Current Natural Sciences

ENERGY

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

Li-ion Batteries

Development and Perspectives

Science Press
edp sciences

Current Natural Sciences

ENERGY

Li-ion Batteries

Development and Perspectives

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

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.

ISBN : 978-2-7598-2555-4

9 782759 825554

Price: 109 €

edp sciences

www.edpsciences.org

Current Natural Science

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

Li-ion Batteries

Development and Perspectives

Science Press
edp sciences

Printed in France

EDP Sciences – ISBN(print): 978-2-7598-2555-4 – ISBN(ebook): 978-2-7598-2567-7
DOI: 10.1051/978-2-7598-2555-4

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 $\mathrm{Wh.kg^{-1}}$ and 1000 $\mathrm{Wh.L^{-1}}$ 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.

Severine JOUANNEAU SI LARBI,
Head of the Electricity and Hydrogen Department
for Transport at CEA/LITEN

DOI: 10.1051/978-2-7598-2555-4.c901

Contents

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 8

CHAPTER 9

CHAPTER 10

CHAPTER 11

CHAPTER 12

CHAPTER 13

CHAPTER 14

CHAPTER 15

CHAPTER 16

CHAPTER 17

CHAPTER 18

CHAPTER 19

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.

DOI: 10.1051/978-2-7598-2555-4.c001

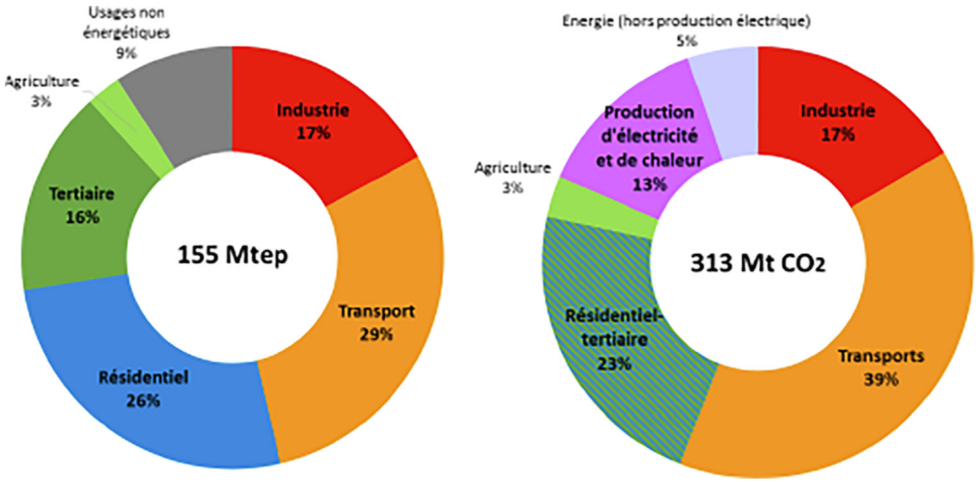

Fig. 1.1 – (a) (left) **Final Energy Consumption by sector, France, 2019**. Transport accounts in France for ≈ 30% of the overall final energy consumed (≈150 MToe), and (b) (right) **GHG emissions corresponding to final energy consumption in France in 2019**. Transport accounts for ≈ 39% of the corresponding 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 fith 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 $\mathrm{Wh.kg^{-1}}$ to almost 270 $\mathrm{Wh.kg^{-1}}$. 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 ($\mathrm{Wh.kg^{-1}}$ or $\mathrm{Wh.L^{-1}}$) and/or power density ($\mathrm{W.kg^{-1}}$), 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

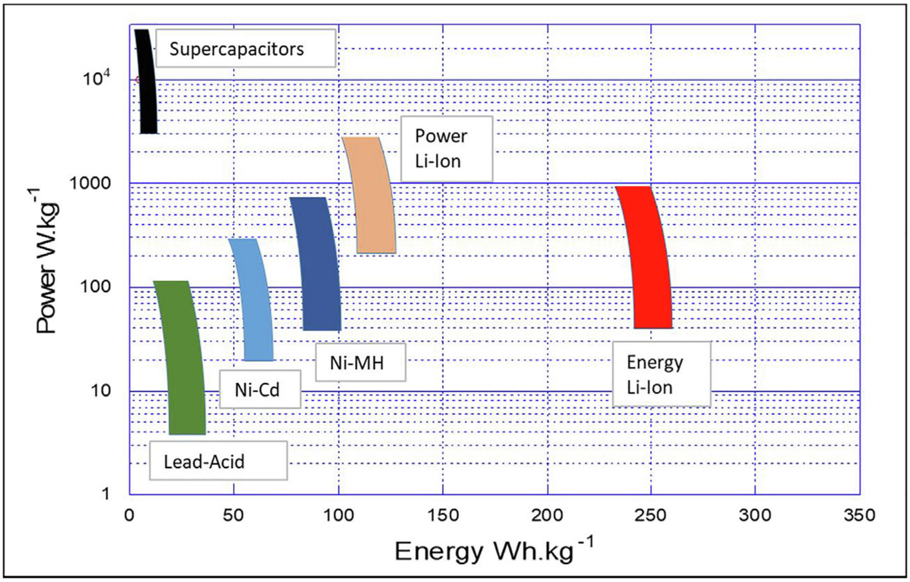

Fig. 1.2 – Ragone diagram of various commercialized battery technologies.

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

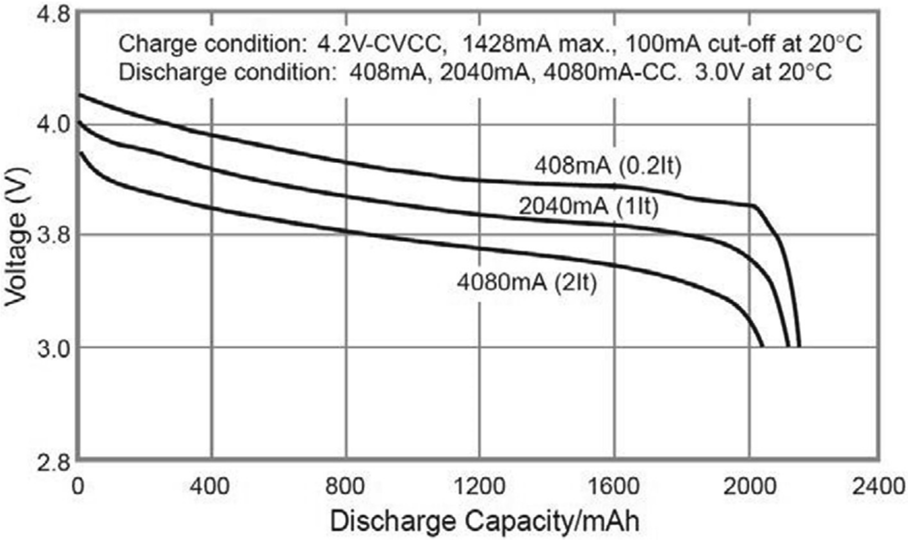

FIG. 1.3 – Discharge curves of a Li-ion cell at various discharge rates: Panasonic CGR18650C [9].

Li-ion cells is focused on the development of All-Solid-State Li-ion Batteries and liquid electrolytes. He is managing several collaborative industrial and European projects.

Romain TESSARD has been a research engineer at the CEA for 10 years, after 10 years as an engineer and R&D project manager for consumer electronic products. He has specialized in the characterization and selection at cell level of storage devices, mainly lithium-ion cells, with a wide knowledge of suppliers and markets.