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High Nickel NMC Cathode Materials for xEV's: What's the price to pay?

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Summary

Since their introduction on the market some 20 years ago, high nickel cathode materials have been somewhat limited to niche applications. This lack of market enthusiasm was mainly due to intrinsic cost, safety and processability issues and better value proposal from competing chemistries.

The ongoing race towards higher energy density allowing longer EV drive range and the lack of innovative high capacity cathode materials forced battery makers and OEMs to reconsider this product family.

This presentation takes a detailed look into high nickel compounds advantages and drawbacks and gives an overview of the potential choices for the chemistries that will enter the market at the end of this decade.

Introduction

Starting with material supply to the Li-ion industry in 1990, Umicore is today one of the leading producers of cathode materials for lithium-ion batteries with a focus on Lithium cobalt dioxide (LCO) and mixed metal oxides (NMC). NMC covers various applications from portables up to stationary and automotive applications (large format cells). The two main development directions over the last years for NMC materials have consolidated around Nickel rich materials and stable high-voltage NMC materials. As a trend, there is great interest in Nickel rich materials in the market, but this comes at a cost. The impact on the cell safety due to the high nickel content, increased dependency on nickel, nickel price stability and finally cycle life stability, which is still far away from today's low and medium Nickel technologies, have delayed market entry. Comparatively challenging is the development of high-voltage stable materials. Operating a cell at cut-off voltages significantly higher than today's solutions results in higher stress to the cathode material. Therefore, the stabilization of the material to achieve sufficient cycle life duration at the increased cut-off voltages is one main development topic. Umicore has developed various NMC grades to deal with these challenges.

This paper will report on results of the material development of medium nickel material operated at high cut-off voltages in comparison to high nickel cathode material with respect to resulting energy densities, material cost evolution as well as on material safety.

The challenges to the industry require an investment pace which can only be handled by financially strong companies. The long-term supply challenge can only be met via sustainable sourcing and recycling. Umicore was the first company worldwide to obtain independent third party verification for this Cobalt sourcing framework.

The success of Li Ion

The Lithium Ion battery (LIB) is an enabler of a success story. The high energy density of LIBs combined with high safety and durability has promoted the broadening demand of consumer electronics like cellular phones, laptops and tablets. This demand is expected to keep on increasing over the next couple of years. Nevertheless new applications, like the electrification of the automobile have entered the market in the last years. This demand will by far exceed the overall volume demand of the other applications (Fig. 1:).

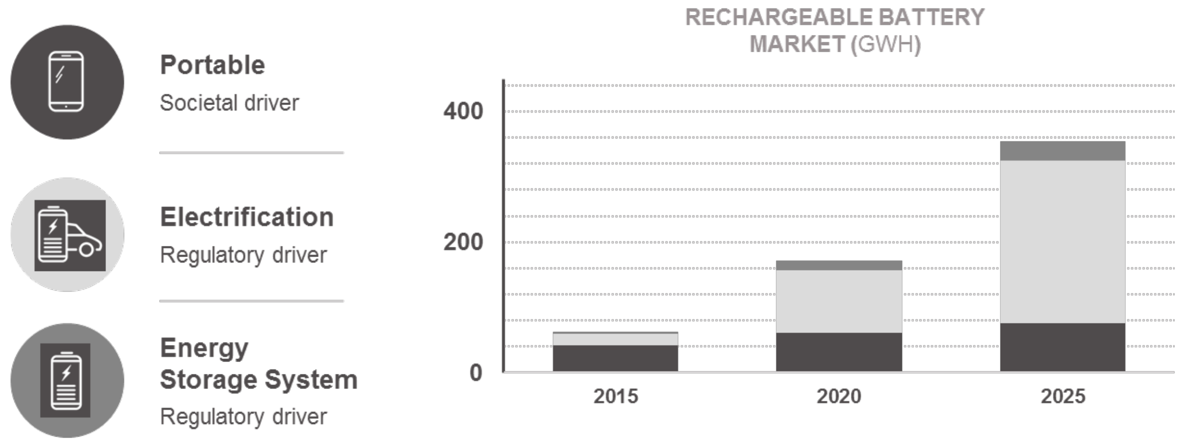

Fig. 1: Expected energy storage capacity till 2025 (Umicore data)

Although the outward appearance of a LIB cells differs between cylindrical, prismatic and pouch type formats, the general internal structure of these cells are comparable: The cathode (= positive side of the cell) consists of an aluminum foil coated with lithium metal oxides, the so called "cathode material". The negative side (anode) is a graphite coated cooper foil. To prevent short circuits the "separator" which is an ion permeable inert membrane separates the cathode and anode (Fig. 2:). The electrolyte fills the space in-between and provides the lithium ions for the reaction. The lithium ions are the actual active species in a LIB but do not form the active material themselves.

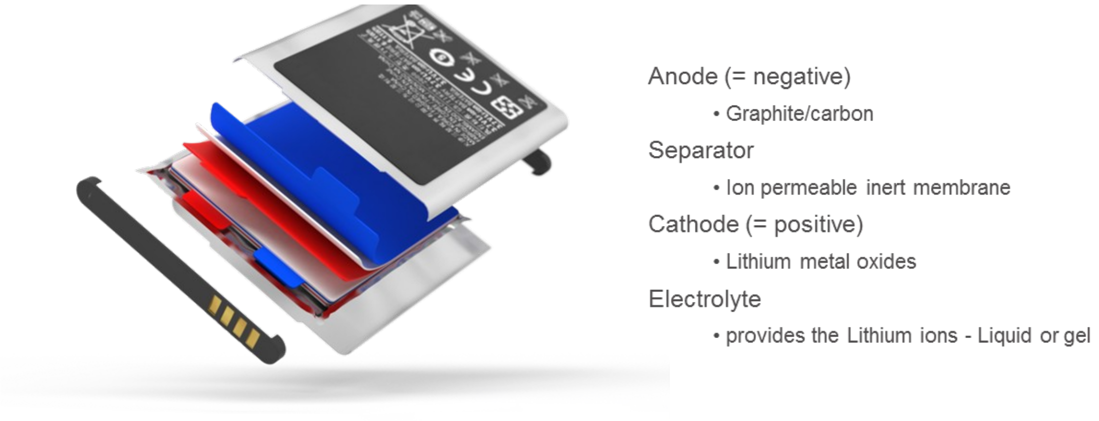

Fig. 2: Schematic plot of a lithium ion battery cell

In today's cells, mainly the cathode material defines the cell performance. The choice of the right cathode material depends on the application. High tech consumer electronics for example rely on lithium cobaltite (LCO) as this material provides high capacity together with high power capabilities. However, for automotive applications, the LCO material is not being considered mainly due to high resulting cost. Various cathode materials are found today in automotive applications: lithium nickel aluminum cobalt oxide (NCA), lithium manganese oxide (LMO), lithium iron phosphate (LFP) and nickel manganese cobalt oxide (NMC). As a trend, the NMC material will continue to dominate the market in this sector going forward.

Cathode material development for automotive applications

For automotive applications, we are facing a high degree of diversification. Applications for electrical storage ranges from Start-Stop applications to hybrid electric vehicles (HEV) and Plug-In Hybrid Vehicles (PHEV) to full electric vehicles (EV). Together with this, the requirements on the performance of the LIB are diversified.

For the full electric vehicle, the focus is on increasing the energy density to expand the driving range of the vehicle and the importance of reducing the total cost of ownership. For a HEV mainly a high power-to-energy ratio is beneficial as for this design the electric drive only supports the internal combustion engine. The PHEV concepts is a combination of EV and HEV and therefore combines those requirements on the LIB.

Strategies to increase energy density for the automotive application are fourfold: Cell optimization by using thinner collectors, higher active material loadings, reducing dead volume inside the cell and substituting some of the conventional graphite anode by new higher capacity anode materials. On the cathode material side the development is ongoing for NMC materials with very high nickel contents and for materials to operate at cut-off voltages significantly above 4.2V (Fig. 3:).

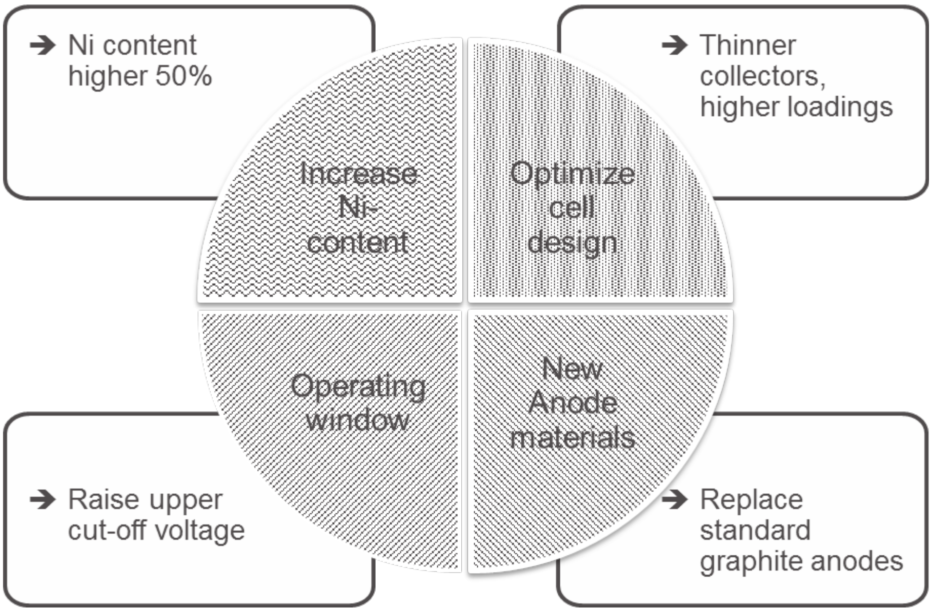

Fig. 3: Strategies to improve energy density in lithium ion batteries

Basic material characterization

The general correlation of the nickel contents and the cut-off voltage on the resulting specific energy density is shown for four NMC cathode materials in Fig. 4:. The three digit number corresponds to the molar content of each metal in the NMC material: A NMC111 material as an example has a nickel content of 33%, while the NMC811 has a nickel content of 80%. The results plotted in Fig. 4: were achieved in a coin cell setup using Lithium as anode.

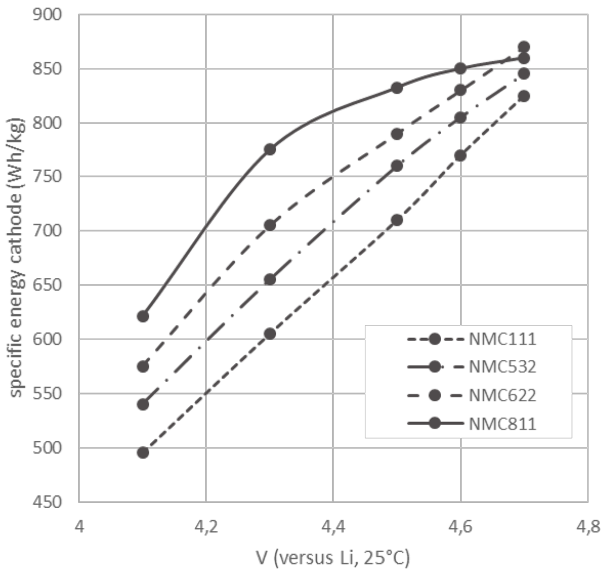

Fig. 4: *Specific energy density of different NMC cathode materials as a function of the upper cut-off voltage (coin cell testing; lithium anode)*

It can easily be seen that for a fixed cut-off voltage the specific energy increases with the higher nickel content in the NMC material - as an example: for a cut-off voltage of 4.2V the NMC111 material (nickel content of 33%) has a specific energy density of 550 Wh/kg while the NMC811 (80% nickel content) reaches up to 700 Wh/kg. Further on, a targeted energy density of e.g. 750 Wh/kg (given on the y-axis) on material level - which would be needed to fulfill future cell energy density requirements - can be reached by more-or-less all NMC materials by raising the cut-off voltage: for the NMC811 a cut-off voltage of ~4.25V is needed while for a NMC111 the cut-off voltage has to be increased up to ~4.6V. Both development directions have pros and cons which have to be taken into account.

The results shown in Fig. 4: derived from testing on coin cell level. To indicate the material performance in a full cell, various full cell tests and simulation works are used. The results from a full cell simulation work are plotted in Fig. 5:. The simulation is based on a 120Ah prismatic hard case cell at a discharge rate of C/5. Shown are the gravimetric energy densities of this simulated 120Ah cell using different cathode materials and cut-off voltages respectively.

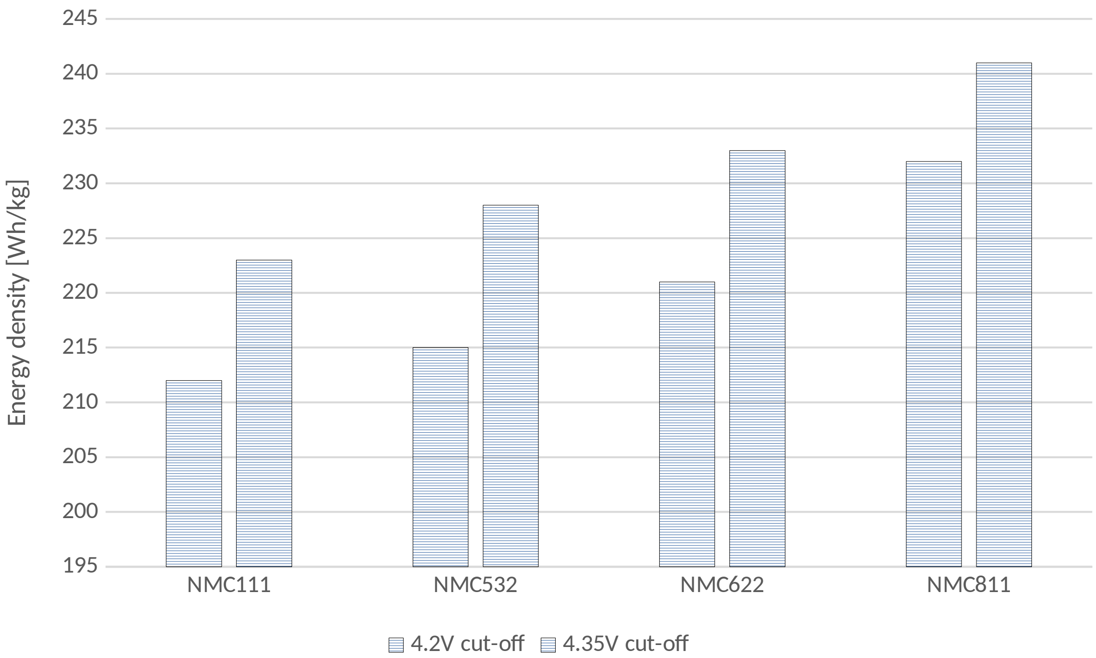

Fig. 5: Comparison of the calculated energy density of a 120Ah cell using different NMC cathode materials and cut-off voltages respectively

Today's mainly used NMC material, the NMC111, reaches an energy density of 212 Wh/kg in this setup at a cut-off voltage of 4.2V. By increasing the nickel content a maximum of around 232 Wh/kg is reached with the high nickel containing NMC811 material - corresponding to a 5 - 10% increase in energy density with each increase in nickel content. A further increase can be achieved by raising the cut-off voltage in this case to 4.35V. These results confirm the evaluation under the coin cell setup. For a given cut-off voltage the energy density can be increased with the nickel content. But, by increasing the cut-off voltage, even lower nickel containing materials can achieve high and comparable energy densities.

It can be concluded, that both development routes - increasing nickel content on the one hand and raising the cut-off voltage on the other - are on a theoretical level appropriate measures to increase energy density on cell level.

Evaluation of material aging behavior

The NMC111 material has proven its technical suitability in automotive applications over years and is used in most of today's EV applications. Therefore the NMC111 can be seen as the reference for energy density and durability.

Fig. 6: shows the retained capacity of different NMC materials during a typical cycling test with a 1C charge and a 1C discharge at room temperature.

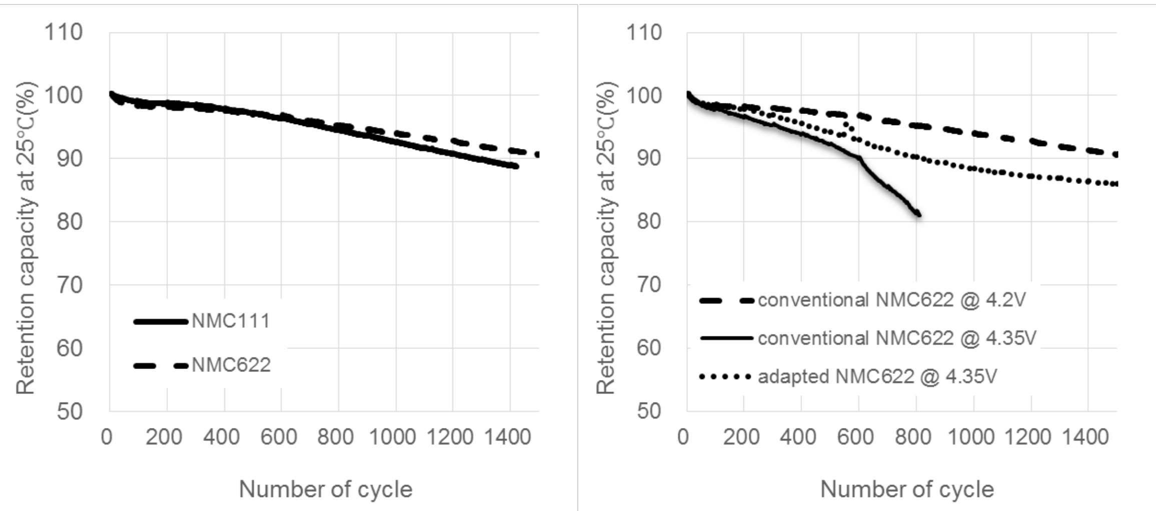

Fig. 6: Comparison of the retained capacity during a 1C/1C cycling at room temperature (25°C). Left diagram shows this for two NMC cathode materials at a fixed upper cut-off voltage; right diagram shows it for a standard and an improved NMC622 at two cut-off voltages

The left diagram in Fig. 6: shows a comparison of the NMC111 material (solid line) and the NMC622 (dashed line) both at cut-off voltage of 4.2 V. Despite the higher resulting specific capacity of the NMC622 material of around 11%, the retained capacity of the NMC622 material is at least comparable to the already very stable NMC111 material.

The right diagram in Fig. 6: shows a comparison of the retained capacity for NMC622 material at different cut-off voltages. Increasing the cut-off voltage of the standard NMC622 from 4.2V (dashed line) to 4.35V (solid line) results in a significant drop in cycle stability, which would be hard to realize in automotive applications. By further optimization of the NMC622 material a similar stability can be reached even at the increased cut-off voltage - by further increased capacity of 11% (dotted line).

Evaluations with high nickel content (NMC811) exhibit inferior stability under these conditions. A comparison of the achieved retained capacity after 600 cycles plotted over the first cycle discharge capacity is shown in Fig. 7: for the NMC811 material and the NMC622 material for different cut-off voltages.

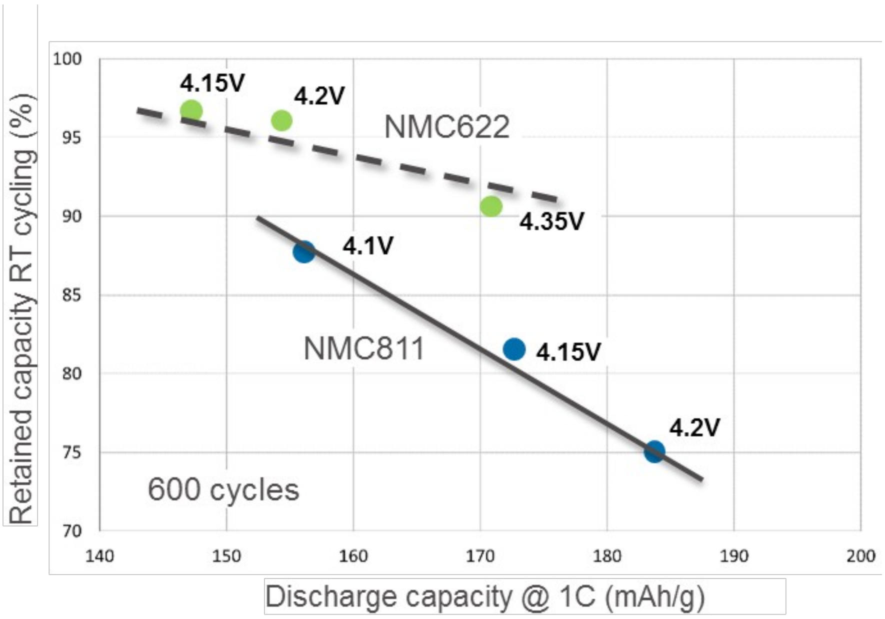

Fig. 7: Comparison of the retained capacity after 600 cycles (1C/1C) at room temperature (25°C) of an NMC622 and NMC811 respectively at various cut-off voltages.

As expected, the discharge capacity increases for both materials with increasing cut-off voltage - e.g. from around 156 mAh/g at 4.1V for the NMC811 to 184 mAh/g at 4.2V. But, the fading of the NMC811 material shows a much stronger dependency on the cut-off voltage as for the NMC622 material.

Improvements to stabilize the NMC811 during cycling are evaluated and show positive effects (without reaching the stability of the NMC622), but this comes at a cost: the discharge capacity of the NMC811 at 4.2V cut-off drops from around 184 mAh/g down to 155 mAh/g.

Towards an affordable EV

In the previous chapter we discussed two possible development routes to increase the energy density on the cathode material side. Either by developing high nickel containing materials (e.g. NMC811) or high-voltage stable medium nickel containing materials (e.g. NMC622). These two development routes are competing with each other and Umicore is developing material solutions for both directions.

From a technical perspective, as indicated by the results given in chapter 2, there is currently a benefit for the medium nickel material operated at higher cut-off voltages due to the higher stability of the material compared to high nickel materials.

Beside the technical aspect, more data is required to find solutions for an affordable EV. Increasing the nickel content further has as a benefit in reduced cobalt content - around 12% for a NMC622 compared to 6% for the NMC811 material. But, on the other hand the nickel content increases from 36% (NMC622) to 48% for the NMC811. This leads to a higher exposure on the nickel-price fluctuations. Today's historically low nickel prices might not be sustainable.

Furthermore high nickel containing materials need a historically more expensive Lithium source. In addition the material production is more complex due to the increasing hygroscopic properties of high nickel materials.

Taking all these facts into account today the medium nickel material seems to offer the best USD/kWh value (Fig. 8:). The increasing bandwidth for high nickel contents is due to the higher dependency on the nickel price evolution.

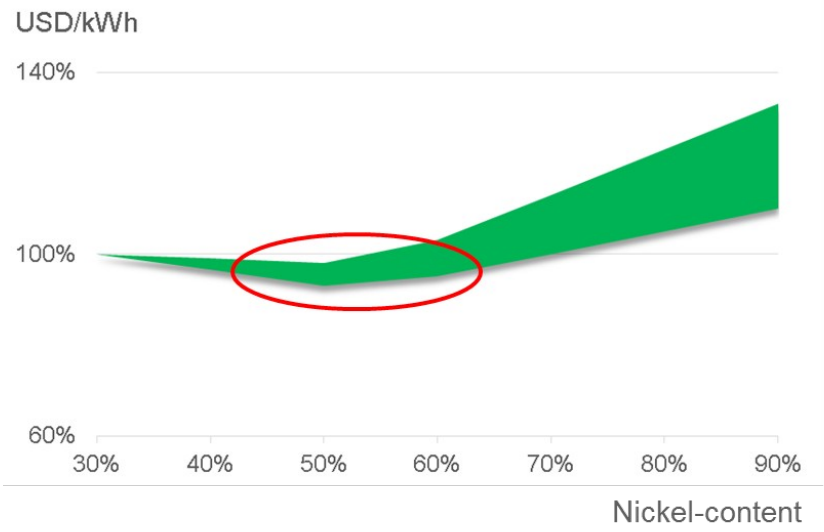

Fig. 8: *Cathode material cost evolvement as a function of the nickel content.*

Summary

For automotive applications, the NMC cathode family offers development paths for increasing the energy density (Wh/kg and Wh/l) and for reducing the total cost of ownership (TCO).

From today's point of view, the cathode material solution based on the medium nickel - high voltage shows advantages compared to the high nickel route. Comparable energy densities are achieved with improved durability and superior safety. In addition the TCO tends to be lower for the medium nickel grades operated at higher cut-off voltages.

The targeted growth of energy storage capacity triggers a significant increase in Co, Ni and Li demand. Beside the material availability of the metals the need for sustainable sourcing from primary sources is essential! Umicore created a “Sustainable Procurement Framework for Cobalt" which is inspired by OECD’s Due Diligence Guidance for Responsible Supply Chains of Minerals from Conflict-Affected and High-Risk Areas. In December 2016, Umicore – as the first company in the world – obtains third party validation for its procurement framework!

Last but not least: Recycling is an additional sustainable source for the required metals cobalt and nickel.

Authors

Tom Van Bellinghen joined Umicore in 2009 as the Marketing & Sales Director taking care of Umicore´s Rechargeable Battery Materials business. Working out of the Umicore HQ in Brussels, he divides his time between Belgium and Asia. In 2012 he became also responsible for raw material purchasing before becoming the VP Marketing and Sales in 2018.

Previously, Tom was a business Development Manager at Intel, and the Country Manager Benelux for Flir Systems.Tom Van Bellinghen holds a Master of Science degree in Electromechanical Engineering from the Catholic University of Leuven and obtained a degree in Business Administration from the Leuven Graduate School for Business Studies.