Project	Lithium-ion battery’s life cycle: safety risks and risk management at workplaces
Work package	WP1: EHS management. Framing the issue: identification of key aspects over the value chain
Task	T. 1.3 Identification of key materials in the production of Li-ion batteries
Responsible organisation	GAIKER
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Abstract

This task report is part of the research project "Lithium-ion battery's life cycle: safety risks and risk management at workplaces" and the task report focuses on identification of key materials in the production of Li-ion batteries. The aim of this task is to classify the materials of Li-ion batteries according to their state of implementation. Currently, there are many industrially established materials for cathodes, anodes, and electrolytes, with different advantages and disadvantages. In this context, and due to the extensive development of electric cars that is foreseen for the near future, much research has focused on the evaluation and selection of the best alternatives for energy storage solutions.

In this report, the identified materials are classified into three main groups according to their market penetration: i) conventional, ii) recently applied and near future materials, and iii) next generation materials.

It must also be highlighted that the battery types are categorized according to their cathode active materials, so the most conventional ones are LCO, LMO, NCA, LFP and NMC-111 materials. Batteries containing these cathodes usually include an anode made of natural or artificial graphite, and an electrolyte composed of an LiPF6 salt together with commonly used DMC, EMC, DEC, and EC solvents and FEC and VC additives.

Finally, NMC 811 was selected as the case study for the purpose of this project as it enables reducing the amount of Co to 20% with an increase of Ni to 80%, achieving a high energy density and a much lower cost than other currently used NMC batteries. Due to these properties, it is also the preferred choice of the automotive industry.

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GLOSSARY

Abbreviations

CE	Coulombic Efficiency
CNT	Carbon Nanotube
CRM	Critical Raw Material
EV	Electric vehicle
GO	Graphene Oxide
HE	High Energy
HV	High Voltage
IL	Ionic Liquid
LCA	Life Cycle Assessment
LCO	Lithium Cobalt Oxide, $LiCoO2$
LFP	Lithium Iron (Fe) Phosphate, $LiFePO4$
LIB	Lithium-Ion Battery
LIS	Lithium-sulphur Battery
LMO	Lithium Manganese Oxide, $LiMn2O4$
LTO	Lithium Titanium Oxide
MWCNT	Multi-walled Carbon Nanotube
NCA	Lithium Nickel Cobalt Aluminium Oxide, $LiNiCoAlO2$
NMC	Lithium Nickel Manganese Cobalt Oxide, $LiNiMnCoO2$
RT	Room Temperature
SEI	Solid Electrolyte Interphase
SIB	Sodium-ion Battery
SSB	Solid State Battery
SWCNT	Single-walled Carbon Nanotube

Chemicals

Al	Bis(2,2, 2-trifluoroethyl) ether
BTFE	Carbon
C	Cobalt
Co	Copper
Cu	Diethyl Carbonate
DEC	Dimethyl Carbonate
DMC	Ethylene Carbonate
EC	Ethyl Methyl Carbonate
EMC	Fluoroethylene Carbonate
FEC	Gallium
Ga	Germanium
Ge	Hydrogen Fluoride
HF	Lithium
Li	Lithium bis(oxalato)borate
LiBOB	Lithium difluoro(oxalato)borate
LiDFOB	Lithium bis(fluorosulphonyl)imide
LiFSI	Lithium Hexafluorophosphate
LiPF6	Lithium 2-trifluoromethyl 4, 5-dicyanoimidazole
LiTDI	Lithium bis(trifluoromethanesulphonyl)imide
LiTFSI	Manganese
Mn	Sodium
Na	Nickel
Ni	Polyethylene
PE	2(2,2,3,3,3-pentafluoro-propoxy)-4-(trifluoromethyl)-1,3,2-dioxaphospholane
PFPOEPi-1CF3	Polypropylene
PP	Poly(tetra fluoroethylene)
PTFE	Poly(vinylidene fluoride)
PVDF	Silice
Si	Tin
Sn	Triethyl phosphate
TEP	Titanium
Ti	Vinylene Carbonate
VC	Bis(2,2, 2-trifluoroethyl) ether

1 Methods

Task 1.1 involved the activities:

- Literature search: most relevant sector information and existing research were reviewed to identify new and already implemented materials.
- Patents search: the patents related to main materials identified in bibliography were also reviewed (See Annex 1 for further detail).
- Interviews in industries: battery recycling and production industries were interviewed to complement the literature information.

Li-ion batteries (LIBs) are categorized according to the active material used in the cathode. This report also describes the materials used in the anode and the electrolytes.

The main active materials integrating these elements (cathode, anode and electrolyte) have been divided into three groups according to their market penetration: i) conventional materials, ii) recently applied and near future materials, and iii) next generation materials.

2 Results

Batteries can be divided into two types, primary and secondary:

- Primary batteries: non-rechargeable, usually irreversible electrochemical reactions or very poor recharging performance.
- Secondary batteries: reversible electrochemical reactions, therefore can be repeatedly charged and discharged (Wu, 2015).

This report focuses on secondary batteries

LIBs can be used in many applications, such as portable electronic devices, power tools, stationary battery energy storage, power trains, EVs, and HEVs. However, the application recently gaining importance is in the automotive industry (Dai et al., 2019).

The sales of electric cars reached 2.1 million in the world in 2019, accounting for 2.6% of global car sales and about 1% of global car stock. This is a 6% growth from the previous year (IEA Global EV Outlook 2020, 2021) (IEA Data and statistics, 2021).

Batteries are essential in EVs, and LIBs are particularly promising due to their exceptional performance and capacity.

However, for some applications (such as transportation and grids) LIBs are currently expensive, and a shortage of Li and some of the transition metals currently used in LIBs may one day become an issue. At the same time, LIBs have certain fundamental advantages over other chemistries. First, Li has the lowest reduction potential of any element, allowing Li-based batteries to have the highest possible cell potential. Also, Li is the third lightest element and has one of the smallest ionic radii of any single charged ion. These factors allow LIBs to have high gravimetric and volumetric capacity and power density (Nitta et al., 2014).

The main components of an LIB (Figure 1) are its two different current collectors, typically copper and aluminium, two electrodes (anode and cathode), and the separator/electrolyte (Chen et al., 2019).

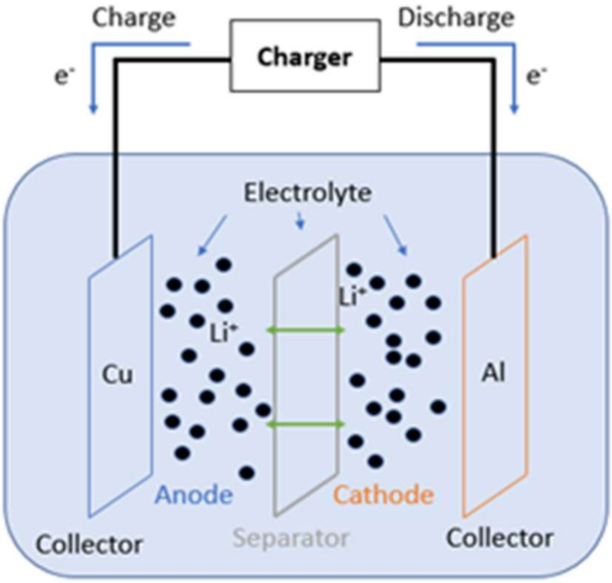


Figure 1. Schematic composition of a Li-ion battery (LIB).

Regardless of their electrode type, batteries consist of an active material, a conductive material, and a polymer binder at different ratios. These three components are typically mixed in a solvent I which the polymer is dissolved, and the active material and the conductive additive are dispersed to obtain good dispersion without sedimentation.

The basic requirements of the cathode material in LIBs are high free energy of Li+ ions and low free energy of electrons. The anode should be at a high energy level, but with low ionic energy of Li+ ions it acts as a reductant in a reversible battery opposite to the cathode (Chen et al., 2019).

Almost all separators are based on semi-crystalline polyolefin materials: polyethylene (PE), polypropylene (PP), combined under the form of a PE-PP bilayer or PP-PE-PP trilayer. In addition, inorganic separators can be used in high-power applications that require separators with excellent thermal stability (Mauger et al., 2017.

For the polymer binder, poly (vinylidene fluoride) (PVDF) and poly(tetra fluoroethylene) (PTFE) are the most used due to their excellent mechanical strength, high chemical resistance, and high melting temperature (Chen et al., 2019).

The main raw materials used in the production of LIB cells are lithium (Li), nickel (Ni), cobalt (Co), aluminium (Al), manganese (Mn), copper (Cu), silicon (Si), titanium (Ti), and carbon (C) as artificial or natural graphite.

Cobalt, graphite, and silicon are classified as critical raw materials (CRM), but nickel and lithium (together with cobalt) are also considered to be of great importance due to their future demand in the production of cathode active materials (Report, 2017).

The next chapter describes and classifies cathode, anode and electrolyte materials according to their degree of penetration in the market for potential application: commonly used or most conventional materials, recently applied and near future materials, and next generation materials.

2.1 Most conventional materials

2.1.1 Cathode

LIBs are categorized according to the active material used in the cathode. The main types of cathode materials are the following (Hannan et al., 2018):

- LCO: Lithium Cobalt Oxide, LiCoO2.
- NMC: Lithium Nickel Manganese Cobalt Oxide, LiNiMnCoO2.
- NCA: Lithium Nickel Cobalt Aluminium Oxide, LiNiCoAlO2.
- LMO: Lithium Manganese Oxide, LiMn2O4.
- LFP: Lithium Iron (Fe) Phosphate, LiFePO4.

The first three belong to the same family of lamellar compounds; the fourth is the LMO spinel and the last is the olivine LFP. The properties of these materials depend greatly on crystal geometry (Mauger et al., 2017). Layered materials are used as cathodes for high-energy systems, whereas spinel oxides and olivines are considered in the case of high-power LIBs due to their low cost and long-life requirements (Julien et al., 2014).

Table 1 summarizes the cathode materials used in the LIBs currently on the market and compares their performance and applications. All cathode materials are used in EVs except LCO.

Table 1. Materials in cathode of different LIBs on the market, and main application of each LIB type (Adolfsson-Tallqvist et al.,2019; Hannan et al. 2018).

Main cathode material	Advantages	Disadvantages	Applications
LCO	High specific energy	Short life, restricted load capacities, moderate safety high cost	Cells, tablets, laptops, and cameras (portable electronic devices)
NMC-111 ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$)	Good overall performance Excellent specific energy	High cost, lower than LCO. Still has Co	EVs, stationary battery energy storages (BES), and others (e.g., power tools and electronic devices)
NCA	High specific energy and power densities Long lifespan	High cost Safety problems	EVs, power trains, stationary battery energy storages (BES) and others (e.g., power tools and electronic devices)
LMO	Specific power, high thermal stability, safety low price	Limited cycle life Poor capacity	EVs, HEVs, medical and others (E.g., Electronic devices and power tools)
LFP	Long lifespan, High load handling capability Good thermal stability, Excellent safety Less expensive than those containing Co	Low resistance, Lower nominal voltage and negative performance Low service life properties due to temperature (cold T reduces performance)	EVs, power tools, portable devices, and stationary battery energy storage (BES).

Figure 2 presents the theoretical voltage of most of the cathodes mentioned in Table 1 versus capacity, giving a measure of the amount of charge contained in the material. The value of energy is obtained by multiplying capacity by voltage. Thus, the higher the voltage and capacity, the higher the energy. Maximum theoretical energy can be expressed in terms of volume (energy density) or weight (specific energy) (Amirault et al. 2009).

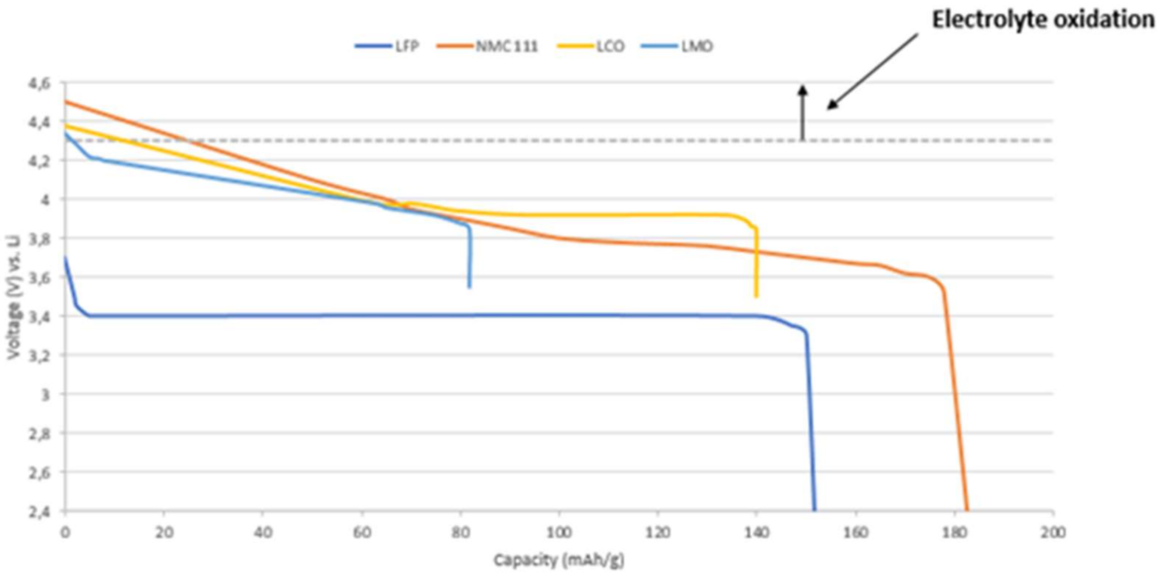


Figure 2. Operating voltage profile of some cathode active materials. Modified from (Amirault, et al., 2009).

Power is also a very important parameter. In contrast to energy, which is a material property, specific power depends on factors such as electrode thickness and the size of the electrode particles, which may be controlled in the manufacturing process (Amirault et al. 2009).

So, whereas specific energy defines battery capacity in weight (Wh/kg), specific power indicates loading capability (Battery University, n.d.).

As shown in Table 1, all materials have advantages and disadvantages, and the key is to find the most balanced ones in terms of the essential aspects. On the technical side, LIB technologies can be compared using five aspects: energy density, power density, safety, costs, and life span (see Figure 3). However, on the business side, cost is one of the main barriers (Ding et al., 2019) to their use.

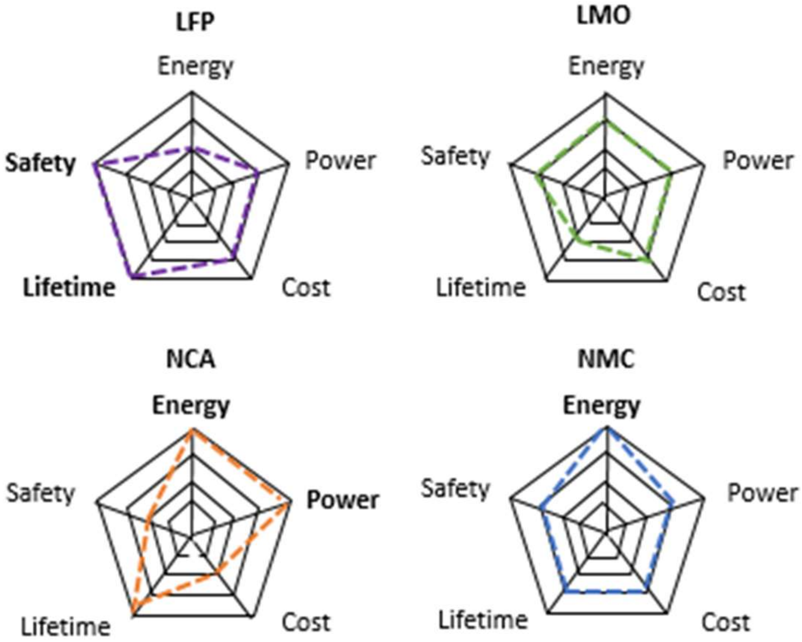


Figure 3. Key performance parameters of four current battery chemistries. Reprinted from (Ding Y., Cano, Yu, Lu, & Chen, 2019).

2.1.2 Anode

Anodes are needed in LIBs to avoid short-circuiting due to the dendrites that Lithium metal can form and which in turn can start a thermal run-away reaction on the cathode and cause the battery to catch fire. Furthermore, Li metal also suffers from poor cycle life (Nitta et al., 2014).

As mentioned above, anodes are organized in layers together with the cathode on aluminium and copper current collectors.

The most commonly used material for the anode is natural or artificial graphite. However, other carbonaceous materials such as meso-phase and amorphous carbon, and more recently tin and silicon oxides and alloys, as well as Lithium Titanium Oxide (LTO) can also be used (Report, 2017). In fact, as mentioned in Section 2.2.2, graphite suffers from poor rate capability and lithium dendrite problems of overcharging, leading to internal short-circuits and safety problems such as fire or explosion (Ding et al., 2019), which could release different gases that may be hazardous to human health.

2.1.3 Electrolytes

The most conventional electrolytes are based on liquid organic solutions that contain a conducting salt, a mixture of linear and cyclic solvents, and additives. Both solvents and additives are composed of carbonate configurations, whereas salts are usually made of fluorinated substances. Table 2the most conventional electrolytes on the market.

Table 2. Summary of most conventional electrolytes

Salts
Lithium hexafluorophosphate (**$LiPF_6$**)
Solvents
Dimethyl carbonate (**DMC)** Ethyl methyl carbonate (**EMC)** Diethyl carbonate (**DEC)** Ethylene carbonate (**EC)**
Additives
Fluoroethylene carbonate (**FEC)** Vinylene carbonate (**VC)**

2.2 Recently applied and near future materials

2.2.1 Cathode

Some materials used in the production of LIBs have many disadvantages. Apart from Li, Co is also a critical element in cathode materials because it enables increased energy density and structural stability, but also has some drawbacks such as toxicity, high price, and limited production (Ding et al., 2019). Moreover, the Democratic Republic of Congo, where the greatest reserves and production are concentrated, is a geopolitically unstable country.

According to LCA studies, the mining and refining of nickel and mainly cobalt represents the most important contribution to the total environmental impacts (Policy, 2018).

Despite all the problems with cobalt, layered lithium transition metal oxides (NMC) have still become the most popular cathodes for automotive battery technologies. The most conventional or commonly used one, as indicated in the previous section, is the **NMC-111**, which has 33% Ni, 33% Manganese, 33% Co. It has a high theoretical capacity of around 275 mAh g-1. However, this capacity cannot be completely extracted upon charging owing to structural instabilities that occur at a high state of charge. Thus, the accessible capacity is usually 160 mAh g-1.

By increasing the Ni content, a higher energy density can be achieved, and other types of NMC batteries are now becoming available: NMC-811 (80% Ni, 10% Mn, 10% Co), NMC-532 (50% Ni, 30% Mn, 20% Co) and NMC-622 (60% Ni, 20% Mn, 20% Co).

The **NMC-811** battery has a specific capacity of 200 mAh g-1, 25% higher than the conventional NMC-111. The rate capability of NMC-811 is also better, owing to its higher electronic conductivity (2.8 . 10-5 S cm-1) and higher ionic diffusivity (10-8 – 10-9 cm2 S-1). In addition to this, battery costs will also be significantly lower due to the reduction of the expensive Co element. Compared with the NMC-532 and NMC-622, it has higher energy densities, so the NMC-811 is the most promising of the NMC technologies.

The promising new NMC configurations mentioned here have been recently applied, and it seems that the interest in their use is continuously increasing. Recently, many battery manufacturers such as LG Chem and SK innovation have announced that they will start production of new NMC-811 battery materials. In addition, BMW also expects to use NMC-811 battery cells in its new BMW i5 in 2021. Figure 4 shows the predicted evolution of NMC batteries in coming years.

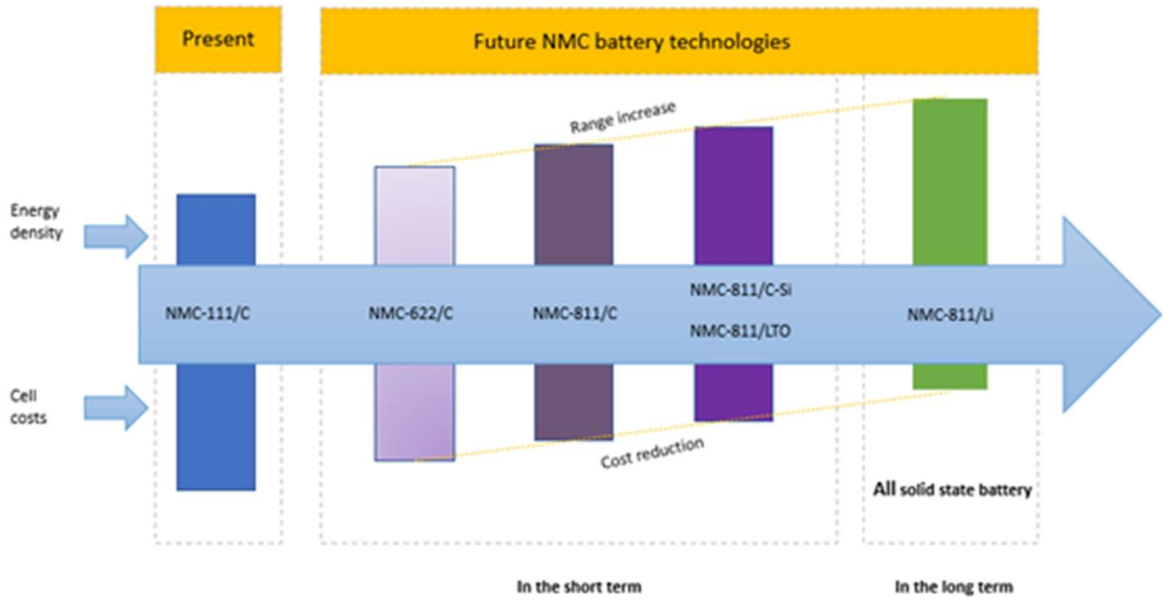


Figure 4. Evolution of the NMC batteries in the next years. Modified from (Ding Y., Cano, Yu, Lu, & Chen, 2019).

However, this type of battery also has some disadvantages. One major drawback is its increased surface reactivity. The reactive and unstable Ni4+ ions in the de-lithiated component tend to form a more thermodynamically stable LixNi1−xO phase, resulting in increased interfacial impedance and poor cycling life. Furthermore, high pH values for NMC-811 cause additional difficulties for cell manufacturing. Thus, mitigating the surface reactivity of the Ni-rich NMC-811 cathode will be an important issue in the near future. A higher Ni content and lower Mn/Co content result in a higher self-heating rate and lower onset temperature for exothermic reactions. Therefore, Ni-rich NMC-811 needs to be protected on the surface to avoid or mitigate the undesirable reaction between the electrode and the electrolyte (Ding et al., 2019).

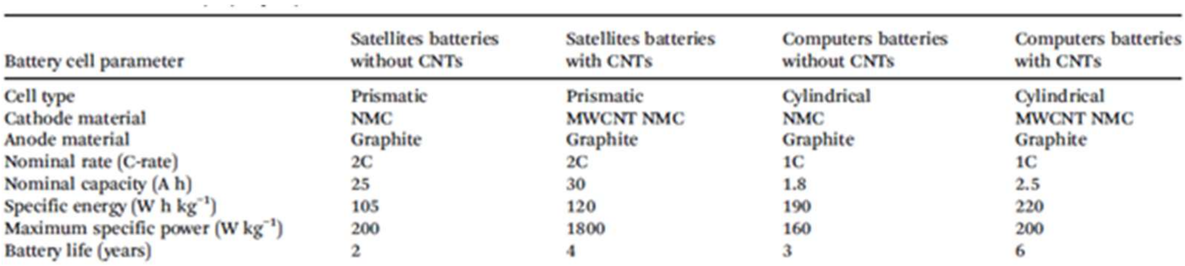
To avoid this problem, new materials are being investigated, for example, graphene and carbon nanotubes (CNTs). CNTs have high conductivity and good mechanical properties, whereas graphene has a high specific area and electrochemical activity (Zang et al., 2019). More details on these materials and their benefits for LIBs are given below.

CNT LIBs. CNTs are nanoscale allotropes of carbon that have a cylindrical structure. Their structure, as well as their exclusive electrical, mechanical, thermal, and magnetic properties place them in a special class of materials for many potential industrial and scientific applications. They can be produced as single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT) and are both lightweight and high-strength materials.

When added to a battery cathode, CNTs can significantly improve LIB performance. The main benefits include increased electronic conductivity of the cathode electrode, increased charge/discharge rate, and higher structural flexibility. Other characteristics that make CNTs desirable for use in LIBs include their high chemical resistance and low flammability. In direct contact with the electrolyte, CNTs in the electrode show high chemical resistance to an extensive range of organic solvents and lithium-ion salts. CNTs may be used for different purposes in different parts of the battery cell, for example, in cathodes or anodes. In research laboratories, different cathode materials are under development to create batteries with a better performance, a longer lifetime, lower thermal tolerance, and higher energy density (Hakimian et al., 2015).

The property improvements in the performance of lithium-ion cells with MWCNTs in comparison to that of the conventional lithium-ion cells in satellites and computers are listed in Table 3. The main drawback in their use is the growing concern about their potential impact on human health and the environment.

Table 3. Lithium-ion cell property improvements with CNTs (Hakimian et al., 2015).



Battery cell parameter	Satellites batteries without CNTs	Satellites batteries with CNTs	Computers batteries without CNTs	Computers batteries with CNTs
Cell type	Prismatic	Prismatic	Cylindrical	Cylindrical
Cathode material	NMC	MWCNT NMC	NMC	MWCNT NMC
Anode material	Graphite	Graphite	Graphite	Graphite
Nominal rate (C-rate)	2C	2C	1C	1C
Nominal capacity (A h)	25	30	1.8	2.5
Specific energy (W h kg^{-1})	105	120	190	220
Maximum specific power (W kg^{-1})	200	1800	160	200
Battery life (years)	2	4	3	6

Graphene LIBs. Graphene has high electrical and thermal conductivities, a unique electronic structure in which charge carriers behave as particles, and every atom in graphene can be considered a surface atom. These properties make graphene a potential candidate in energy applications. Since its discovery, its possible use in computer chips, flexible transparent screens and desalination membranes has been investigated. Now, its use in transparent batteries, smaller capacitors and quick charging devices with high capacity is being explored due to its impressive ability to store high amounts of energy. Graphene can be produced using different methodologies that include mechanical exfoliation, epitaxial growth, chemical vapor deposition and reduction of graphene oxide (GO), which is the most economical.

There are many types of graphene batteries (Dasari et al., 2020):

Graphene Composites for Cathode Materials in LIBs:

- Graphene/ LiFePO4 composites in LIBs
- Graphene/ FePO4 composites in LIBs
- Graphene/ Li3V2(PO4)3 composites in LIBs
- Graphene/ LiMnPO4 composites in LIBs
- Graphene/ LiMn2O4 composites in LIBs

Graphene Composites for Anode Materials in LIBs:

- Graphene/ Si composites in LIBs
- Graphene/ transition metal oxides composites in LIBs
- Graphene/ Sn composites in LIBs

Graphene-based Materials for Sodium-Ion Batteries (SIBs)

- Graphene-based cathode materials in SIBs
- Graphene based anode materials in SIBs

Graphene-based Materials for Lithium-Sulphur Batteries (LISs)

- Graphene-based cathode materials in LISs
- Graphene-based anode materials in LISs

Many production techniques for both graphene and graphene electrodes are reported but graphene's full potential is yet to be explored. More insight is needed to investigate the interaction of graphene with base materials and electrolytes to form electrodes with self-assembled structures that will increase potential industrial applications.

Below are some other cathode materials under investigation and which could also be used in the future (Policy, 2018):

Lithium sulphur. This still contains lithium, but avoids the use of nickel and cobalt. Sulphur is a cheap and abundant resource, but these batteries currently have low volumetric energy density.

Lithium air. This uses oxygen for the cathode. In theory, it could reach energy densities ten times greater than most of the batteries currently on the market. However, at a system level, it is likely to require significant peripheral components to prevent the pure oxygen from degrading in ambient air, such as oxygen tanks or air separation units, which in practice, would drastically reduce its energy density.

Sodium-ion. This is the most appealing alternative to LIB from the viewpoint of sustainability. It does not contain Li, and Na is an abundant resource that is not associated with any geopolitical issues. It has a lower energy density than lithium-based batteries, but a high potential for stationary energy storage systems in which weight and volume are less critical.

2.2.2 Anode

As mentioned in Task 2.1.2, conventional graphite anodes suffer from poor rate capability and lithium dendrite problems upon overcharging, leading to internal short-circuits and safety concerns including fire or explosion owing to their flammable nature (Ding et al., 2019).

Much of the research over the years has focused on the improvement of electronic conductivity being the main cause of poor rate capability. Doping with various atoms, anodizing, nano structuring, and applying various coatings have been the main strategies. Synthetic routes, incorporating conductivity-improving strategies, have led to LTO materials being capable of extremely high rates and unprecedented cycling stability, making LTO highly relevant for the mass production of batteries.

Titanium oxides, especially lithium titanate (LTO), have a substantially higher potential and are appealing alternatives with which to overcome safety issues. However, improved safety comes with a significantly lower energy density due to its halved specific capacity of 175 mAh g-1 in comparison to graphite, and the reduced voltage window of the battery cell by -1.5 V. Nonetheless, LTO offers several advantageous characteristics in addition to improved safety, as its unit cell volume only changes by 0.2% upon lithiation and de-lithiation, which is referred to as “zero strain”. Therefore, it is an inherently structurally stable material with excellently reversible Li+ de-/insertion. It also features an extremely flat potential plateau on both charge and discharge, characteristic of a two-phase reaction mechanism. LTO, with a 3D structure, is expected to have excellent rate performance. However, it is characterized by rather low intrinsic electronic conductivity (< 10-13 S cm-1) and low Li+ diffusion coefficient, and therefore performs poorly at high rates.

Both graphite and LTO are now established commercial materials. As already mentioned, graphite anodes are the industrial standard for LIBs, and only minor improvements can be expected in the future.

LTO anodes occupy a market niche in which extreme safety is of the utmost importance, such as medical devices and public transportation. The use of LTO-comprising batteries might increase with the development of electrolytes that are stable at high voltages, thus allowing the use of high-voltage cathodes, as in such cases, energy densities that are comparable to the current graphite-based batteries might be reached – with the valuable add-on of avoiding lithium plating.

Other promising materials for anodes are the alloying type, which generally offer much higher capacities than carbonaceous anodes.

Silicium (Si) is a very promising candidate for replacing graphite as:

1) it is abundant, eco-friendly and non-toxic,

2) it offers extremely high gravimetric and volumetric capacities and

3) it displays an appropriate average voltage of ca. 0.4V vs Li+/Li.

However, Si suffers from poor cyclability due to the large volume change (280%) during full-capacity cycling at room temperature (RT), which leads to subsequent mechanical and chemical degradation. Mechanical degradation occurs as pulverization of silicon particles, loss of electronic contact between the Si particles and the electrode conductive network, and delamination from the current collector. Chemical degradation takes place along with the irreversible consumption of the electrolyte and active lithium due to the continuous growth of an unstable SEI, which lowers coulombic efficiency (CE) (Armand et al., 2020).

Nevertheless, although using Si as a complete replacement for graphite is not currently realistic, Si/graphite or Si/carbon composite electrodes could be a suitable choice in the near future. Such a partial replacement for graphite in battery anodes not only increases specific energy, but also effectively overcomes electrode expansion issues upon charge/discharge cycles (Ding et al., 2019).

Other possible materials for the anode are (Nitta et al., 2014):

Tin (Sn). It has similar properties to those of Si but has lower gravimetric capacity, and slightly lower cell voltage but higher electrical conductivity. However, Sn appears to suffer from easy fracturing, even when the particle dimensions are decreased to the 10 nm range.

Germanium (Ge) does not fracture even at larger particle sizes, but it too expensive for most practical applications.

Gallium (Ga) also has an interesting property of being liquid near room temperature, but is also too expensive.

2.2.3 Electrolytes

As mentioned before, the most used electrolyte is the LiPF6. The main advantages of this electrolyte are:

1) low dissociation energy and good solubility in carbonate solutions, affording superior ionic conductivity,

2) the perfluorinated PF6 anion is stable in oxidation, thus allowing the use of > 4V positive electrodes,

3) the Al current collector used for the positive electrode does not corrode at high potentials (> 4V vs Li+/Li) due to the formation of a stable passivation layer, and

4) The electrochemical reduction of the EC solvent together with FEC or VC as additives on the graphite electrode yields a high-quality solid electrolyte interphase (SEI), which ensures the reversible intercalation of the Li+ cations for hundreds (and even thousands) of cycles.

Nonetheless, $LiPF_6$ based liquid electrolytes have also some drawbacks:

1) thermal decomposition at a relatively low T (ca. 105 oC)

2) highly flammability of the organic carbonate solvents (Armand et al., 2020).

So, the addition of $LiPF_6$ salt electrolyte is justified because: i) it is highly conductive and ii) the creation of a passivation layer of AlF_3 at the surface of the aluminium current collector protects the current collector against the corrosion of the electrolyte (Mauger et al., 2017).

Apart from being highly flammable, current lithium-ion electrolytes can potentially form a toxic atmosphere if accidentally released in a (semi-) enclosed space, such as a garage, tunnel (in the event of a car crash, for instance) or recycling facilities. This is due to the solvents used and the formation of HF, a highly toxic and corrosive decomposition product of the $LiPF_6$ salt that forms when the salt comes into contact with atmospheric moisture or traces of water (Policy, 2018).

To overcome these safety problems by replacing the PF_6 anion, numerous other anions have been studied in recent years. Among them, the most studied and produced is LiTFSI (bis(trifluoromethanesulphonyl)imide), which is used as co-salt for LIBs, as well as electrolyte salt for post-lithium-ion batteries such as Li-S batteries. LiTFSI is thermally stable at up to 380 oC, readily soluble in most donor solvents, and the resulting solution shows decent ionic conductivities. However, the practical application of LiTFSI as the sole conducting salt is hindered by the anodic dissolution of the aluminium current collector in LiTFSI-based carbonate electrolytes.

Another alternative is LiFSI, due to its higher ionic conductivity and better stability against the Al current collector compared to LiTFSI. Consequently, LiFSI is being commercialized by Suzhou Fluolyte and Nippon Shokubai, and is added to $LiPF_6$-based electrolytes to improve the rate capability of LIBs while maintaining Al passivation.

Another class of lithium salts that has attracted considerable attention in view of their film-forming ability on electrode/electrolyte interphases are borate salts such as LiBOB (lithium bis(oxalato)borate) and LiDFOB (lithium difluoro(oxalato)borate). However, its C_2O_4 moieties tend to oxidize at high voltage resulting in gassing.

LiTDI (lithium 2-trifluoromethyl 4, 5-dicyanoimidazole)-based electrolytes have also recently been spotlighted. An optimal amount of LiTDI effectively suppresses the degradation of $LiPF_6$-based electrolytes and stabilizes the SEI layer on graphite, which could considerably improve the performance of LIBs.

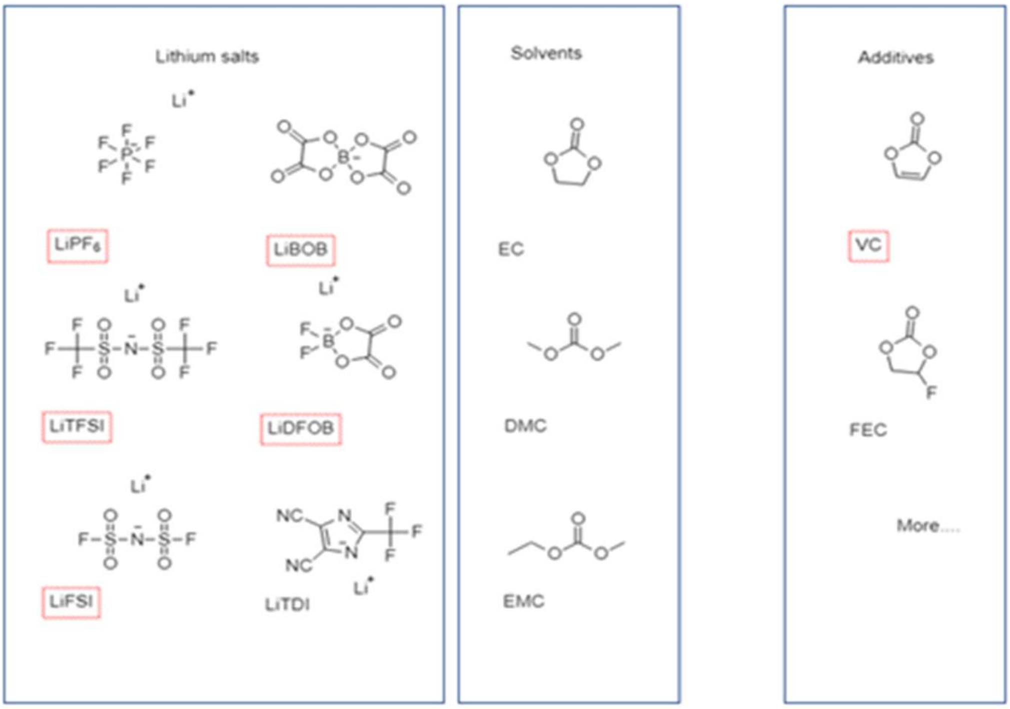


Figure 5. Chemical structures of lithium salts, solvents and additives of the most common electrolytes Modified from (Armand, et al., 2020).

However, to improve the safety of liquid electrolytes, the replacement of carbonate solvents with non-flammable ionic liquids (ILs) and the incorporation of flame-retardant additives (e.g., organic phosphorus compounds) have been intensively investigated. IL-based electrolytes are inherently safer, but their ionic conductivities are somewhat lower than those of carbonate-based ones, which results in relatively poorer rate-capability at room temperature. Due to the (currently) significantly higher cost of ILs, such electrolytes have not yet been commercially used in LIBs.

Alternatively, flame-retardant additives could sufficiently block the combustion process, but usually at the expense of cyclability. Recently, new additives such as 2(2,2,3,3,3-pentafluoro-propoxy)-4-(trifluoromethyl)-1,3,2-dioxaphospholane (PFPOEPi-1CF3) have been reported to have a positive impact on cell performance by contributing to the formation of a robust SEI layer on graphite for >1200 cycles. Localized high-concentration electrolyte (LCE) containing LiFSI and a ternary solvent, i.e., triethyl phosphate (TEP), EC, and bis (2,2, 2-trifluoroethyl) ether (BTFE), also enables the stable cycling of graphite NMC-811 cells. Hence, using electrolyte additives or co-solvents tends to be an economical and effective approach (Armand et al., 2020).

Table 4 and Table 5 summarize the advantages and disadvantages of the main materials used in LI-ion batteries.

Table 4. Recently applied materials in cathodes, anodes, and electrolytes.

Recently applied		
Cathode	**Advantages**	**Disadvantages**
NMC-811	Higher specific capacity (25% higher than NMC-111) Higher electronic conductivity and ionic diffusivity Lower cost	Still has Co Surface reactivity
Graphene for LIBs, SIBs and LIs	High electrical and thermal conductivities Unique electronic structure Large surface area	Needs further investigation to increase potential industrial applications
CNT	Increased electronic conductivity, charge/discharge rate, and higher structural flexibility High chemical resistance and low flammability	Increasing use has raised concerns about their potential impact on human health and the environment
Anode	**Advantages**	**Disadvantages**
LTO	Improved safety "zero strain"	Significantly lower energy density than graphite due to its halved specific capacity, and reduced voltage windows of cell Low intrinsic electronic conductivity and low Li+ diffusion coefficient and thus performs poorly at high rates
Graphene for LIBs, SIBs and LIs	High electrical and thermal conductivities Unique electronic structure Large surface area	Needs further investigation to increase potential industrial applications
Electrolyte	**Advantages**	**Disadvantages**
LiTFSI	Thermically stable up to 300 °C, readily soluble in most donor solvents and decent ionic conductivities	Practical application as sole conducting salt is hindered by anodic dissolution of Al current collector
LiFSI	Higher ionic conductivity and better stability against Al current collector than LiTFSI Added to $LiPF_6$ → to improve rate capability of LIBs while maintaining Al passivation	Able to form HF when in contact with atmosphere moisture or traces of water
LiBOB	Film-forming ability on electrode/electrolyte interphases Does not form HF	C_2O_4 moieties (fractions) tend to oxidize at high voltages, resulting in gassing
LiDFOB	Film-forming ability on electrode/electrolyte interphases Does not form HF	C_2O_4 moieties (fractions) tend to oxidize at high voltage, resulting in gassing

Table 5. Near-future materials in cathodes, anodes, and electrolytes.

Near-future		
Cathode	**Advantages**	**Disadvantages**
Li-S	Avoids Ni and Co S is cheap	Low volumetric energy density
Li-air	Avoids Ni and Co Higher energy density	Requires significant peripheral components
Na-ion	Does not contain Li Na is abundant with no geopolitical issues High potential for stationary energy storage systems where weight and volume are less critical	Lower energy density
Anode	**Advantages**	**Disadvantages**
Si	Abundant, eco-friendly and non-toxic Extremely high gravimetric and volumetric capacities Appropriate average voltage	Poor cyclability due to large volume change, leading to subsequent mechanical and chemical degradation
Si/Graphite	Better capacity retention and rate-capability than conventional carbonate electrolytes	
Electrolyte	**Advantages**	**Disadvantages**
LiTDI	Optimal amount effectively suppresses degradation of $LiFP_6$-based electrolytes and stabilizes SEI layer on graphite	
Non-flammable ILs (solvents)	Safer	Lower ionic conductivity and poorer rate capability than carbonate ones
Flame-retardant additives	Blocks combustion process	Lower cyclability

2.3 Next Generation Materials

As mentioned above, LIBs could be the key to the reduction of gas emissions. Many studies have been carried out in recent years and highly promising technologies could be applied in the future. These technologies are known as next generation LIBs, and the most interesting are the solid states batteries (SSB) and the new NMC technologies.

Solid State Batteries (SSBs)

Many authors consider these batteries to represent the next big leap forward in battery technology. Compared to conventional LIBs, SSBs would be safer and could also have a longer cycle life, higher energy density and less requirements in terms of packaging and the state of charge monitoring circuits.

Like the other members of the Li-ion family, numerous chemical technologies can be used for the electrodes. This battery version has a solid electrolyte, usually made of a ceramic (inorganic electrolyte) or a polymer (organic electrolyte). This solid electrolyte also acts as a separator and enables the use of different electrode materials, notably, lithium metal, as the anode material (as shown in Figure 4 above). Such a battery configuration effectively decreases the "dead volume" (Figure 6) between single cells, leading to more compact space and higher specific energy for battery packs (Ding et al., 2019).

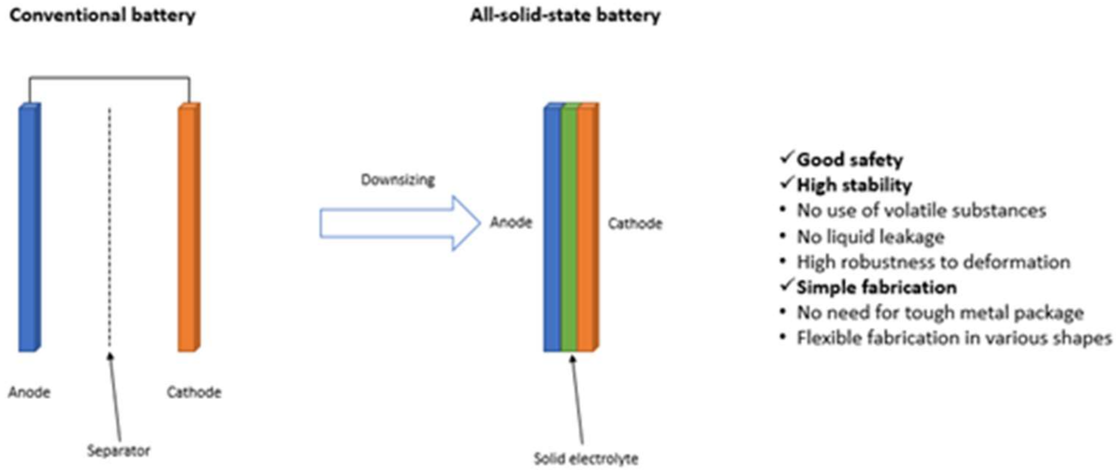


Figure 6. Schematic comparison between conventional and SSB. Modified from (Ding Y., Cano, Yu, Lu, & Chen, 2019).

There are two types of SSB (Ding et al., 2019):

- Non-Li-Metal based SSB
- Li Metal Anode based SSB

Thus, a solid configuration based on an NMC-811 cathode with Li as anode could be the most demanded in the far future.

NMC Technologies

Despite a move towards nickel-rich NMC technologies due to their higher specific energy and low cost, it is very hard to exceed their theoretical limitation (350 Wh/kg at a cell level). Thus, high-voltage spinel and high-energy NMC technologies could become promising alternatives in the long-term.

High Voltage Spinel (HV-Spinel- $LiNi_{0.5}Mn_{1.5}O_4$)

Since its discovery, the high-voltage spinel ($LiNi_{0.5}Mn_{1.5}O_4$—LNMO) has been presented as a tantalizing option for cathodes in next generation LiBs.

The combination of high operating voltage and excellent rate capability makes this material particularly attractive for automotive applications (Kim et al, 2014). It possesses a high operating voltage of 4.7V and a specific capacity of 130 mAh g-1, which leads to a specific energy of around 580 Wh kg-1. Even though it shows a modest energy improvement, it is attractive due to its easy synthesis, low costs, environmental friendliness, good safety, and excellent conductivities owing to both high electron and ionic (Li^+).

However, such material suffers from some disadvantages, such as severe capacity fading at elevated temperature (60 °C) (Ding et al., 2019). Therefore, recent studies suggest that the most critical barrier for the commercialization of this type of batteries is the electrolyte decomposition and the concurrent degradation reactions at electrode/electrolyte interfaces (Kim et al., 2014).

High Energy NMC ($xLi_2MnO_3 \cdot (1-x)LiMO_2$ where M= Ni, Mn, Co)

These materials, $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (where M= Ni, Mn, Co), have raised considerable interest in the automotive industry because they exhibit the highest specific energy (around 900 Wh kg-1) of all cathode materials. With this composite structure, the layered $LiMO_2$ component can be stabilized by the structurally compatible Li_2MnO_3 component. In the cut-off voltage range of 2.0–4.4 V vs. Li^+/Li, $LiMO_2$ is the only electrochemically active component: Li_2MnO_3 is inactive as the manganese ions are already tetravalent and cannot be further oxidized. In this regard, the main function of Li_2MnO_3 is to stabilize the $LiMO_2$ layered structure by providing Li^+ ions for the active $LiMO_2$ component. However, when voltage is increased to 4.4–4.6 V, Li_2MnO_3 becomes active and capacities above 250 mAh g−1 can be theoretically obtained. In the higher voltage range, the removal of Li_2O from Li_2MnO_3 will generate the electrochemically active MnO_2 phase.

Despite its favourably high capacity, HE-NMC still suffers from poor cycling stability, seriously limiting its practical application in the EV industry. This is mainly attributed to the extensive removal of Li_2O from Li_2MnO_3, resulting in damage to the electrode surface and increased impedance, especially at high current densities. In addition to cycling performance, low electronic conductivities and low tap densities need to be enhanced before HE-NMC could be considered as a potential battery technology for next-generation EV applications. Table 6 summarizes the main materials used for its components and presents the most important advantages and disadvantages.

Table 6. Next generation materials in cathodes and anodes.

Next-generation		
Cathode	**Advantages**	**Disadvantages**
HV-Spinel	Facile synthesis, low cost, environmental friendliness, good safety and excellent owing due to both high electron and ionic (Li+) conductivities	Modest energy improvement Seve capacity fades at elevated T (60 ºC) Electrolyte decomposition owing to higher operating voltage
HE-NMC	Highest specific energy among all the cathode materials	Poor cycling stability Needs the enhancement of low electronic conductivity and low tap densities
Anode	**Advantages**	**Disadvantages**
Non-Li-Metal in SSBs (HV→ Graphite and LCO as anode Large-current type→ LTO as anode)	Excellent electrochemical performance owing to their SSE superior conductivity High power density and ultrafast charging capability	
Li-Metal in SSB	Increased volumetric and gravimetric energy density	Low ionic conductivity and limited chemical stability of SSEs against metallic Li, and large interface impedance between Li anodes and SSEs

3 Discussion

This report has described the current and next generation materials for the production of Li-ion battery.

The safety issues of the anode and electrolyte materials are mainly related to their flammability. In this context, different alternatives have been recently applied (E.g., LTO or lithium titanate). Promising alternatives are still under research, but Sn, Ge and Ga and mainly Si could be implemented in the near future. Safer alternatives have also been identified for the PF6 anion salt, including LiTFSI, LiFSI, LiBOB and LiDFOB. The LiTDI salt could already be introduced to the market in the near future.

For the cathode, the most successful combination developed to date is that of nickel, manganese, and cobalt, abbreviated as NMC. This is currently being used as the cathode powder to develop batteries for power tools, e-bikes and other electric powertrains due to its strong overall performance, excellent specific energy, and the lowest self-heating rate of all mainstream cathode powders. These features also make it the preferred option for automotive batteries. Figure 7 schematically represents the current and future state of NMC batteries (Ding et al., 2019):

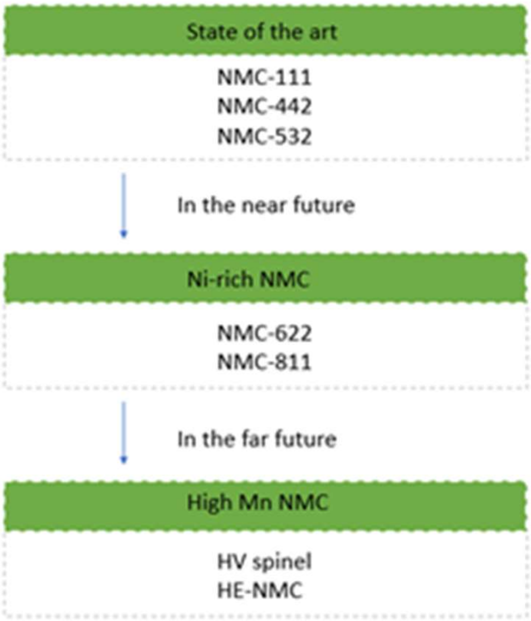


Figure 7. Schematic state of art of NMC batteries. Modified from: (Ding et al., 2019).

The main disadvantage of cathode materials is that most of them contain Co (cobalt), which can lead to toxicity, high costs, and geopolitical issues (extraction is mainly concentrated in the Democratic Republic of Congo). However, they also provide high technical benefits such as high energy density. In this way, it is important to replace or to reduce the quantity of Co in the cathode active materials. Different NMC batteries with increased quantities of Ni have been developed. Together with graphene and carbon nanotubes, these are technologies that have been recently applied due to the exceptional properties they provide for batteries. However, ongoing research has also identified other technologies that could be interesting in near future applications, such as lithium sulphur, lithium air, and sodium ion batteries.

Regarding next-generation Li-ion batteries, Solid-State Batteries are considered the most promising, but some NMC technologies such as the High Voltage Spinel and High Energy NMC, have also gained attention in recent years although they are still far from the market.

NMC-811 was chosen as the case study for this project. It is an attractive alternative that is already used by the automotive industry, and enables reducing the amount of Co to 20% with an increase of the Ni to 80%, achieving a higher energy density and a much lower cost of the battery. Compared to conventional NMC-111 technology, this battery has advantages such as higher energy density and reduced problematic Co content.

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Annex 1: Patent search

Title	Inventors	Applicants	Earliest priority
CNT-LTO complex for lithium secondary battery, and preparing method of the same, and lithium secondary battery including the same	Cho Yong Jae [KR] Roh Young Bae [KR] Seo Hyun Seung [KR]	EIG LTD [KR]	2014/12/31
Range-extended electric vehicles having lithium titanate oxide (LTO) battery with super high charge and discharge rates	Hou Junwen [US] Xu Jianguo [US]	HYBRID KINETIC MOTORS CORP [US]	2018/05/04
A lithium secondary battery with improved power property	Cho Sang Eun [KR] Kim Jae Kyung [KR] Lee Hyun Seok [KR] Park Min A [KR] Park Cung Chul [KR]	LG CHEMICAL LTD [KR]	2014/10/31
Lithium ion electrolyte and lithium ion battery using same	Li Junyi Li Suli Xu Yanming Zeng Chang'an	ZHUHAI COSLIGHT BATTERY CO LTD	2018/12/19
Novel process for synthesizing fluorinated conductive salt for lithium ion batteries	Cui Weilong Du Hongjun Wu Wenting Zhou Changyue	FUJIAN YONGJING TECH CO LTD	2019/08/22
Electrolyte composition for lithium secondary battery and lithium secondary battery using the same	Choi Nam Soon [KR] Lee Jae Gi [KR] Lee Yong Won [KR]	ULSAN NAT INST SCIENCE & TECH UNIST [KR]	2016/12/16
Electrolyte solution for lithium ion battery	Toyama Hiroshi	TOYOTA MOTOR CORP	2016/05/27
Electrolyte solution for lithium secondary battery and lithium secondary battery comprising the same	Chae Jong Hyun [KR] Choi Young Cheol [KR] Choi Young Geun [KR] Chung Geun Chang [KR] Jung Jong Mo [KR] Lee Chul Haeng [KR] Yoon Seung Jae [KR] Yoon You Rim [KR]	LG CHEMICAL LTD [KR]	2012/11/23

Lithium ion battery electrolyte containing LiFSI	Ding Xianghuan Guo Ming Xia Nannan	DONGGUAN SHANSHAN BATTERY MATERIALS CO LTD	2013/12/31
Lithium battery electrolyte solution and lithium primary battery using same electrolyte solution	He Xianwen [CN] Liang Hui [CN] Pan Wenshuo [CN]	HUIZHOU HUIDERUI LITHIUM BETTERY TECH CO LTD [CN]	2016/06/17
Lithium secondary battery	Ahn Seung Ho [KR] Kim Dong Hui [KR] Kim Sa Heum [KR] Lee Sang Joon [KR] Lee Yoon Ji [KR] Lee Yoon Sung [KR]	HYUNDAI MOTOR CO LTD [KR] KIA MOTORS CORP [KR]	2018/12/13
Battery having electrolyte including organoborate salt	Yoon Sang Y [US] Nakahara Hiroshi [US] Tsukamoto Hisashi [US] Yoon Sang Young [US]	QUALLION LLC [US]	2004/02/04
Electrolyte for rechargeable lithium battery and rechargeable lithium battery including the same	Han Su-hee [KR] Kim Jin-Sung [KR] Jim Jin-Hyunk [KR] Oh Mi-Hyeun [KR] Park Na-Rae [KR]	SAMSUNG SDI CO LTD [KR] HAN SU-HEE [KR] KIM JIN-SUNG [KR] LIM JIN-HYUNK [KR] OH MI-HYEUN [KR] PARK NA-RAE [KR]	2009/11/26
Method for manufacturing lithium secondary battery, lithium secondary battery, and lithium secondary battery system	Matsui Masaki [JP]	MATSUI MASAKI [JP] TOYOTA MOTOR CO LTD [JP]	2008/04/04
Lithium ion battery electrolyte with wide-temperature-range discharge characteristic	Guo Shaoxiong Wu Yushuang	FUJIAN JINDE POWER TECH CO LTD	2018/11/30