16}O_{55}$, of renewed academic interest since 2010.[xiv]

These systems reportedly offer high-rate capabilities. However, they typically have relatively low energy density in full-cells; practical capacity of ~171 mAh/g for $W_5Nb_{16}O_{55}$. This is due to the high atomic weight and high redox couple of tungsten that pushes up the nominal voltage vs Li/Li^+ >1.6 V.

So, for practical use, systems containing tungsten require a wider voltage range of operation from low to high SoC than other Nb-based materials. This limits application to uses with low sensitivity to voltage drop changes over a battery's SoC. Or, alternatively, where power electronics design permits a wide range of current handling.

Reducing this wide voltage range may be possible at the battery module or pack level. However, that would increase the system's cost and complexity.

Examples of smaller block materials include titanium-rich niobates like $TiNb_2O_7$, also rediscovered in 2010. Titanium's low atomic weight and redox couple enables higher practical capacities (~225 mAh/g with a 1.1 V cutoff).[14] But these materials can suffer from significant side-reactions and gas generation during high-rate cycling, and at elevated temperatures.[xv]

Additional complexity can be introduced in these structures when they contain cations in a tetrahedral coordination in addition to octahedral. As in H-Nb_2O_5 and VNb_9O_{25}, for example. These tetrahedral sites can act as Li-ion traps, leading to lower first-cycle columbic efficiencies. They can also add structural instability and lower battery lifetime. This happens if the tetrahedral cation is redox active and shifts with poor reversibility to octahedral sites during cycling.

As such, XNO's third-generation formulation has been developed with:

- All sites in octahedral coordination, no unstable tetrahedra are present, increasing first-cycle columbic efficiencies, overall stability, and cycle life
- Additional structural stabilisation from tuning the composition to lock the structure in place during cycling
- Superior, stable high-rate performance through optimising ionic, electronic, and physical properties. Focus is on processability for a drop-in solution to standard electrode preparation processes
- Ease of manufacture at scale, with 50 t/y scale proven

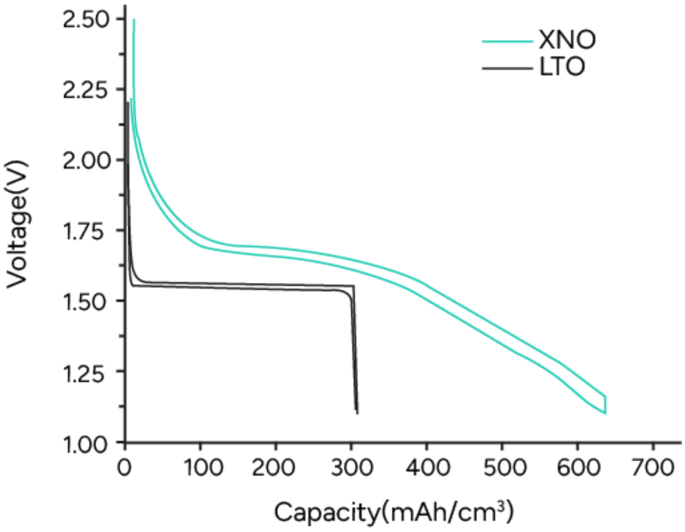


Figure 5: Half-cell electrode volumetric capacity of XNO and LTO vs Li/Li+. Note 2x volumetric capacity vs LTO due to higher specific capacity, material density, and possible electrode density: 2.8 g/cm^3 vs 1.9 g/cm^3 for LTO.

Our in-house cell development work creates clear, effective application notes, enabling XNO users to reach their own cell performance targets. Figures 6 and 7 emphasise our ongoing internal coin cell development.

Figure 6 shows 80% capacity retention is achievable after 5000 0-100% SoC cycles for an NCA/XNO full coin cell. These include no electrolyte additives, prepared using 20 mg/cm^2 aqueous-based electrodes.

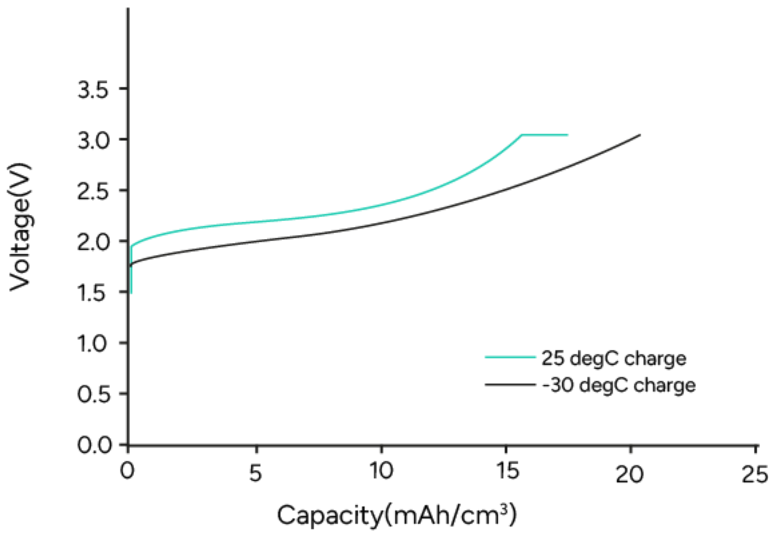
Figure 7 demonstrates >80% capacity retention is achievable at a charge rate of 10C, depending on the cell design. The mechanical design of coin cells can limit high C-rate tests in favour of higher performance.

These results demonstrate XNO's excellent stability and rate capability in laboratory scale conditions. We expect further optimisation within commercial cell formats will be able to achieve >10,000 cycles.[15]

XNO's properties have also been demonstrated in multiple large-format cell designs by existing customers, and by our own cell builds. Highlights include:

- Demonstrations of a >12,000 cycle life forecast

- >400 Wh/L cell design
- Excellent performance at temperatures as low as –30°C (limited by test chamber capability)[xvi]



CC retention vs 25 degC: 78%

CCCV retention vs 25 degC: 88%

Standard organic electrolyte

Figure 6: Prototype aqueous slurry-based full cell life test, demonstrating 5000 cycles to 80% capacity retention. Coin Cell Test Conditions: XNO 92.5% active material content, 35% porosity, 20 mg cm^{-2} *mass loading; NCA 92% active material content, 24% porosity; LiPF6 in organic electrolyte without additives, 25oC; 1C/1C with a 0.2C/0.2C reference cycle every 100 cycles, 100% SoC window, reference cycles shown.*

Prototype 20 Ah tabless 4690 cells have demonstrated 97%/95% capacity retention at 7C discharge and charge respectively. Cycle life studies are ongoing.[xvii]

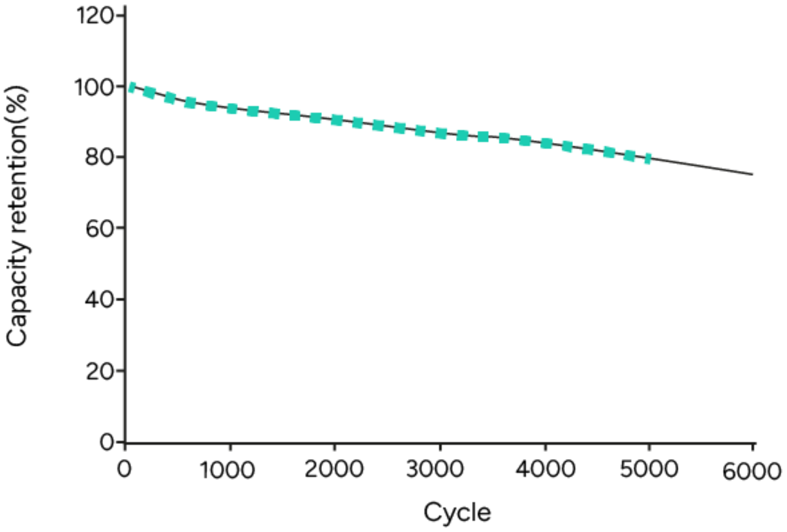


Figure 7: Prototype aqueous slurry-based full cell life test, demonstrating 5000 cycles to 80% capacity retention. Coin cell test conditions: XNO 92.5% active material content, 35% porosity, 20 mg cm^{-2} mass loading; NCA 92% active material content, 24% porosity; $LiPF_6$ in organic electrolyte without additives, 25°C; 1C/1C with a 0.2C/0.2C reference cycle every 100 cycles, 100% SoC window, reference cycles shown.

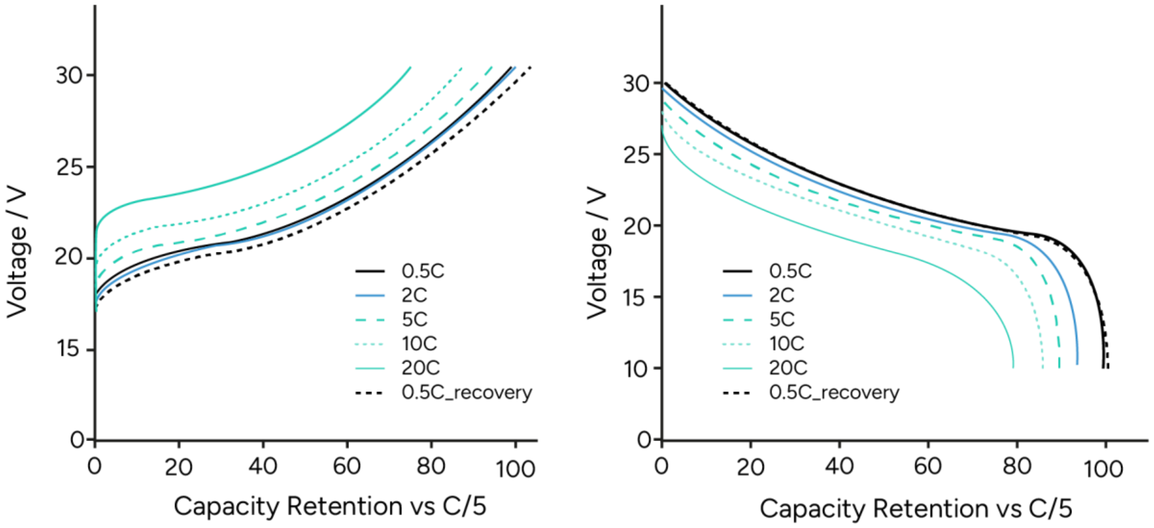


Figure 8: NCA/XNO rate capability, demonstrating XNO-based cells can continuously charge and discharge in up to 3 minutes. Coin cell test conditions: anode and cathode 92% active material content, 33% porosity, 7 mg cm^{-2} mass loading anode, $LiPF_6$ in organic electrolyte without additives, 25°C; asymmetric cycling 0.2C/xC.

Using XNO, our cell development programme is enabling the highest-performing Li-ion cells for our cell manufacturing customers, in a range of cell designs and formats. We're helping accelerate further optimisation and advancements, tailored to both OEM's and end-users' specific requirements.

Anode performance summary*

Table 1: Comparison of anodes for Li-ion batteries

	Echion XNO	Graphite	LTO	Silicon	Li metal
Charge Time to 80% SoC CC (mins)	3-10	20-60	3-10	10-60	15-60
Cycle Life	>10,000	500-5,000	>10,000	500-1000	200-500
Power Density	+++	++	+++	++	++
Safety	+++	+	+++	-	-
Temperature range during charging (°C)	-40-60	-10-60	-40-60	-10-60	-10-60
Cell Energy Density (Wh/L)	Up to 425	Up to 600	Up to 230	Up to 1000	Up to 1000
Ready for market?	Now	Now	Now	2025	2030+

*Dependent on factors like cell design and cycling conditions

XNO lifecycle analysis

A full lifecycle analysis of XNO was completed in 2023 and published in the Journal of Sustainable Materials and Technologies. Compared to LTO batteries, XNO offers a 51% reduction of global warming potential (GWP) on the material production level. On energy delivery level, it offers 61% lower GWP than LTO batteries.

That also represents a 64% reduction vs graphite, based on publicly available figures.[xiii] As markets aim to further lower their kgCO2e/product, selecting the right active anode material is important. This study demonstrates that XNO helps achieve this objective.

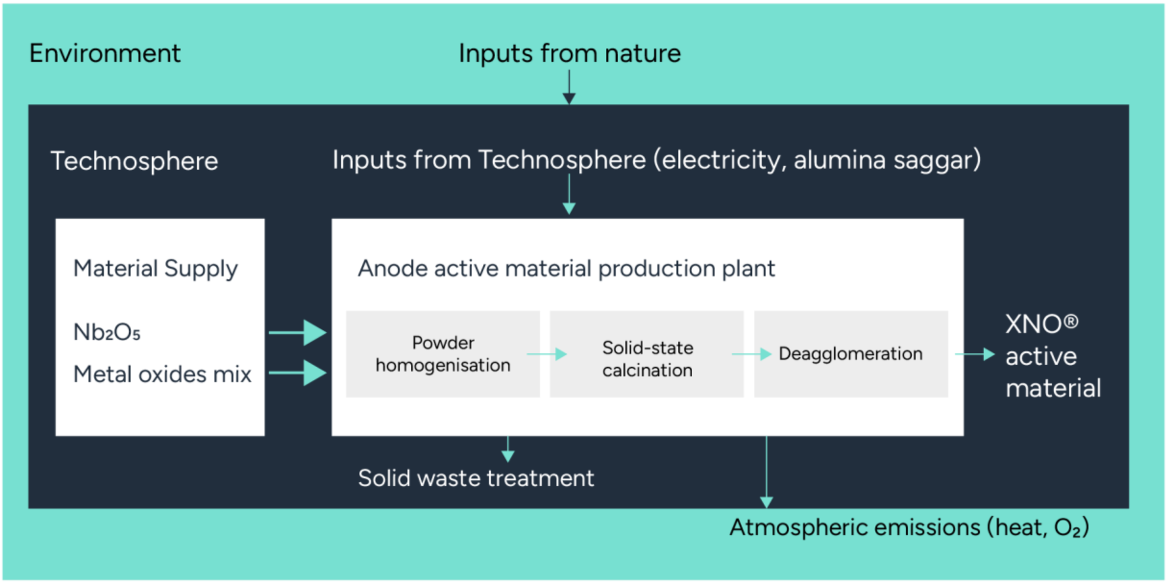


Figure 9: XNO's low carbon intensity is driven by low-carbon CBMM mining practices, plus high energy density and cycle life.

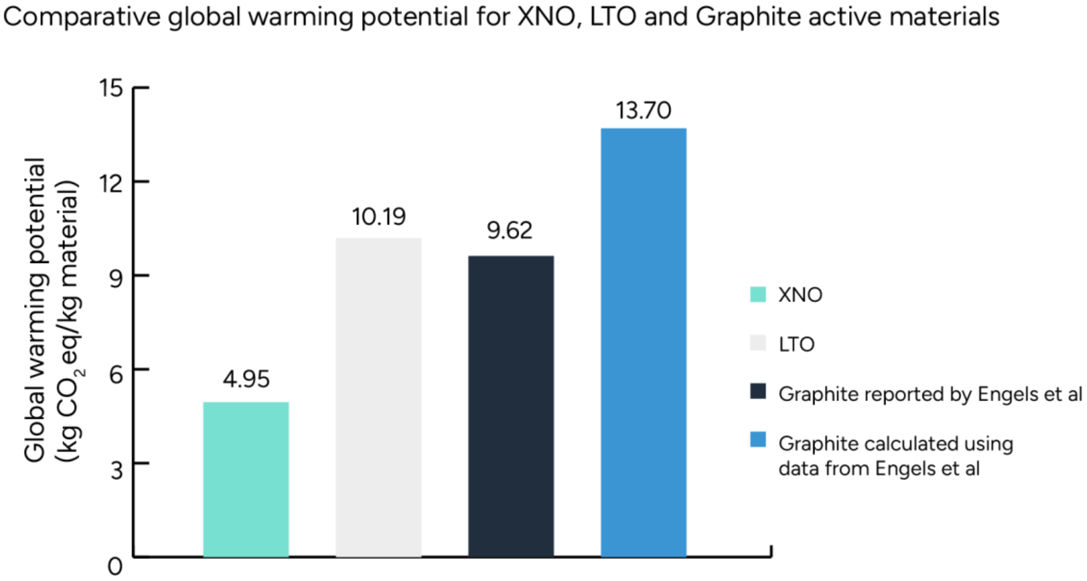


Figure 10: Comparative global warming potential (GWP) for XNO, LTO, and graphite active materials.

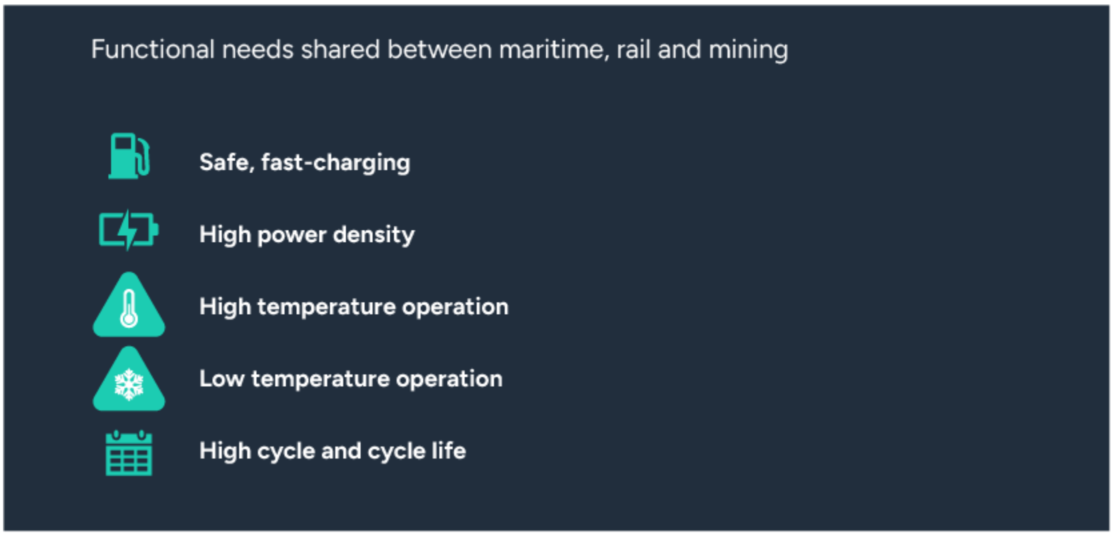
XNO: The opportunity

Niobium-based active anode materials like XNO enable cell performances which are well aligned to industrial and commercial needs.

Legislation and market factors like carbon intensity indexes and safeguarding mechanisms[xviii] are driving need for electrification. Shipping aims to go emission-free by 2050, for example.

Short-range vessels like inland ferries and tugs suit all-electric propulsion, while medium to long-range vessels need battery-supported hybrid propulsion. Battery power supports transient loads, peak shaving, and pure propulsion in shorter-range vessels.

Then there's rail. Battery electric (electrification without overhead line and third rail's infrastructure costs) improves urban aesthetics and expands the accessible network. Li-ion batteries' viability depends on their performance, safety, lifespan, and cost. Finally, the mining sector faces a significant challenge to decarbonise its haul truck operations.



Functional needs shared between maritime, rail and mining

- **Safe, fast-charging**
- **High power density**
- **High temperature operation**
- **Low temperature operation**
- **High cycle and cycle life**

Figure 6: The unique performance combination achievable with XNO

These markets represent an underserviced and largely untapped ~100 GWh opportunity by 2030. Most require batteries which deliver the highest safety, lowest total cost of ownership, and highest operational productivity across long lifespans. Some need to last for decades.

XNO addresses the shortcomings of graphite and LTO-based chemistries, offering both long life and superfast charging capabilities. For these and other applications, it's unlocking new battery electrification design possibilities and benefits. Two examples include:

Smaller battery packs

In charge or discharge power-limited applications, excess energy capacity is typically installed to achieve the necessary power requirements.

XNO's increased power density in charge and discharge lets smaller battery packs be specified instead. Reducing weight and volume improves design packaging, consuming fewer raw materials and resources, improving cost and environmental footprint.

Higher available battery capacity

In applications requiring faster charging, capacity retention and cycle life diminishes with graphite-based battery chemistries at charge rates >3/4C.

XNO's higher capacity retention and cycle life when charging at over 5C, across a wider temperature range, boosts available battery capacity. Despite the same volume and weight, higher total energy delivered across the lifetime of the battery lowers total cost of ownership.

Conclusion: XNO is powering better batteries

The needs of essential industries like rail, mining, and shipping aren't being met by today's Li-ion batteries.

XNO delivers the fast charging, long cycle life, safety, low cost of ownership, and energy density these vital sectors need.

The battery industry can now move into these sectors with confidence, armed with a new, competitive anode material. At Echion, we're committed to increasing the industry's reach and knowledge base, helping cell manufacturers drive the energy transition faster.

Contact us

You've seen how XNO is stepping up to help cell manufacturers meet the demands facing today's Li-ion batteries. Want to know more? Get in touch with Echion, we welcome enquiries from anyone looking to evaluate our anode material, and end users interested in XNO-powered cells.

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