Current Natural Sciences

ENERGY

Coordinated by Didier BLOCH, Sébastien MARTINET,
Thierry PRIEM and Christian NGÔ

Li-ion Batteries

Development and Perspectives

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Thanks to their improved performance and the continuous decrease of their manufacturing costs, lithium batteries, initially marketed in 1991 by SONY to power portable equipment, now play a key role in the expected massive development of electric mobility.

Connected to the electricity grid via the electrified vehicles they will power, lithium batteries will also be used as a massive means of buffering renewable energies, as well as tools for supporting the network (peak shaving, frequency regulation, etc.), making it possible to multiply their usefulness beyond their primary function (ensuring vehicle mobility).

These developments will profoundly transform our societies, and will not only make it possible to significantly reduce CO_2 emissions and the consumption of fossil fuels (oil, gas, coal), but also, if they are conducted and coordinated effectively, to contribute to economic growth.

The development of electric mobility thus offers a unique opportunity to reconcile legitimate environmental protection requirements with industrial development objectives.

The aim of this book is to provide the reader with an overview of lithium battery technologies, to give an overview of current initiatives around the world, and to outline some perspectives for the future.

The authors of this book, who are researchers at the CEA and the CNRS, all have expertise based on several years of experience in the development of lithium batteries and post-lithium ion batteries, covering all the elements of the value chain, from the design and synthesis of electrode materials to integration in the vehicle.

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Preface

In order, in particular, to support energy transition, necessary and essential to safeguard our planet, energy storage needs will increase very sharply in the coming decades, whether for stationary applications or for mobility with a global market which should increase from 100 GWh in 2016 to 3 TWh (3000 GWh) in 2030.

Li ion batteries have a number of advantages that help meet these needs. The current challenges are to increase performances (to reach more than 350 $Wh.kg^{-1}$ and 1000 $Wh.L^{-1}$ at cell level) while aiming for increased safety and a cell target cost of around € 80–120 per kWh. The so-called traditional Li ion is now reaching its limits in terms of mass and volume energy densities, which is pushing all scientific and industrial players towards the identification of new technological breakthroughs on new generations of batteries. Particular attention is also fundamental with regard to the sustainability of the solutions proposed by securing supplies, avoiding so-called "critical" materials in terms of environmental impact, using solvent-free processes, but also more generally by considering recycling and full battery life cycle analysis.

This book, by addressing the topic of batteries across the entire value chain from materials to the system, offers readers elements of understanding and reflection allowing everyone to have a better knowledge of the expected assets, but also of the hurdles and issues related to the development of present and new generations of Li-ion or post Li-ion Batteries. The development of these new batteries as a storage solution, beyond being useful for the development of clean energies to support the energy transition, will have a certain environmental and societal impact in the years to come.

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Chapter 1

Introduction

Didier Bloch, Sébastien Martinet, Thierry Priem and Frédéric Le Cras

After a brief introduction, this first chapter introduces a short history of battery technologies, as well as the operating principles of Li-ion batteries.

It is now clear to everyone that the rapid and drastic greenhouse gases (GHG) emissions is an absolute imperative. This necessarily implies achieving a massive reduction in the consumption of fossil fuels (oil, gas, and coal).

Provided the electricity used to recharge vehicles is decarbonized, the deployment of battery powered electric vehicles could significantly contribute to make this possible, as it shifts the consumption of oil to electricity.

In addition, the deployment of electrified vehicles offers another decisive advantage: as electric motors happen to be much more energy efficient than internal combustion engines, it should make it possible to decrease significantly the overall energy consumption.

This is why the accelerated development of vehicle electrification is a top priority.

In France, for example, in 2019, transport, which is currently essentially oil-based (excluding rail), accounted for about 29% of the country's ∼150 MTep *final energy consumption*, and contributed to ∼39% of the 313 Megatons corresponding GHG emissions (figure 1.1a & b).

Slightly less than half of these emissions come from passenger vehicles alone.

The complete electrification of *e.g.* all French passenger cars and small and medium sized commercial vehicles fleets would therefore make it possible to save 32 Mtoe of oil imports (out of a total of 62 Mtoe, *i.e.* more than 50% of all oil imports), and reduce the country's overall GHG emissions by approximately 25%. Considering the 20–25 years required to completely renew a fleet of vehicles, an ambitious and proactive policy could allow achieving this goal as soon as 2040–2045.

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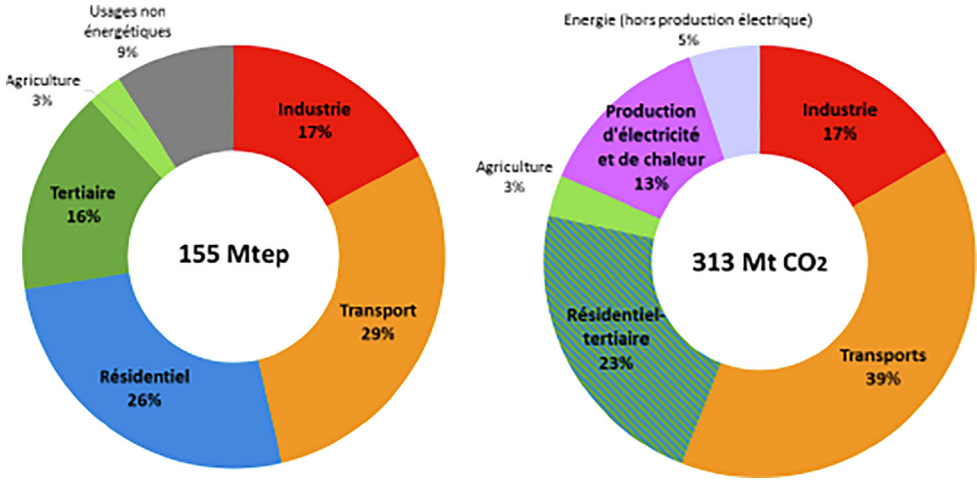

FIG. 1.1 – (a) (left) **Final Energy Consumption by sector, France, 2019**. Transport accounts in France for ≈ 30% of the overall final energy consumed (≈150 MToe), and (b) (right) **GHG emissions corresponding to final energy consumption in France in 2019**. Transport accounts for ≈ 39% of the corresponding overall CO_2 emissions (122 Mt out of 313 Mt). (Note that the 313 Mt CO_2 final-energy-consumption-related GHG emissions correspond to only 70% of the country's global GHG emissions, which take into account additional emissions due to, *e.g.*, industrial or agricultural processes). (source : « Integration de l'electromobilite dans le systeme electrique » RTE-AVERE Report, 15 April, 2019).

In addition, the expected electromobility surge will also spread to other modes of transport, such as, to a certain extent, public and heavy transport, thus multiplying its benefits, and making it possible to achieve this objective earlier than expected.

On the other hand, the deployment of the so-called "renewable" energy (RNE), mainly solar photovoltaic and wind energy, is often being put forward, rightly or wrongly [1], as one of the other possible solutions to help meet the GHG emissions reduction challenge mentioned above. Beyond the fact that the deployment of these electrical energy production devices does not reduce GHG emissions in countries whose electrical energy is *already* decarbonised, these energies are by nature not dispatchable on demand because of their intermittency. Their deployment requires the availability of additional dispatchable electricity production means, as well as massive electricity storage buffers, capable of storing the RNE electricity when it is produced in excess, and delivering it to the grid when there is no wind or sun to meet consumer demand.

A simple calculation shows that these energy storage buffers could be partially made of the storage capacity offered by a fleet of electrified vehicles (which would simultaneously obviate the need to develop and implement specific and costly additional stationary storage means). Let us indeed consider the reasonable assumption of a French fleet of personal electrified vehicles of around 5 million units by 2030 (*i.e.* around 15% of the French personal vehicles fleet). If one considers that approximately

5 kWh are required to recharge every vehicle due to its average, daily, 35 km mileage, and taking advantage of the fact that more than 80% of personal vehicles at parked at any given time of the day, one can see that on board batteries could become a controllable electricity storage buffer system capable of storing approximately 25 GWh (5 million times 5 kWh), that can be stored at any time of the day when solar or wind energy is available. This amount represents approximately one fifth of the average daily ENR French production in 2020. It therefore appears on a first hand quite smart and easy to store a significant part of the energy produced by RNE in electrified vehicles, provided the simultaneous deployment of RNE and electrified vehicles is efficiently coordinated. It is even possible to take on a second hand the logic one-step further: the deployment of bi-directional V2G/V2H (Vehicle to Grid/Vehicle to Home) connections could in return allow the vehicles to provide services to the power grid, such as peak power demand shaving, frequency regulation, and substitution of electricity for fossil fuels (oil and gas) whenever possible. Parked vehicles could also be recharged during off-peak hours and be used to directly power homes during peak hours (self consumption). These additional features will reduce the need to build additional power plants generally using fossil fuels, which would otherwise be required to produce the electrical energy in the absence of wind or sun.

Of course, the legitimate question is whether carbon-free electricity power stations will be sufficient to meet the growing electricity demand due to the take-off of the EV's market. To consider, once again, only as an example, the French case, one can reasonably imagine that if the nuclear and hydropower power capacity is *at least* maintained at its present, ≈ 450 TWh, 2021 production level, sufficient electricity should be available to meet the 100 TWh additional annual demand of the personal and light/medium sized delivery vehicles' batteries fleets. This assumes, however, a strong hypothesis: batteries should mainly be recharged at night during off-peak hours, and fast charge (>7–11 kW) during day hours should be minimized as much as possible to reduce the risk of grid instability. Additional 2–11 kW recharging could be envisaged, for example, on company's car parks charging stations during low electricity demand periods. Large scale development of fast recharging would undoubtly require additional power means, and probably a costly reinforcement of the power grid.

Properly coordinated, the concept should lead to a win–win situation for all stakeholders: every citizen will personally contribute to effectively combating climate change, and, finally yet importantly, partially amortize the purchase of the battery in his or her vehicle by selling energy back to the grid. Governments will be able to keep their word and efficiently reduce their GHG emissions, as well as their financial and political dependence on fossil fuels. Car manufacturers will sell as much cars as today. Electricity operators will play with offer and demand to reduce their investments in new power stations and offer additional, profitable services.

The implementation of this vision requires foremost the effective and vigorous coordination of public authorities, which will have to play the role of an orchestra conductor. They will have to foster the implementation of bidirectional recharging infrastructures, which will be a relatively easy task to deal with, but, above all, in close coordination with all industrial players implicated all along the energy value chain, promote the large scale implementation of batteries offering a very long cycle

life (>2000–5000 charge/discharge cycles), since these batteries will be expected to perform a dual function: mainly for mobility, and also to provide grid services. Such a long cycle life will, by the way, drastically reduce their Total Cost of Ownership (TCO), expressed in €/Wh exchanged, and contribute to a significant reduction of the battery environmental footprint. The expected evolution of the current technical specifications, for which the battery only provides the "mobility" function, therefore, invites to explore new technical options or to improve existing ones, from the material to the complete system.

Lithium-ion batteries will be the catalyst, the pivot of all these expected industrial and societal transformations. Initially developed to replace the nickel–cadmium batteries used at the time to power portable electronic devices, the continuous improvements in their performance and the sharp drop in their production cost now pave the way for their large-scale use as a massive, dispatchable on-demand, electricity storage means. As of today, the battery manufacturer controls a key part of the vehicle's performances and cost.

This is why the very large-scale production of lithium batteries has become a top priority issue, which conditions primarily the future of the automotive industry. As the first one built in Nevada by the Tesla company (Elon Musk) allied with the Japanese Panasonic, "Gigafactories" are now being built all over the world. Each of them mobilizes investments of several billion euros. In the majority of cases, their deployment is based on the technical know-how detained by world leaders, currently Asian (Japan, Korea, and China). As a matter of fact, these countries anticipated and prepared, as early as the beginning of the 20th century, for the major developments in mobility that are taking shape today. China has become the world's largest producer and consumer of lithium batteries in 2020, driven by its domestic market, and by a very proactive political regulation. In Europe, the construction of more than 20 Gigafactories, mainly operated by Asian industrial players, is also underway or planned: Samsung SDI and SK Innovation (Korean) are implementing factories in Hungary; LG (Korean) in Poland; Envision (Chinese) in France; CATL (Chinese) in Germany... [2].

Until then, most European car manufacturers considered batteries to be a simple commodity and expected competition from their Asian suppliers to continue to lower costs and improve performance. However, several factors combined, leading to a gradual awareness in Europe – in 2016 in Germany, mid-2018 in France – of the mandatory need to master the battery manufacturing know-how. As a matter of fact, electrified vehicles are now built "around" the embarked battery, which obviously becomes a critical component. Moreover, the expected growth of the world market will most likely lead to possible issues in battery supply, thus increasing the risk of dependence on manufacturers whose interests are likely to change rapidly depending on the geopolitical context. This awareness led in 2019–2021 to the emergence of European-born consortiums such as those led by Stellantis, Volkswagen, and other car or battery manufacturers such as Northvolt in Sweden, with the perspective to build >30 GWh Gigafactories in Sweden, France, Germany or Italy, with the partial support of European and national funding [3].

If Europe wishes to maintain a strong car industry, it must reasonably play both sides of the coin:

- Rebuild a complete industrial sector, across the entire value chain, to manufacture, in the shortest possible time, high-performance and economically competitive batteries, and take a significant share of the fast-growing electric mobility market. As batteries will be manufactured in millions in the near future, it seems unlikely that technologies that are too far from the current state of the art will be used. This is the purpose of the "Present" of lithium-ion batteries presented in this book, to give the reader the most accurate possible idea of the technology used not only today, but in the next 10 years, as long as present-generations Gigafactories will operate.
- Actively encourage the R&D activity necessary for the development of next-generation batteries, since it will be necessary to remain competitive in the long term: this is the purpose of the Post-Li-ion or other types of batteries, presented in this book through dedicated chapters, which will provide the reader with an overview of the options explored to date.

Although the two types of initiatives are closely coupled, the first type of action appears to be more the domain of industrial leadership, and the second type of action more the domain of institutional action. In both cases, the game will involve European industrial and research players, who will be able to coordinate their efforts and select the relevant technical options. They should control and secure the entire battery value chain in a context of intense competition. The manufacture of a battery requires the mastery of a large number of skills in a wide variety of fields, from the extraction of raw materials to their recycling at the end of the battery's life and their reuse in new batteries, *via* the synthesis of active materials, the very large scale manufacture of electrodes, cells, modules, packs, and complete systems including electronic and thermal management.

The avenues for progress are real. From the point of view of the materials used as well as that of the complete on-board system, they depend largely on the functional specifications of the intended application, which has a direct influence on them.

As an example, the trend seems presently to priviledge the development of "all electric" vehicles with >50–70 kWh batteries, in order to offer the longest possible driving range. In this case, materials designed to cycle 500 times (200 000 km with 400 km per cycle) may well meet the demand. But what if the same vehicle must also be used as a grid service provider? Then the material's behaviour must be improved to meet >2000 cycles without major degradation. And what if the battery is supposed to power a Plug-In Electric vehicle (PHEV), which 12–15 kWh, much smaller, and much less material-intensive consuming battery, has on the other hand to cope with much more heavy power discharge rates to power the vehicle, must prove a much larger (>5000–10000 cyles) life expectancy to be recharged every day and offer grid services at the same time? One can see that electrode and electrolyte materials will probably be designed differently in each case. In the end, all doors remain open, in order to adapt materials and batteries to the preferences of the final consumer, the good news being that such design adaptation to meet various needs seem now within reach. Regardless of the option selected, the consortia that

will be set up will have to deal with numerous, sometimes contradictory specifications, in order to comply with the final target (reduction of greenhouse gas emissions):

- To ensure user's safety.
- To offer the battery's best possible performance: energy density and power density, of course; but also high cyclability, so as to reduce the cost of ownership per cycle, and enable the vehicle not only to meet mobility needs but also to provide other types of services to the power grid, and reduce the environmental footprint.
- To reduce the presence of sensitive or critical materials to a minimum, and if possible to zero.
- To effectively coordinate all players involved in the entire value chain, including energy producers and operators, manufacturers of electronic materials or components, car manufacturers, recycling industries, etc.
- To manufacture vehicles, especially entry-level and mid-range vehicles, accessible to the greatest number of people. Commercial success will indeed depend on many parameters: social acceptance of the electrified/connected vehicle, changes in consumer purchasing power, renewal rate of the vehicle fleet, availability of recharging systems, and development of alternative mobility solutions.... A great deal of pedagogical work will be necessary in order to answer the legitimate questions of all citizens.

Europe is late, but has the skills and assets needed to catch up with the Asian industry. France and Sweden have, in Europe, key assets in this area, particularly thanks to their decarbonated energy mix. R&D collaborations are already in place and have been established for a long time (European joint projects for example).

Hurdles will be numerous but the European automotive industry survival is at stake and success is the only possible option [3].

1.1 Brief History of Primary and Secondary Batteries

The discovery of the working principle of primary batteries took place in 1800, by Alessandro Volta with the eponymous battery [5] using two different metals, zinc and copper discs, separated by a felt soaked in sodium chloride. It was not until 1859 that Gaston Planté discovered the first rechargeable lead-acid battery [6].

In 2021 battery technologies include only three major families in addition to lead-acid batteries (this latter remaining so far dominant in terms of Wh produced, but not any longer in value): alkaline nickel–cadmium (Ni–Cd), nickel-metal hydride (Ni-MH), and, since 1991, lithium-ion (Li-ion) batteries, which gradually dominate all others.

Two major breakthroughs allowed the large scale commercialization of Li-Ion batteries. In 1980, J. Goodenough *et al.,* discovered $LiCoO_2$ as a high-potential positive electrode material [7]. Shortly after, in 1983, R. Yazami and P. Touzain showed that lithium could intercalate reversibly in low-potential graphite [8]. This

made it possible to dispense with the use of metallic lithium, which posed serious safety issues. The combination of these two innovations allowed the development of Li-ion systems and their first commercialization, in 1991, by Sony.

Since 1991, the gravimetric energy density of Li-ion batteries has almost tripled from 100 $Wh.kg^{-1}$ to almost 270 $Wh.kg^{-1}$. At the same time, their cost has fallen very sharply, thanks in particular to the reduction in manufacturing costs. These improvements, coupled with initiatives of visionary industrial players such as Tesla/Panasonic in USA; LG in Korea; or BYD or CATL in China, made it possible for the electric vehicle market to take off.

Battery technologies are generally compared in terms of their energy density ($Wh.kg^{-1}$ or $Wh.L^{-1}$) and/or power density ($W.kg^{-1}$), especially for embedded systems. These performances are usually synthesized by plotting the power density as a function of the mass energy density in a so-called *Ragone* diagram as shown in figure 1.2. For each technology, these performances are described by a beam representing the possibility of modulating the performances according to whether one seeks to favour the energy density or the power density, *via*, for example, the use of thin electrodes to favour the latter. These notions are discussed in chapter 13, which describes the batteries manufacturing processes. It is also worth noting the presence of supercapacitors in this diagram, a technology based on capacitive phenomena and the use of electrochemical double layers. Supercapacitors are covered in chapters 9 and 10.

Of course, the performances of batteries are also measured during use, *i.e.* during charging and discharging cycles, for example. To characterize these performances, one usually reports the evolution of the voltage at the terminals of the cell as a

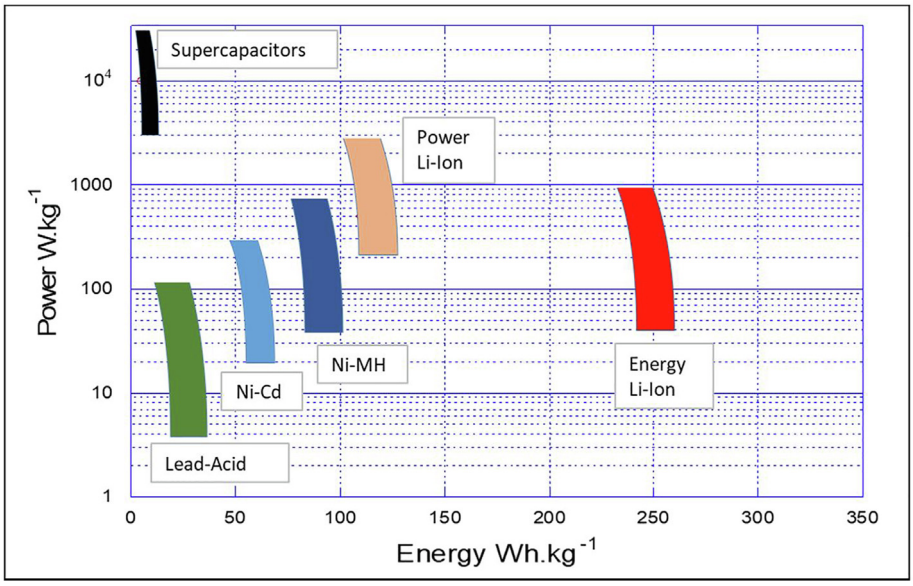

FIG. 1.2 – Ragone diagram of various commercialized battery technologies.

function of the discharged capacity, given in ampere hours (Ah) (1 Ah corresponds to the flow of a current of one ampere over a period of 1 h, *i.e.* 3600 Coulombs), and for various current values. An example is shown in figure 1.3 for the case of a cylindrical "18 650" cell (18 mm diameter and 65 mm height) for currents ranging from 0.2 times the nominal discharge rate (discharge in 5 h) to 2 times the nominal discharge rate (discharge in ½ h). The nominal discharge rate (or C-Rate) is defined as the current that allows the cell capacity to be totally discharged in 1 h. This then allows the use of C/n or nC ratings which represent slower rates, discharge in n h for C/n, or faster, discharge in 1/n h for nC.

In concrete terms, the Li-ion cell shown in the example of figure 1.3 has a nominal capacity of 2040 mAh, *i.e.* is able to withstand a nominal discharge rate C (noted "It" in the figure) and to deliver during one hour a discharge current of 2040 mA. A more rapid discharge rate at 4080 mA, or 2C, lasts almost 30 min, during which time nearly all of the rated capacity is recovered. At slower C/5, or 408 mA, the delivered capacity is close to 2200 mAh. The curves show a significant decrease in the mean voltage when the discharge rate is increased. This is due to an increase in ohmic and/or diffusive losses within the battery cell, which degrades the energy efficiency (energy losses between charge and discharge).

It should be noted that the accumulators (or unit cells) are the elementary cells constituting the batteries in which they are assembled in series and/or in parallel in order to increase the operating voltage (series connection) and/or the on-board capacity (parallel connection). An electronic management system called BMS (Battery Management System) always controls the battery operation and ensures safety. The pack constituting the cell/BMS assembly (see chapter 14) is referred to

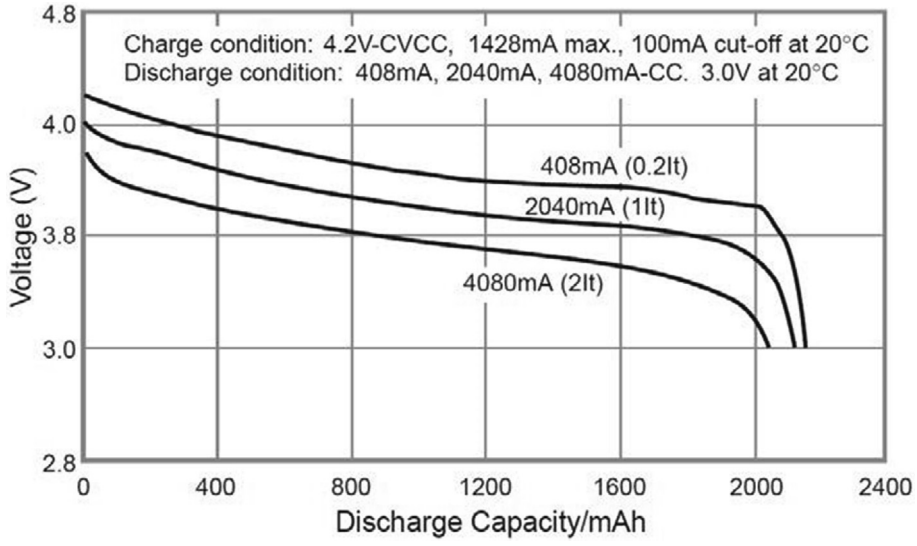

FIG. 1.3 – Discharge curves of a Li-ion cell at various discharge rates: Panasonic CGR18650C [9].

as the "battery pack". It often includes a thermal management system, in order to ensure a uniform temperature between the unit cells, which in turn allows the battery to behave as expected throughout its lifetime.

As mentioned above, after more than 150 years of development, only four main battery technologies have been widely commercialized. Today, Li-ion batteries are taking a growing share of the market thanks to their versatility, performance and cost. At the same time, faced with the challenge posed by the large-scale development of the electric vehicle, and of stationary energy storage, many other options are explored, either to improve the performance of the current Li-ion ("all-solid"…) sector, or to develop alternative solutions – lithium–sulphur, sodium-ion, organic materials… – less demanding in terms of sensitive materials for example.

1.2 General Information on Li-ion Batteries

"Traditional" Li-ion batteries are based on the use of two lithium intercalation materials: a lithiated transition metal oxide at the positive electrode ($LiCoO_2$, NMC, NCA, LFP...) and graphite at the negative electrode. Chapters 2 and 3 introduce new electrode materials which may be used as alternatives to these reference materials. The operating principle is shown in figure 1.4. The battery is manufactured in the discharged state, the positive electrode being the source of lithium, and the graphite of the negative electrode being initially free of lithium ions. During the first charge, lithium ions de-intercalate from the positive electrode, diffuse through the electrolyte and intercalate into the negative graphite electrode. In order to respect the rule of electro-neutrality, the flow of one Li^+ ion in the internal circuit of the accumulator is exactly compensated by the flow of one

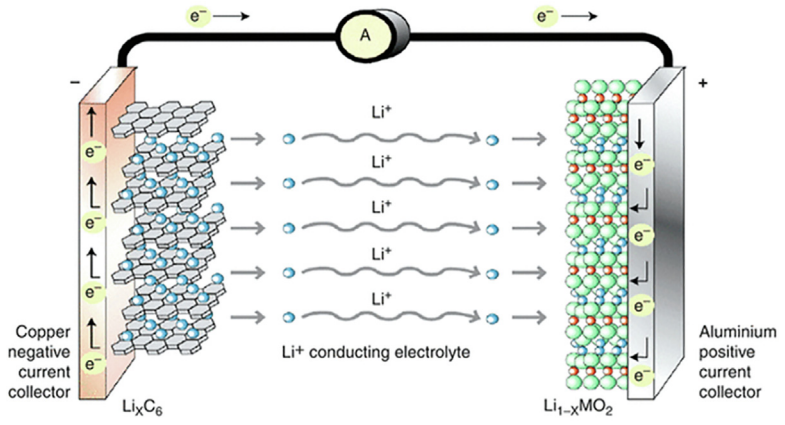

FIG. 1.4 – Working principle of a traditional lithium-ion battery, using a transition metal oxide $LiMO_2$ as positive electrode active material, and graphite as negative electrode active material. From reference [10].

electron in the external electrical circuit. The opposite phenomena occur during discharge.

It should be noted that, during the first charge, a passivation layer, known as SEI (Solid Electrolyte Interphase), is formed on the negative graphite electrode, which ensures the cell's good cycling behaviour. However, it does lead to an irreversible loss of capacity in the order of 5%–10%.

The high voltage difference between the two electrodes – typically 3.6 V nominal voltage – contributes greatly to the high energy density of this battery technology. This compares to 2 V for lead batteries and 1.2 V for alkaline batteries. This is due to the highly reducing nature of lithium metal and the fact that lithium ions are intercalated in graphite at a potential fairly close to the Li^+/Li redox couple potential (−3.04 V *vs.,* SHE, SHE for Standard Hydrogen Electrode), typically on average 100 mV above this value.

Figure 1.5 illustrates the positioning of the various positive and negative materials discussed further in this book. Positive electrode materials (described chapter 2) are mainly positioned at the top left with maximum insertion capacities often well below 300 $mAh.g^{-1}$ (typically 150–190 $mAh.g^{-1}$), while the range of negative electrode materials is wider with three families: conventional carbon-based materials, titanium-based compounds (power-oriented) and materials corresponding to the p-block elements such as silicon with a very high specific capacity (see chapter 3). To promote energy density, it is necessary to select both positive and negative compounds with high specific capacities, but also as far as possible on the scale of potentials.

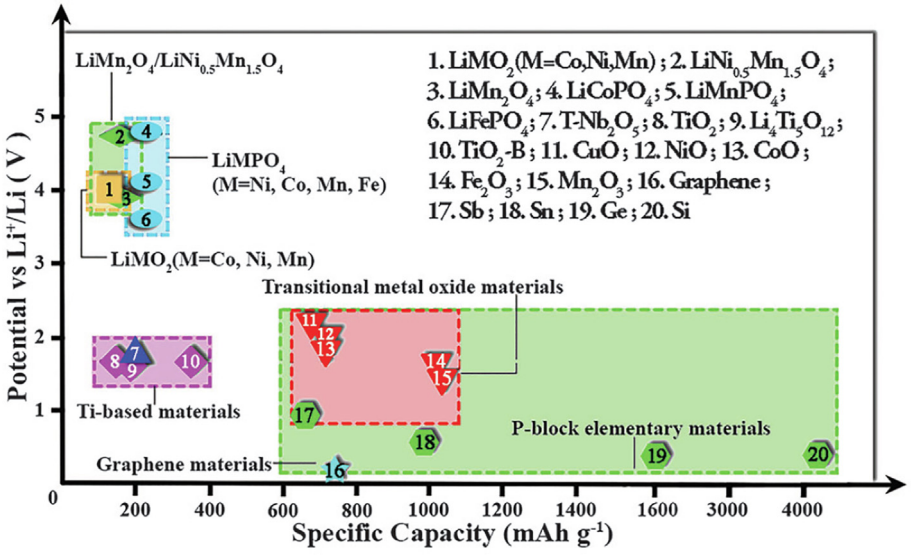

FIG. 1.5 – Li-ion batteries materials mapping. From reference [11].

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Chapter 2

Positive Electrode Materials for "Lithium-ion" Accumulators

David Peralta, Frédéric Le Cras, Jean-Baptiste Ducros, Carole Bourbon, Jean-François Colin and Sébastien Patoux

The positive electrode (or cathode) is a key component of a Li-ion cell: it is the most limiting element, for several reasons.

The first of these reasons deals with material's cost: more than 60% of the cost of the electrochemical unit cell is due to the raw materials that make it, and in 2021, the cost of the cathode materials represents 27% of the cell cost (figure 2.1). The cell material's cost share should increase in the next future, with the Gigafactories expected mass production ramp up, which will mechanically reduce production and administrative cost share.

The cathode material market grows rapidly from year to year (410 000 tons in 2021 *vs.* 184 000 tons in 2016) due to the rapid development of the electric vehicle market [1]. However, cobalt, for instance, used in the composition of the cathode active material, is considered as a critical metal: its known resources are relatively limited (it is mined as by-product of nickel and copper extraction) and mainly located in geopolitically unstable countries. This is why compositions with lower cobalt content are currently developed, with a real success. The lithium battery industry remains however exposed to a risk of material's supply shortage. Significant fluctuations in the raw materials cost may be expected in the future, not considering the environmental impact of their extraction conditions.

The second reason deals with the intrinsic performance of the cathode material (energy and power density, electrochemical reversibility, temperature stability…), which largely conditions the behavior of the cell during cycling. The selection of cathode material's blends, and the way in which these blends are implemented, implies a necessary compromise between cost, safety, life expectancy, and energy/power density performance.

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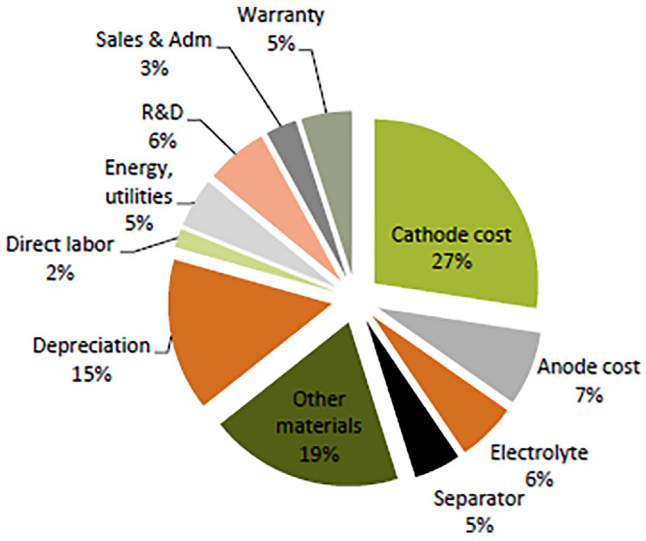

FIG. 2.1 – Li-ion unit cell cost breakdown. Source: Avicenne [1].

Currently, there are very few cathode materials available for lithium-ion battery applications. These compounds belong to three different crystallographic families that give materials special properties: spinels, layered oxides and olivines [2].

The main purpose of this chapter is to provide an overview of these three material families.

2.1 Positive Electrode Materials of "Spinel" Structure

Interest in spinel positive electrode materials was born in the early 1980s with the emphasis on the possibility of chemically and electrochemically extracting lithium from $LiMn_2O_4$ without significantly disrupting the spinel structure of the initial compound [3, 4]. From the outset, this material, free of expensive or toxic elements, has a theoretical specific capacity equal to 148 $mAh.g^{-1}$ at a potential of 4 V *vs.* Li^+/Li. Because the spinel structure is favorable to rapid ionic exchange kinetics, this material family was considered as an alternative to the $LiCoO_2$ layered oxide. With its substituted variants, spinel structure materials were specifically targeted for use in Li-ion power cells.

Description of the Spinel Crystallographic Structure

A number of compounds of the general formula $A[B_2]X_4$ (A and B being cations, X being an anion such as O, S, Se, Te) adopt a crystalline structure isotype of the $MgAl_2O_4$ spinel. This structure is characterized by a pseudo-close-packed anion stacking, and by cations' occupancy of 1/8 of tetrahedral sites and 1/2 of interstitial octahedral sites. In normal distribution, cations A occupy tetrahedral sites, while

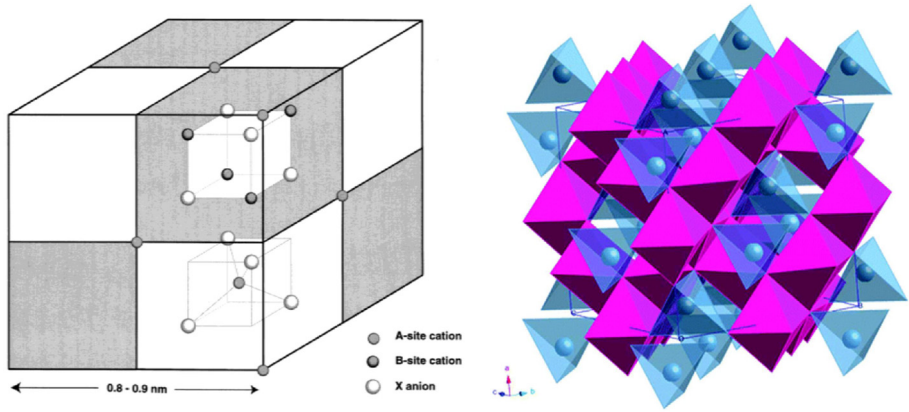

FIG. 2.2 – Left: AB_2X_4 spinel structure consisting of two site types. The mesh parameter of 8–9 Å corresponds approximately to that of oxides [5]. Right: picture of the spinel structure consisting of BX_6 and AX_4 tetrahedrons [6].

cations B occupy octahedral sites of the crystal. However, there may be an inverse B $[AB]X_4$ distribution in which half of the B cations occupy the tetrahedral sites, while the octahedral sites are occupied by both cation types, and also intermediate distributions $A_xB_{1-x}[A_{1-x}B_{1+x}]X_4$. When the cation distribution on each site type is random, the cubic crystalline structure is indexed in the Fd-3 m space group and includes 8 formula units (figure 2.2).

$LiMn_2O_4$ (LMO), a "Low Cost" 4 V Electrode Material for Power Cells

In the case of the $LiMn_2O_4$ spinel compound, lithium alone occupies an interstitial network (tetrahedral sites (8a)) delimited by the Mn_2O_4 skeleton, which consists of octahedral sites (16c), which makes it possible to diffuse Li^+ ions within a three-dimensional network of channels. In the case of intercalation materials, such a three-dimensional geometry of the diffusion paths is in principle particularly well suited for applications that require high current densities. At room temperature, $LiMn_2O_4$ is an n-type semiconductor with an electronic conductivity of about 10^{-4} S.cm^{-1} [7, 8]. The *gap* value measured on thin-layer samples is in the order of 1 eV [9].

The deintercalation of Li^+ from $LiMn_2O_4$ occurs primarily at around 4.0 V *vs.* Li/Li^+ and is accompanied by the oxidation of Mn^{3+} manganese contained in the Mn^{4+} structure (figure 2.3) according to the equation:

$$LiMn^{3+}Mn^{4+}O_4 \rightleftarrows \square_x Li_{1-x}Mn^{3+}{}_{1-x}Mn^{4+}{}_{1+x}O_4 + xLi^+ + xe^-$$

Additional Li^+ can also be intercalated in $LiMn_2O_4$. This reaction results in a potential plateau of around 2.95 V *vs.* Li^+/Li typical of a two-phase process

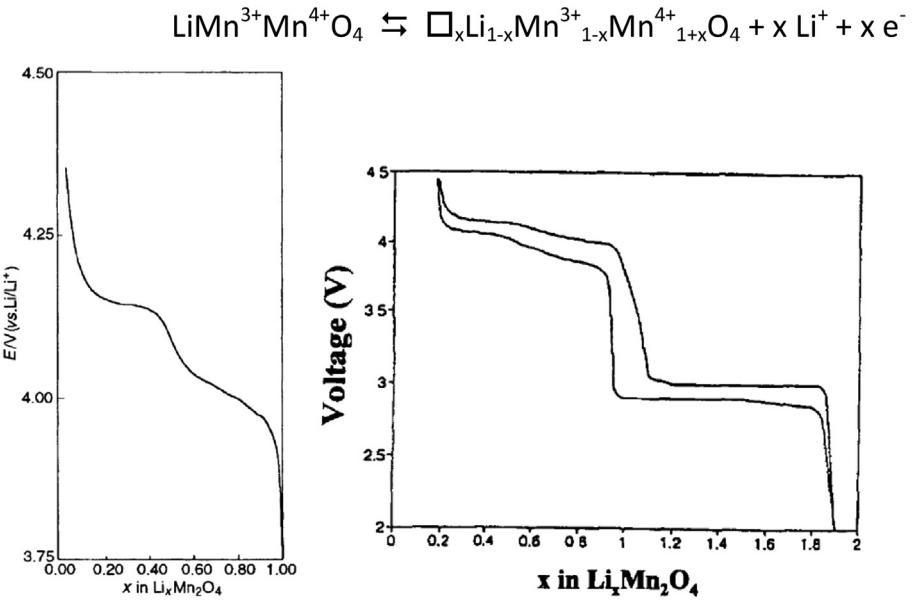

FIG. 2.3 – Left figure: The evolution of the potential of a Lithium/Lithium Electrolyte/$Li_xMn_2O_4$ cell as a function of the amount x of lithium contained in the $Li_xMn_2O_4$ cathode material, with $0 < x < 1$. The potential decreases during the cell discharge – the cell functions as an energy source – while the lithium content in the material increases between $x = 0$ (Mn_2O_4 composition) and $x = 1$ ($LiMn_2O_4$ composition). Right figure: The potential evolution of a Lithium/Lithium Electrolyte/$Li_xMn_2O_4$ cell, depending on the amount of lithium in the material (charge and discharge of the cell), with $0 < x < 1.8$ [10, 11].

(figure 2.3b). It leads to the formation of a $Li_2Mn_2O_4$ phase with a quadratic cell ($I4_1/amd$, $\sqrt{2}a = \sqrt{2}b = 7985$ Å, $c = 9.250$ Å) resulting from a significant distortion of the initial cubic cell induced by a cooperative Jahn–Teller effect [12, 13]. Thus, lithium occupies the 16c octahedral sites of the initial cell, making $Li_2Mn_2O_4$ an ordered NaCl compound [14].

At room temperature, $LiMn_2O_4$-based electrode cycling shows the good reversibility of the lithium intercalation/disintercalation reaction in the high potential '4 Volts' part. However, a progressive loss of capacity is systematically observed, the latter becoming particularly rapid at a higher cycling temperature (55 °C) (figure 2.4). This behavior does not meet requirements of commercial batteries. Numerous studies have attempted to understand the reasons for this and to remedy it. A great number of factors can explain this performance degradation during charge/discharge cycles, among which: formation of the $Li_2Mn_2O_4$ phase on the surface of the particles, generation of Mn^{2+} on the surface of the material (dismutation of Mn^{3+}, formation of Mn_3O_4) [15] followed by dissolution in electrolyte, decomposition of $LiPF_6$ and organic carbonates electrolytes, non-stoichiometry in oxygen, loss of electron percolation in the electrode…

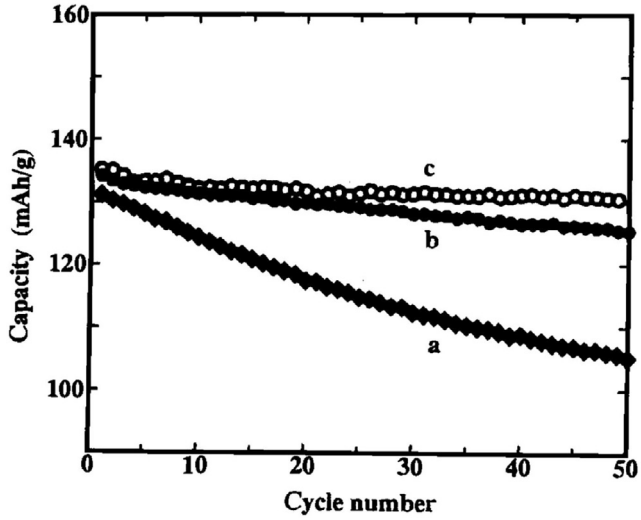

FIG. 2.4 – Specific capacity evolution of $LiMn_2O_4$ cycled at different temperatures between 3.5 and 4.5 V/Li^+/Li in medium 1 M $LiPF_6$ EC : DMC 1 : 2 volume: (a) 55 °C, (b) 25 °C, and (c) 0 °C [16].

The first proposed strategy to limit this capacity loss during cycling is to reduce the Mn^{3+} content in the spinel, to limit the formation of the NaCl-type phase and/or slow down the dissolution of the material. This can be achieved easily by substituting a fraction of manganese with a valence cation of 3 or less and stable in the octahedral environment: $LiM_yMn_{2-y}O_4$ (M = Li^+, Mg^{2+}, Ni^{2+}, Cr^{3+}, Co^{3+}, Al^{3+} among others) [17–20]. As hoped, the electrochemical behavior of these substituted spinels is actually much better, especially for those with an initial average degree of Mn oxidation greater than +3.55 (lithium, magnesium or aluminum doped materials) [21].

At the industrial level, the synthesis of these materials is carried out by thermal treatment at a temperature of 700–900 °C of a mixture based on manganese oxide type γ-MnO_2, lithium carbonate Li_2CO_3 and additives. Commercial powders of spinel materials are generally in the form of pseudo-spherical particles of 10–15 μm in diameter, consisting of crystallites of submicronic size (figure 2.5). The specific capacity obtained is about 105–110 $mAh.g^{-1}$, corresponding to 430 $Wh.kg^{-1}$ (*vs.* Li^+/Li).

Thanks to their interesting compromise in terms of cost and power density, "LMO" spinel materials have so far been mainly used in applications such as electric portable tools or as blends for EV's applications [23]. Global production of these materials has however stabilized to about 15 600 tons since 2016 and their share in cathode production is expected to decrease in ne next decade, due to the expected domination of the layered oxide compositions (figure 2.6) offering a higher energy density and a better life expectancy.

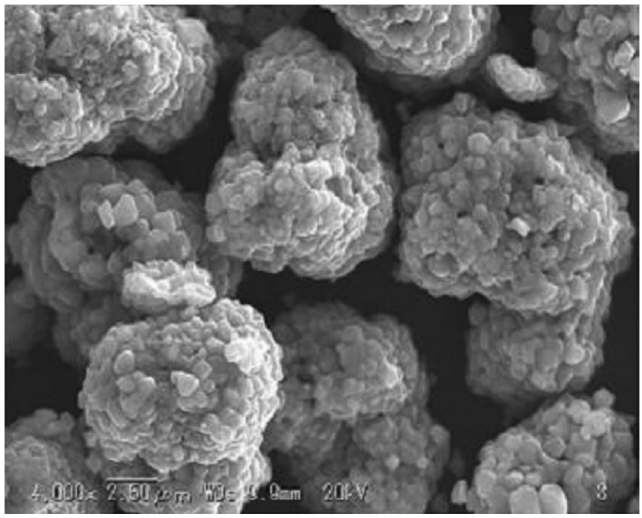

FIG. 2.5 – Morphology of a commercial LMO powder (Nichia) [22].

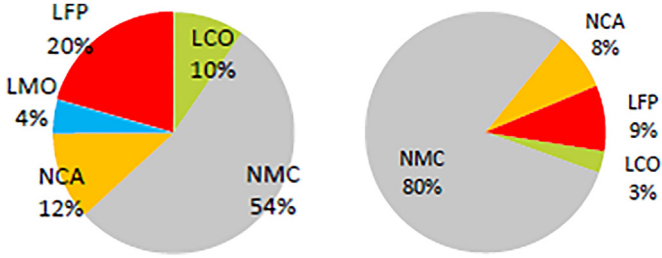

FIG. 2.6 – Cathode active material world's production by composition (left: 2019 : 390 ktons) and 2030 (realistic scenario: 1570 ktons). Nickel-Manganese-Cobalt « NMC »-based compositions will probably be mostly used. Uncertainty remains for LFP composition, free of sensitive materials, which may see a strong resurgence of interest [1].

Manganese Spinels Operating at High Potential – '5 V' Spinels "LNMO"

Work on substituted "LMO" spinels to improve their stability at high temperatures has revealed the presence of processes of de-intercalation/intercalation of lithium at 'high potential', *i.e.* close to 5 V *vs.* Li^+/Li, in particular for "LNMO" spinels of $LiNi_{0.5}Mn_{1.5}O_4$ composition (figure 2.7).

The theoretical specific capacity of this material (corresponding to the exchange of one Li^+ per unit formula) is 147 $mAh.g^{-1}$. Given the potential of 4.8 $V/Li^+/Li$ at which this step takes place, the theoretical energy density of this material is 705 $Wh.kg^{-1}$. This very high value (LCO: 625, NMC: 630, NCA: 695 $Wh.kg^{-1}$),

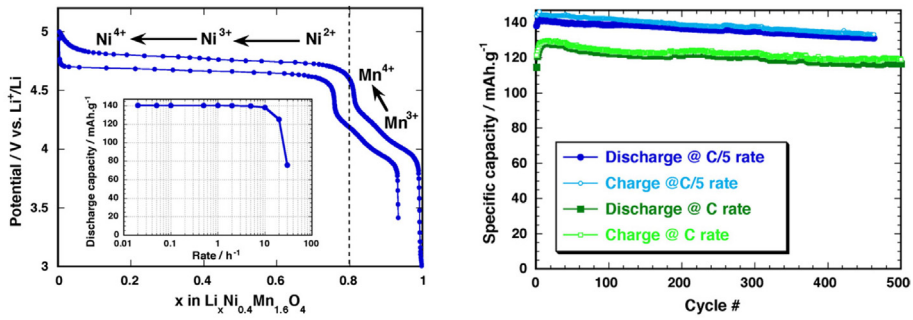

FIG. 2.7 – Left figure: Electrochemical behavior of Li/electrolyte/spinel accumulator $LiNi_{0.4}Mn_{1.6}O_4$ cycled on the 3–5 V domain, highlighting the successive electrochemical steps at different potentials involving manganese and nickel [24]. Right figure: Evolution of the capacity of a Li/electrolyte/spinel $LiNi_{0.4}Mn_{1.6}O_4$ cell cycled on the 3–5 V domain in relation to the number of cycles, under two different charge/discharge rates (C-rate: discharge and charge in 1 h; C/5: discharge and charge in 5 h).

combined with a spinel structure favorable to high load/discharge speeds and a 'cheap' composition, should make it a particularly attractive material for applications in the electric vehicle (EV, HEV, PHEV).

However, the ageing processes identified for the "LMO" "4 V" spinels are also observed with the "LNMO" "5 V" spinels. Moreover, due to the particularly high value of the working potential of this electrode at 4.7–4.8 V, *i.e.* significantly above the electrolyte's electrochemical stability domain, the reaction with the electrolyte is exacerbated. In addition, the electrochemical electrode/electrolyte reactivity of the system leads to a rapid self-discharge of the positive electrode, which, while having little effect on the cyclability of the Li/LNMO half-cells, leads to an extremely rapid loss of capacity in Li-ion configuration due to the imbalance of the $Li_xC_6/Li_{1-y}Mn_{0.5}Mn_{1.5}O_4$ system.

Thus, the introduction of '5 V' electrode materials (including in particular the "LNMO" spinels) into commercial cells remains more than ever an ambitious goal. Many researches are ongoing to assess solutions and eliminate or reduce degradation processes at different levels. These studies aim in particular at limiting the specific surface of the particles; modifying the composition of the spinel material by different doping methods; or modifying the composition of the liquid electrolyte to make it more oxidative-resistant (fluorinated carbonates solvents: FEC, TFEC; sulfonates or nitriles; additives such as tri-allyl phosphate). They also explore other, complementary approches, such as generating a passive film on the material's surface. This type of coating can be carried out by different techniques (sol-gel, ALD or Atomic Layer Deposition,...) of inorganic deposits (carbon, lithiated metal oxides and other lithium compounds). The final objective is to reduce the dissolution of the active material, and act as an artificial "SEI" (Solid Electrolyte Interphase) on the surface of the spinel material and/or the complete electrode. Given that none of these pathways is a 100% effective solution to all issues, a breakthrough combining

different approaches is required to lead to a satisfactory behavior of LNMO materials, and counterbalance its deficiencies.

2.2 Positive Electrode Materials with Lithiated Layered Oxide Structure

Generalities

Materials called lithiated lamellar oxides meet the general $LiMO_2$ formula with M that can be an element or a mixture of elements including Co, Ni, Mn and/or Al. MO_6 octahedrons sharing edges are arranged as sheets (figure 2.8). The cross-leaf space is occupied by lithium ions, which can diffuse in two dimensions into the material (thanks to the layered structure).

The best-known layered oxide is without any doubt the formula material $LiCoO_2$ (LCO). This material was the first layered oxide marketed as cathode material, and, despite many years of research, it remains widely used today, especially for the manufacture of batteries used in mobile phone or laptops. The use of LCO as a battery material was first proposed by Goodenough in 1981; the first commercial

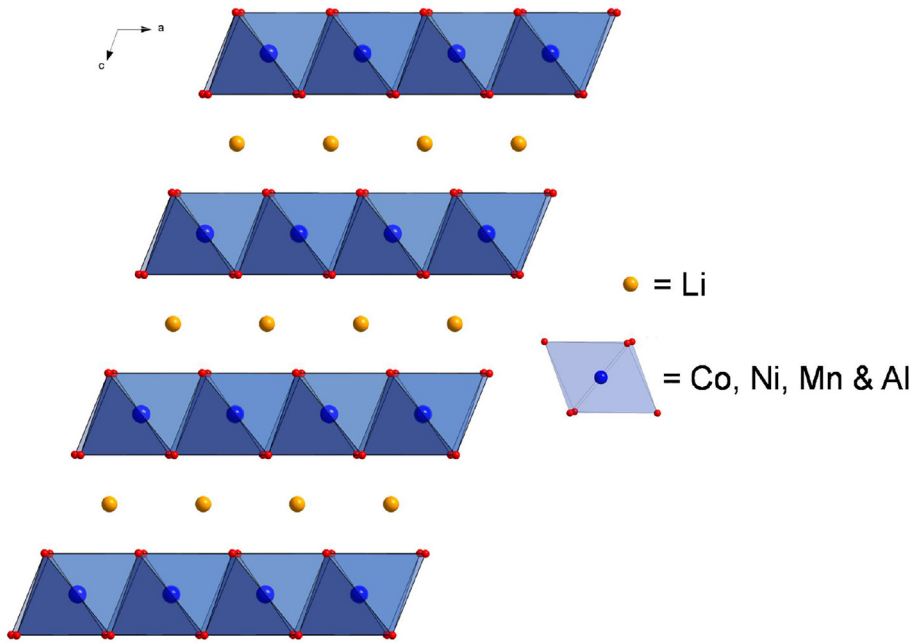

FIG. 2.8 – Structure of a $LiMO_2$ layered oxide with M that can be Ni, Mn, Co, Al or a mixture of these elements.

accumulators using this material were marketed by Sony corporation in 1991 [25–27]. Since then, the major improvements to these materials have been to replace a part of the cobalt with nickel and manganese, or even aluminum [28–31]. These substitutions have increased reversible capacity while reducing toxicity and product cost. The most well-known material developed for this purpose is the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ formula commonly referred to as NMC 111 because metal elements of MO_6 layers have identical concentrations of nickel, manganese and cobalt. When a cell is cycling between 2.7 and 4.3 V, 0.6 lithium can be extracted, thanks to the electrochemical activity of the Ni^{2+}/Ni^{4+} and Co^{3+}/Co^{4+} electrochemical couples, which is particularly interesting because lithium is extracted from the material in a potential area where the electrolyte is stable. For this reason, the main development concerning layered oxides is to increase nickel content in materials. To do this, two routes are followed: the first is to reduce the level of cobalt and manganese contents in the case of $LiNi_xMn_yCo_zO_2$ (NMC) formula materials; the second is to reduce cobalt content and replace manganese with aluminum to obtain $LiNi_xCo_yAl_zO_2$ (NCA) formula materials. Some of these nickel-rich materials are currently commercialized for "high energy" applications (NMC 532, NMC 622 or NCA for electric vehicles); others are still under improvement (NMC 811 and NMC 9-0.5-0.5). While the increase in nickel content in materials allows extracting more lithium at a constant potential, issues related to safety of use happen [29]. The main benefits of each compound are detailed below in this chapter.

To increase the specific capacity, rather than increase the nickel content, another solution is to increase the lithium content in materials. These materials named "over-lithiated layered oxides" have supplementary lithium in their structures. This lithium can be inserted/disinserted thanks to the electrochemical activity of nickel and oxygen couples. This family of materials would significantly improve the energy density of batteries: it is still under research [32].

This part of the chapter provides a brief overview of the state of the art commercial lithium layered oxide structure materials and those still in search.

The "LCO": $LiCoO_2$

The "LCO" material is mainly composed of cobalt. It is mainly used as battery cathode material for applications in mobile electronics (smartphones, laptops, tablets…). The main suppliers of "LCO" in the world are Umicore, L&F, Pulead and B&M, that share 55% of the world market (figure 2.9).

LCO can crystallize in two structures named "high temperature form" ("HT-LCO") and "low temperature form" ("LT-LCO"). The obtained structure depends mainly on the synthesis temperature (>700 °C to obtain "HT-LCO"). The material used commercially is the "HT-LCO", a layered structure with rhombohedral symmetry (space group $R\bar{3}m$ (figure 2.10). In the "LT-LCO", some of the Co atoms substitute lithium atoms in their sites and vice versa. The result is a material with cubic symmetry (spinel with space group Fd-3 m) [33–35].

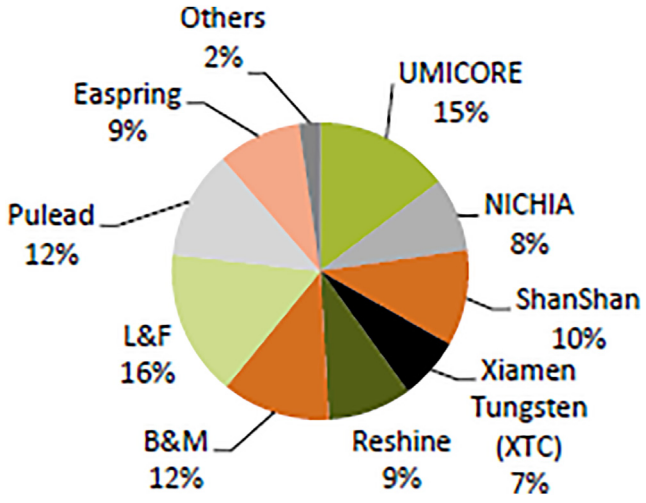

FIG. 2.9 – Main suppliers of LCO materials in the world [1].

The "HT-LCO" structure has a reversible potential of 3.93 V in relation to lithium, while the "LT-LCO" structure suffers from a significant polarization phenomenon (potential of 3.75 V in charge/oxidation versus 3.45 V in reduction/discharge [36, 37]). It is therefore important to take the greatest care to avoid the forming of the LT-LCO phase of spinal structure when synthesizing the material.

The layered structure "LCO" has a hexagonal structure (space group $R\overline{3}m$ with $a = b = 2.816$ Å and $c = 14.08$ Å). The stacking formed by the atoms of Li, Co and O is ABC and the structure can be assimilated as alternating layers of CoO_6 and liO_6 [25, 38, 39].

The insertion and disinsertion of lithium result in several phase modifications [2, 40]. The first modification happens between $0.75 < x < 0.94$. On the corresponding potential tray, two hexagonal phases with different cell parameters coexist ($a = 2.82$ Å, $c = 14.08$ Å and $a = 2.82$ Å, $c = 14.19$ Å^3). Between $0.6 < x < 0.75$, only one hexagonal phase is present. Between $0.56 < x < 0.51$ a monoclinic phase is observed. Between $0.5 < x < 0.35$ a new hexagonal phase is observed. Beyond $x = 0.35$, there are two phases, hexagonal and monoclinical (respectively, $a = 2.82$ Å, $c = 14.26$ Å and $a = 4.91$ Å, $b = 2.82$ Å, $c = 5.02$ Å, $\beta = 111.4°$). The monoclinic phase becomes majority when more lithium is removed (figure 2.11).

Because of these numerous phase changes, $LiCoO_2$ is usually cycled by limiting the extraction of lithium to 0.6 mol of Li per material mole, which represents a theoretical capacity of 140 mAh.g^{-1}. Research is still being conducted to "smooth" these phase transitions to extract more lithium from the material. For small cells, the "LCO" material is often preferred, but for larger batteries, manufacturers favor another lamellar oxide named "NMC".

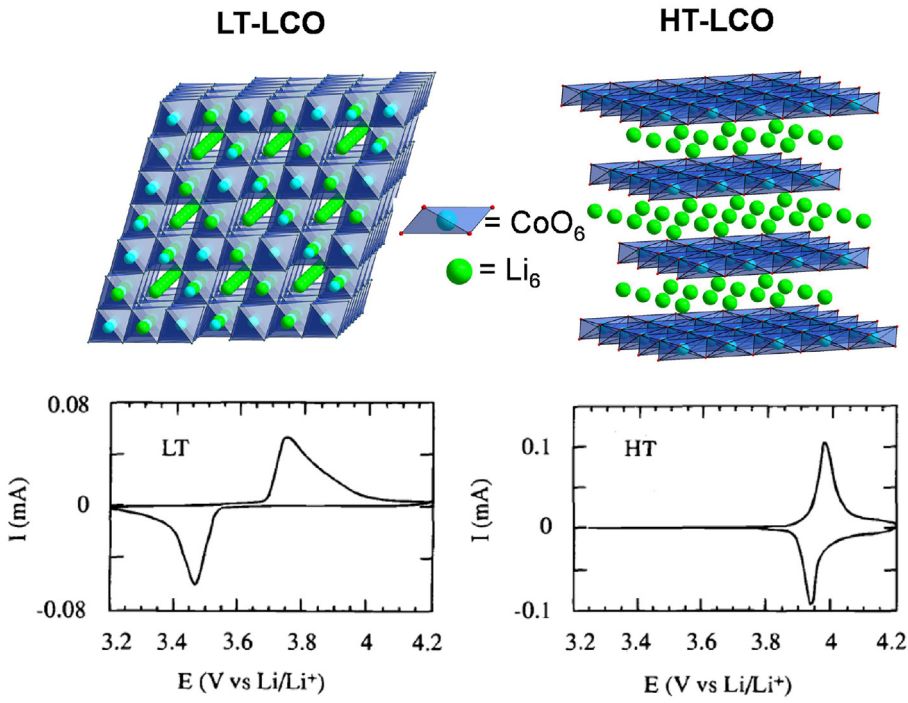

FIG. 2.10 – Associated structures and voltammetries of "LT-LCO" and "HT-LCO" [36]. Potential scanning voltammetry is an electrochemical spectrometer technique that reveals the behavior of active electrode materials: a Lithium/liquid electrolyte/active cathode material cell is submitted to a slow, step-by-step scanning of potential from its equilibrium position. At each stage of the voltage scan, the average current (supplied or consumed by the cell until it reaches its electrochemical equilibrium state) is recorded.

The NMC: $LiNi_xMn_yCo_zO_2$

NMCs consist of a mixture of cobalt, nickel and manganese. The result is a higher energy density and a lower material cost than the LCO material. This family of materials is often used in combination with "LMO" for the manufacture of cathodes for electric vehicles. For example, car manufacturers such as Nissan, Toyota, Mitsubishi and Honda use "NMC" batteries. The main suppliers of materials are Umicore and ShanShan. Battery manufacturers such as LG, Panasonic and Samsung control the production of their proprietary "NMC" material to meet their own needs [1] (figure 2.12).

The formulation $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (commonly referred as "NMC 111") is proposed by Ohzuku in 2001 [42]. The theoretical capacity of this material is 277 mAh/g when 1 mol of lithium is removed. Ohzuku studies the behavior of the material in cycling and shows that the cell parameters change rapidly beyond $x = 0.6$ (figure 2.13). Beyond this value, the life of the cycling material is

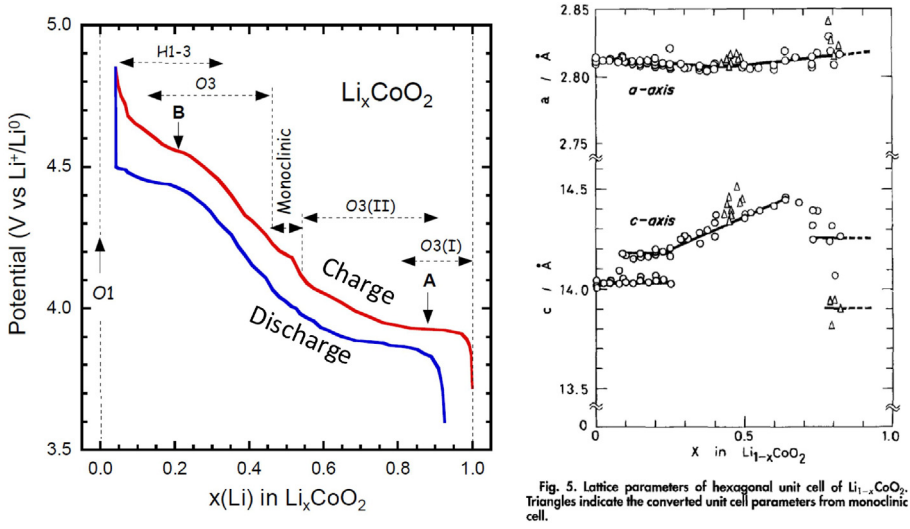

FIG. 2.11 – Evolution of the LCO structure in relation to cycling [2, 41].

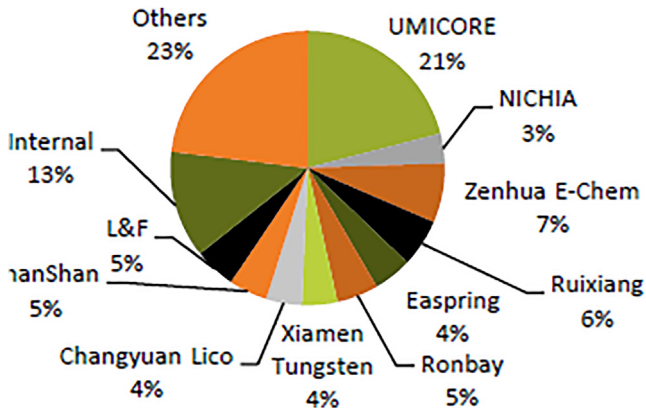

FIG. 2.12 – Leading NMC materials suppliers in 2019 : China represents 65% of the market [1].

significantly affected. Therefore, the cycling point of this material is limited to about 4.3 V and the capacity reached by this material is 160 $mAh.g^{-1}$.

For several years, there has been a gradual increase in the nickel content of the "NMC". By increasing the amount of nickel, it becomes possible to disinsert and reinsert a greater amount of lithium while remaining in the field of electrolyte stability. Demand for "NMC 111" has strongly reduced during the past 5 years: this composition has been replaced by compositions such as $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (respectively, "NMC 622" and "NMC 811"), which make it possible to manufacture batteries with even higher energy density (figure 2.14).

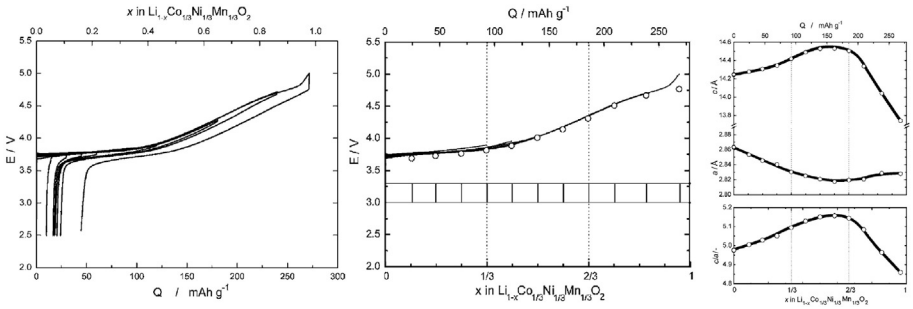

FIG. 2.13 – Electrochemical performance and structural evolution of an NMC 111 based on the amount of lithium dis/insert [43].

These materials with a high nickel content are commonly referred to as Ni-Rich. The theoretical capacity of the materials can be directly related to the amount of nickel in the oxides. The nickel contained in the structure can be completely oxidized from its oxydation state 2–3 to 4+ while it is difficult to oxidize cobalt beyond 3.6 + without oxidizing the oxygen of the structure [32, 44]. It is important to note that in these structures, manganese oxidation state is 4+ and remains inactive in cycling conditions.

We see that it is interesting to increase the density of energy of materials by increasing the ratio of Ni/Co concentration in the material. Another benefit of this substitution is the small amount of manganese contained in the structure. The average potential in the first cycle decreases when the amount of manganese decreases and the nickel content increases, allowing to extract more lithium in the first charge in the same voltage windows [32, 44]. It should be noted that, on the other hand, the discharge potentials are similar regardless of the composition of the material. The capabilities of the manganese-poor "NMCs" are therefore higher.

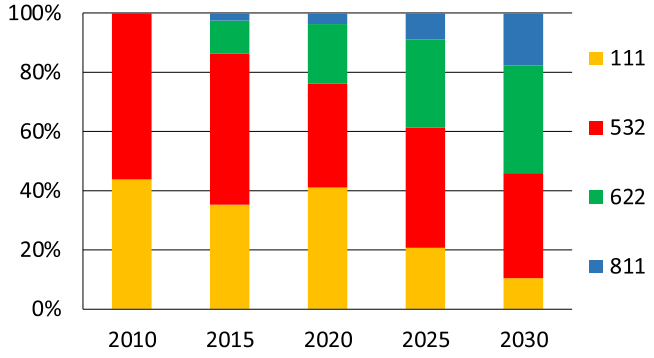

FIG. 2.14 – Evolution of the composition of "NMC" materials over time [1].

Thus, by changing the formulation and substituting more and more cobalt with nickel, it is possible to increase the energy density while reducing the cost of raw materials (cobalt being the most expensive element).

However, the increase in the nickel content of the material unfortunately does not have only advantages: there is a price to pay for it (figure 2.15).

The stability of the material, and thus the safety of its use, is directly related to the amount of nickel in the structure. The more nickel the structure is enriched with, the less thermally stable the material [29]. In addition, the battery cycling behavior is also degrading when the nickel content of the cathode material increases. Battery capacity is decreasing, and the number of charge/discharge cycles that can be made with high nickel-rich materials is currently below the specifications required by car manufacturers. This reduction in cycling capacity is partly explained by the volume expansion of the electrode and also by an evolution of the surface structure of the materials (the latter evolves gradually from a lamellar structure to a rocksalt or spinel structure) [29, 32, 45, 46].

Among the materials called "Ni-Rich", the "NMC 532" and "NMC 622" are now commercial and used in recent generations of electric vehicle batteries. Much of the research effort currently aims at stabilizing the "NMC 811" and "NMC 9-0.5-0.5" materials. As mentioned above, the lack of stability of these materials during cycling can be mainly attributed to an evolution of the material's surface. The solutions envisaged to stabilize these materials imply therefore the modification of their surface [47]. To this end, two approaches are explored: "coating" solutions, or the creation of a "core shell" structure. In the case of a "coating", a thin layer of a stable material is deposited on the surface of the "Ni-rich" particles to stabilize the

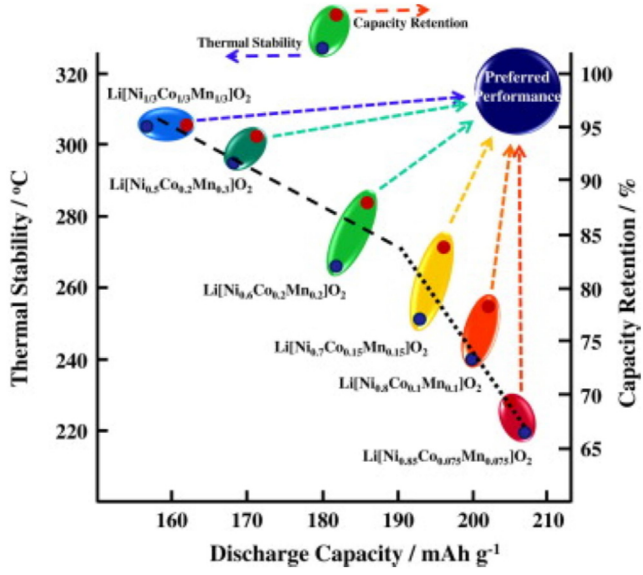

FIG. 2.15 – Advantages and disadvantages of different NMC compositions [29].

electrolyte/material interface. Different types of "coating" are assessed in the literature: fluorinated materials (AlF_3…), glasses, but most of the materials used are oxides (Al_2O_3…) [48–53]. The effectiveness of the coating has been demonstrated on numerous occasions, and coated materials are already being marketed. However, the concept of "coating" can be pushed further by creating a "core–shell" structure. The core shell can be seen as a multilayer composite material [54–59]: a very rich nickel material is fully covered by a thick shell of a more stable material, usually with a high manganese content. The main problem with this solution is the appearance of cracks in the material during prolonged cycling. In fact, nickel-rich or nickel-poor materials do not exhibit the same volume expansion during cycling, resulting in particle stress and rupture. As a result of this limitation, a new concept called "full-gradient concentration" has recently been proposed [60–62]. In this material configuration, the internal and external compositions of the particles are different. The core of the particles is made of nickel-rich material and the surface is rich in manganese, but the material is not multi-layer: the concentration of nickel and manganese changes gradually througout the particle's thickness. This allows to homogenize the volume expansion and makes it possible to considerably improve the cyclability of the material. The main disadvantage of this concept is the difficulty encountered to perform a synthesis that must tune the material's composition at the nanoscale (figure 2.16).

The "NCA": $LiNi_xCo_yAl_zO_2$

"NCA" materials also belong to the family of layered oxides. In this case, the material is composed of nickel, cobalt and aluminum. This material is used not only in power portable electronics equipment but also in power portable tools requiring a good power/energy compromise. It is also important to note that a large part of the production of NCA material is dedicated to the automotive sector, particularly for

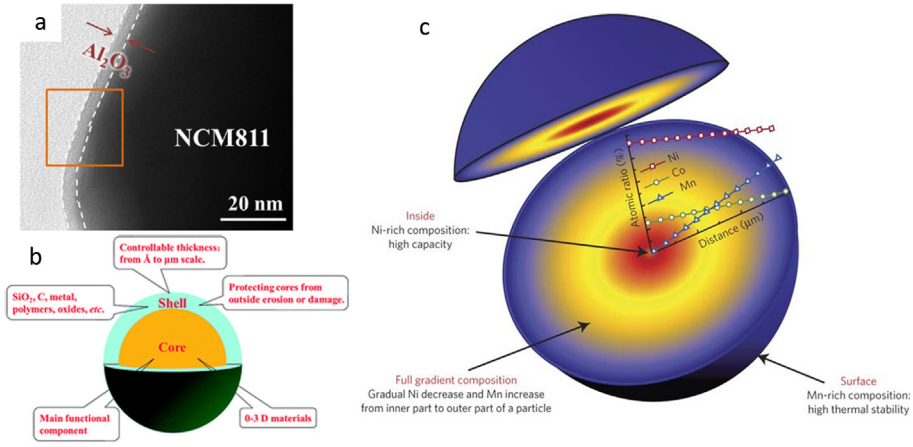

FIG. 2.16 – Comparison of (a) "coating", (b) a "core shell", and (c) a "full-gradient concentration" [48, 54, 60].

the supplying electric cars of the Tesla brand. Sumitomo is the world's leading supplier of "NCA" material because it supplies Panasonic and Tesla companies (figure 2.17).

NCA materials are high nickel layered oxides. The formula material Li $(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ is currently the only commercial representative of this subfamily of compounds. This material can reach capacities close to 200 $mAh.g^{-1}$ [63–65]. In NCA-type layered oxides, nickel provides high capacity, cobalt improves power performance and limits lithium-metal exchange in the structure, whereas aluminum improves the structural and the thermal stability of the material.

Similarly to NMC, the nickel content is likely to increase in the coming years in order to increase the specific capacity of these materials (figure 2.18).

The issues associated with these materials and the optimization perspectives explored are very similar to those of "NMC" materials: problems related to the modification of the structure of the material during cycling also lead to problems of

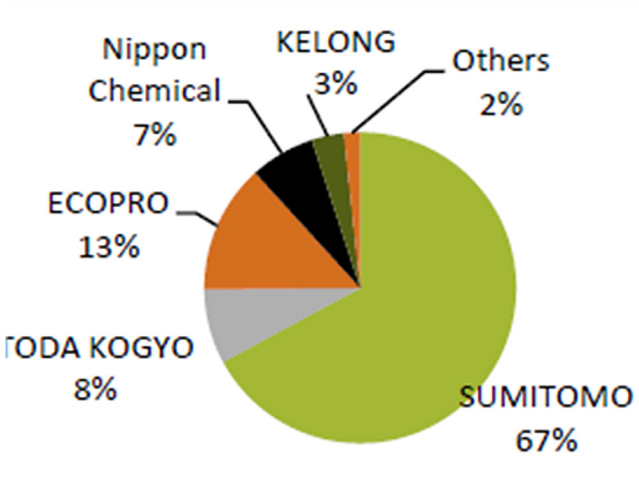

FIG. 2.17 – Leading NCA materials suppliers in 2019 [1].

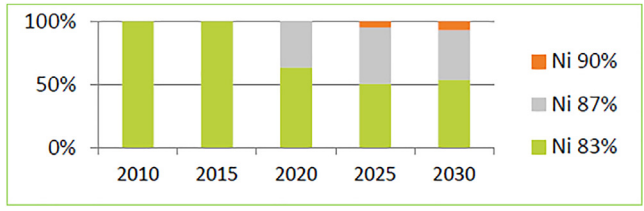

FIG. 2.18 – Expected evolution of the composition of the NCA materials over time [1].

stability in cycling [66]. The "coating" and "core–shell" are also studied to stabilize the material/electrolyte interface [67–71].

The Lithium Rich Layered Oxides

Layered oxides commonly referred to as "Li-rich" are not commercial materials. Indeed, these high capacity materials present many issues that have not yet been resolved. The literature dealing with these materials is extremely dense and we will here only briefly explain the advantages and disadvantages of this material family.

The "lithium rich" layered oxides can be seen as a mixture of $LiMO_2$ and Li_2MnO_3 compositions [72–74]. It is possible to index their structures according to two groups of space, $R\overline{3}m$ if indexed according to the $LiMO_2$ part or C2/m if indexed with the Li_2MnO_3 part [75]. The local structure of the material is controversial among scientists, some consider the structure as a composite material (made up of Li_2MnO_3 independent sheets and $LiMO_2$ sheets), others consider the material as a solid solution (figure 2.19) [76, 77]. This explains why it is possible to write the same formula for a material in two different ways: for example, $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (compact formulation) may also be written in composite form $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Mn_{0.5}O_2$.

In all cases, the $LiMO_2$ and Li_2MnO_3 components provide a compact cubic structure defined by oxygen atoms, where all octahedral sites are filled by alternating lithium, transition or lithium layers, and transition metals. An X-Ray diffraction analysis (XRD) of this material reveals that, with the exception of peaks between 20 and 25°, each peak can be indexed with a hexagonal structure of the type, α-$NaFeO_2$ (space group $R\overline{3}m$) [78]. The peaks between 20 and 25° result from

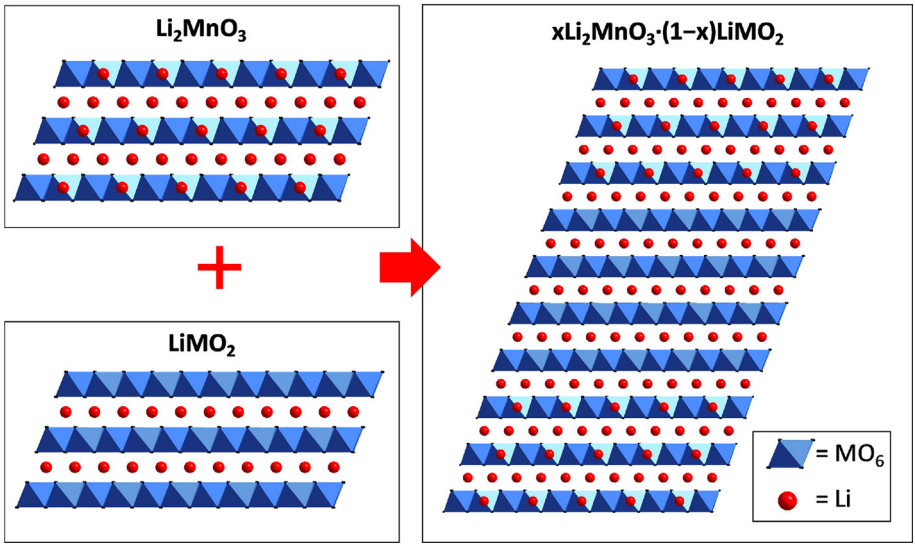

FIG. 2.19 – Structure of a Li-rich layered oxide (010).

an order between lithium and metallic ions in transition metal sheets, giving a Li_2MnO_3 type structure with a C2/m space group (figure 2.20).

The particularity of this material lies in the oxidation mechanisms used to extract lithium from the structure. Typically, the specific capacity achieved with these materials is much higher than the theoretical capacity calculated by Ni^{2+}/Ni^{4+} couple (manganese remains at oxidation level 4 + and is therefore inactive). For example, $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$, for which the theoretical capacity is 126 $mAh.g^{-1}$, but the specific reversible experimental capacity is greater than 250 $mAh.g^{-1}$, can be cited (figure 2.21). This phenomenon has been particularly studied in the literature in order to elucidate the origin of this additional capacity.

During charge, the first part of the curve can be attributed to the oxidation of the transition metals, then a plateau corresponding to the activity of the oxygen

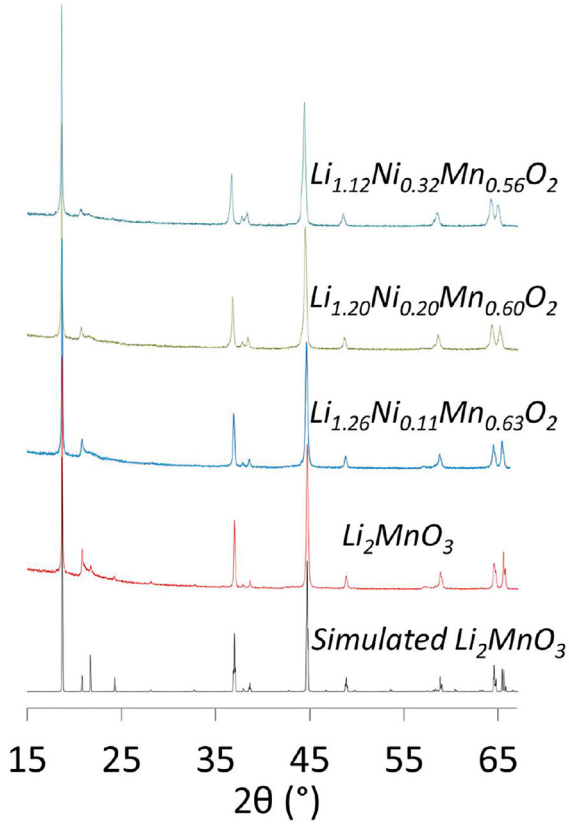

FIG. 2.20 – Example of XRD (X-ray diffraction) analysis of different Lithium rich layered oxides [79].

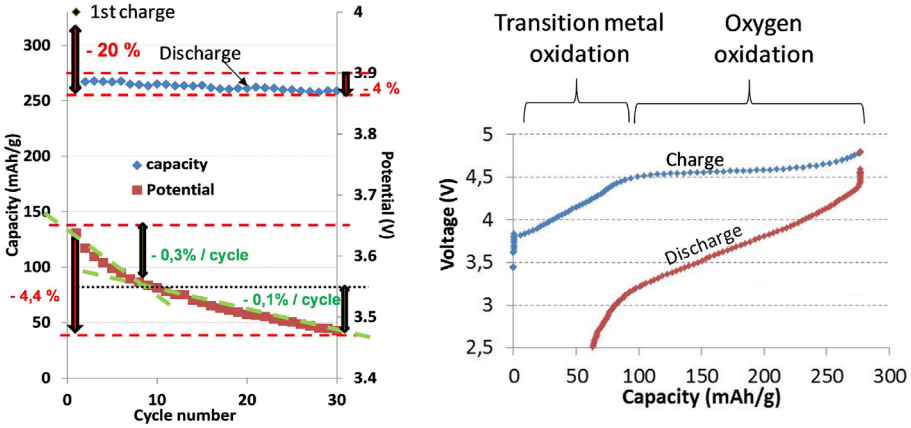

FIG. 2.21 – Highlighting the drawbacks of lithium-rich and the galvanostatic curve of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ [ref: Source CEA].

contained in the structure can be observed [80–83]. It has been shown that during this partially reversible cycle, oxygen is found in the form of peroxides or superperoxides [84]. The result is a very high capacity with an inexpensive material, which justifies the great enthusiasm of many research groups to optimize this material. In return for these advantages, lithium rich layered oxides suffer disadvantages that prevent their commercialization (figure 2.21) [85, 86]. The first and main limitation of these materials is the decay of the average potential during cycling, resulting in a loss of energy density and making it difficult to measure the battery state of charge. Many "coating" and doping agents have been considered, but none of these solutions has so far been able to solve the problem [87, 88]. Phenomena involved in this material are very complex and many studies have focused on their understanding [73, 89]. It is shown that the drop in potential during cycling is not due to a single phenomenon, but to the contribution of various mechanisms that are well summarized by Passerini *et al.* [90]. Peralta *et al.* show that the drop in potential during the first cycles is due to two phenomena occurring at high potential: activation of Li_2MnO_3 sheets and migration of some of the transition metals into the lithium interslab [79]. Currently, the only way to stop material evolution is to cycle below 4.3 V, but unfortunately, under these conditions, the reversible capacity recovered is too low to make this material competitive (figure 2.22). To date, many groups are still working in hope to make this material viable.

Several possible solutions have recently been proposed in the literature to limit voltage decay, for example, the possibility of using O_2 layered phases instead of O_3, or by inserting defects into the structure, or by replacing manganese with ruthenium [84, 91, 92].