

Empowering the Future: Exploring the Construction and Characteristics of Lithium-Ion Batteries

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How to cite this paper: Dan, D.T. (2024) Empowering the Future: Exploring the Construction and Characteristics of Lithium-Ion Batteries. *Advances in Chemical Engineering and Science*, 14, 84-111.

<https://doi.org/10.4236/aces.2024.142006>

Received: February 2, 2024

Accepted: April 27, 2024

Published: April 30, 2024

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Abstract

Lithium element has attracted remarkable attraction for energy storage devices, over the past 30 years. Lithium is a light element and exhibits the low atomic number 3, just after hydrogen and helium in the periodic table. The lithium atom has a strong tendency to release one electron and constitute a positive charge, as Li^+ . Initially, lithium metal was employed as a negative electrode, which released electrons. However, it was observed that its structure changed after the repetition of charge-discharge cycles. To remedy this, the cathode mainly consisted of layer metal oxide and olive, e.g., cobalt oxide, LiFePO_4 , etc., along with some contents of lithium, while the anode was assembled by graphite and silicon, etc. Moreover, the electrolyte was prepared using the lithium salt in a suitable solvent to attain a greater concentration of lithium ions. Owing to the lithium ions' role, the battery's name was mentioned as a lithium-ion battery. Herein, the presented work describes the working and operational mechanism of the lithium-ion battery. Further, the lithium-ion batteries' general view and future prospects have also been elaborated.

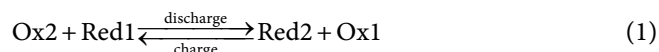
Keywords

Lithium-Ion Batteries, Battery Construction, Battery Characteristics, Energy Storage, Electrochemical Cells, Anode Materials, Cathode Materials, State of Charge (SOC), Depth of Discharge (DOD), Solid Electrolyte Interface (SEI)

1. Introduction

A battery is a device intended to store electrical energy to be able to use it later. It is composed of several elementary cells connected in series and/or parallel to

obtain the desired voltage and capacity. The elementary cell consists of a positive electrode (cathode) and a negative electrode (anode) immersed in an electrolyte [1]. The functioning of a battery is based on a chemical reaction of oxidation-reduction that allows the reversible exchange of ions between the positive and negative electrodes, throughout the charge or discharge cycles. Once these electrodes are connected (at the terminals), two electrochemical reactions take place to produce simultaneously (oxidation at the anode and reduction at the cathode) giving rise from the passage of electric current. The overall reaction of the system is therefore:



Each of the electrodes is therefore composed of materials that can be inserted or uninserted in their crystal structure. For battery designers, the problem is finding pairs of materials capable of releasing or inserting these ions the most quickly and as long as possible to increase battery performance (life cycle, energy density, etc.). **Figure 1** compares the energy densities of various current electrochemical storage technologies. Indeed, to date, the lithium batteries have a higher mass density (180 Wh/kg) than that of Nickel-Cadmium Ni-Cd (75 Wh/kg) or Nickel metal hydride Ni-MH (100 Wh/kg).

Designed more than 30 years ago, so-called “lithium-ion” batteries have become ubiquitous in our daily lives. They can be very small in size in a mobile phone or assembled by dozens in an electric car. They are the subject of intense research around the world given the importance of storing electricity [3]-[10].

Currently, the transport sector is changing, especially the automotive area. Facing regulatory pressure demand from customers, and the ecological awareness of citizens, car manufacturers have launched a general movement to reduce pollutant and CO₂ emissions from vehicles. The development of hybrid and pure electric vehicles belongs to this underlying trend.

The electrification of transport involves incorporating, more or less massively a reversible electrical storage system within vehicles. Today lithium-ion (Li-ion) batteries have established themselves in the field of transport, mainly because of their very good performance in terms of energy and power density.

2. Lithium Batteries

2.1. Lithium-Metal

Usually, there are two types of lithium batteries developing: lithium-metal battery (Li Metal) and lithium-ion battery (Li-ion). The difference between the two technologies is related to the nature of the material used as anode. Li-Metal batteries implement a metallic deposit of lithium at the negative electrode and the positive electrode. Thus, during the discharge, the lithium ions (Li⁺) are stripped from the lithium anode and migrate through the electrolyte to insert into the sites provided by the structure of the insertion compound cathode. Conversely, during recharging, the Li⁺ ions are extracted from these sites, to go deposit on

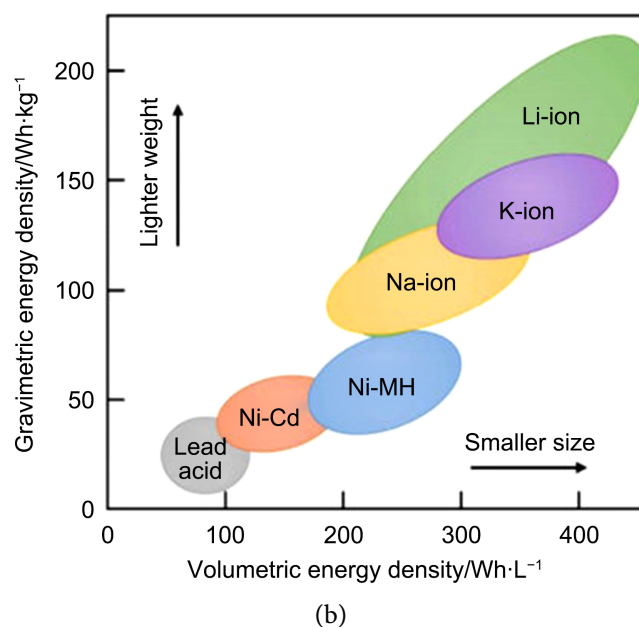
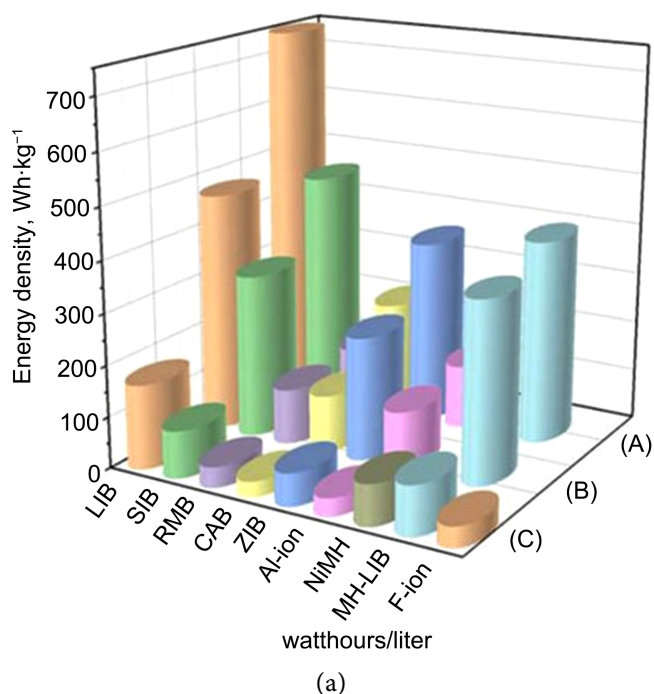


Figure 1. The energy density of major energy storage devices [2].

the surface of the metallic lithium electrode. The transfer of a Li^+ ion in the internal circuit of the accumulator is compensated exactly by the passage of an electron in the external electric circuit, thus generating an electric current. Nevertheless, the violent reaction of lithium metal in the presence of oxygen and the deposition of lithium on the anode with each recharge, induce the problem of dendrite formation which causes thermal instability sometimes leading to battery explosion. Therefore, very few manufacturers have now oriented their choice towards this technology.

2.2. Lithium-Ion

The principle of operation is based on the same principle as Li Metal accumulators, with the only difference; the anode material is an insertion compound instead of a pure lithium electrode.

Given the increase in energy storage needs in a large number of applications, the development of cheaper materials and components leading to more efficient batteries is therefore essential.

3. Different Constituents of a Li-Ion Battery

Li-ion batteries are composed of active materials (cathode, anode, electrolyte) and inactive materials (separators, current collectors, etc.). We give below some examples of the main materials used.

3.1. Cathode Materials

The cathode is the electrode capable of delivering one or more ions (here Li^+) in charge and performing the opposite phenomenon in discharge. Positive electrode materials that are currently marketed, can be grouped into three groups, according to their crystallographic structures: lamellar oxides (NMC, etc.), materials polyanionic (LFP, etc.), and spinel structure oxides (LMO, etc.). These three groups of compounds show different properties: specific capacity, potential, etc. **Figure 2** shows the potential curves corresponding to these different materials. The lithium cobalt mixed oxide (LCO) material has the best characteristics in terms of potential and specific capacity. However, the price of cobalt being high other families have generated interest where the amount of Cobalt is reduced and compensated by other less expensive materials such as manganese or aluminum.

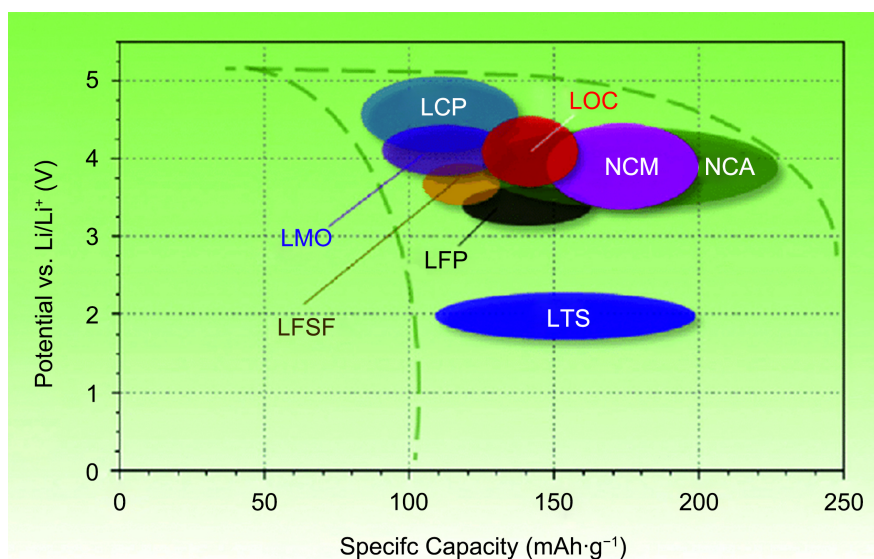


Figure 2. Potential curves as a function of specific capacities for the different cathode materials [11].

On this account, the lithium iron phosphate, Li_xFePO_4 , which we will note below LFP, belongs to the family of promising materials to replace LCO-type cathodes for automotive applications. Despite its potential close to 4V vs. Li/Li^+ which confers a moderate theoretical specific energy, it however has the advantage of not integrating metals such as cobalt (Co) or nickel (Ni) into its composition.

3.2. Anode Materials

The two main families of anode materials used today are graphite (and its derivatives) and lithium titanate (LTO). As a materials negative electrode, Graphite has a large theoretical mass capacity (370 mAh/g) [12]. Lightweight, he is also inexpensive and has a very low average potential, close to that of lithium metal. Nevertheless, the formation of a layer called “Solid Electrolyte Interphase” (SEI) on its surface (passivation process) is the source of a large part of the aging of lithium-ion batteries. This type of material is widely used and is present in almost all lithium-ion batteries currently on the market: In addition, LTO is not subject to massive passivation like graphite, which makes it a material with a very long life. Moreover, its structure allows it to accept high load regimes, unlike graphite. These qualities make lithium titanate a credible alternative to graphite, especially for power-oriented applications. On the other hand, its high potential plateau (1.55 V vs Li/Li^+) does not make it possible to obtain a high energy density and the presence of titanium makes also this electrode more expensive than graphite.

3.3. Electrolyte

The electrolytes used in Li-ion batteries consist of a salt of lithium (ex: LiPF_6 , LiBF_4) dissolved in a mixture of organic solvents to obtain a suitable electrolyte: high dielectric constant, low viscosity, good conductivity, a wide range of thermal stability (from -20°C to 70°C), a wide range of electrochemical stability (from 0 to 5 V vs Li^+/Li). Commercialized Li-ion cells contain liquid electrolytes [13] which are produced by incorporating into a solvent organic liquid highly dissociated lithium salt. The most widely electrolyte used today is thus lithium hexafluorophosphate, LiPF_6 [13]. It exists also solid electrolyte batteries [13] [14]. The latter is a gelled polymer of solid consistency, which makes it possible to give the cell a flexible envelope and the shape wanted. But the performance is also altered since the specific energy is reduced.

3.4. Separator

The separator is a membrane made up of one or more layers of polymers that separate the active materials. It is thanks to this separation of the charge that the battery can produce electricity. During the discharge or charge cycle, the ions move from one electrode to the other passing through the separator, while the electrons migrate from the negative electrode to the positive electrode and pass

through the external circuit. The main characteristic of the separator is its porosity.

3.5. Current Collectors

The current collectors are the support elements for the active material on the electrodes. As their name suggests, it is through them that electrons are collected/distributed to the different regions of the electrode and on a smaller scale, to the different particles of active material. They are found in the form of metal sheets whose thickness varies from about ten to about fifty microns, depending on the type of cell and the application for which it is intended. The conductive compounds found are aluminum, copper, or nickel.

3.6. The Packaging or “Casing”

Current battery technologies come in different cell formats. For a given application, this directly influences the overall packaging of the ESS due to mechanical properties, resulting in mass and thermal management.

Generally, electrodes are either stacked or coiled. Cell packing can be flexible or rigid. We, therefore, distinguish three types of cells: “pouch”/“stack”, cylindrical and rolled up crushed (or “jelly roll”).

3.7. Characteristics of an Electrochemical Cell

A lithium-ion battery can be defined by several quantities or indicators. Issues from the literature [11], let's look here at the different definitions that are generally used which will be used in this thesis.

3.7.1. Capacity

Storage capacity represents the amount of charge the battery is capable of storing in chemical form. In general, the capacity of a battery corresponds to:

$$C = \int_{t_i}^{t_f} \frac{I_{\text{batt}}}{3600} dt \quad (2)$$

With C , the capacity of the cell (Ah), I_{batt} , the current delivered (A), to the initial time (s), and t_f the final time (s). Battery manufacturers often provide rated capacity which is achieved at rated discharge current, within voltage limits specified, and under given temperature conditions.

3.7.2. Voltage

Expressed in volts, the voltage (or electromotive force, reduced to E.m) corresponds to the potential difference that exists between two terminals of an accumulator. When this is at equilibrium or in an open circuit, we then speak of no-load voltage or OCV. This voltage is directly linked to the technology used within the accumulator because it depends directly on the activities of the active species which often vary with the state of charge and sometimes with temperature. When the circuit is closed, we then speak of a drop in tension, which corresponds to the decrease (respectively the increase) of the tension observed when

the battery is traversed by a current in the direction of the discharge (respectively the load).

3.7.3. The Current Regime

In the description of the batteries, the discharge or, by extension, charging currents are generally expressed as a function of the discharge rate (“C-rate”). It defines a current value normalized about the capacity of the battery. For example, for a battery with a capacity of 100 Ah, the discharge rate of 1 C (100A) means that the battery will be fully discharged in one hour. A rate of 0.5C (50A) will discharge the cell in 2 hours and so on.

3.7.4. Power/Energy

A performance indicator of an electrochemical cell is the electrical power that it can deliver. Power, measured in watts (W), is the amount of electricity that a cell can supply at a given time. Like capacity, battery energy represents an amount stored by the cell. This time, it takes into account the voltage variation that occurs across the terminals of the cell. It is, in general, measured during the same protocol as the capacity. It corresponds to:

$$E = \int_{t_i}^{t_f} \frac{V_{\text{cell}} \cdot I_{\text{batt}}}{3600} dt \quad (3)$$

With E, the exchanged energy of the cell (Wh), I_{batt} the delivered current (A), V_{cell} , the cell voltage (V), to the initial time (s), and t_f the final time (s).

3.7.5. Internal Resistance

In general, in electricity, resistance is the property of a body to oppose the passage of an electric current. In operation, when the battery is traversed by a current, there appears a voltage drop between the voltage at rest (OCV) and the voltage of the element, which characterizes the resistance of the battery to deliver the requested current [14]. Expressed in ohm, its value can vary within a wide range depending on the electrochemical couples used, the materials, the state of charge of the accumulator, the temperature, and well other parameters. Electrochemically, the internal resistance of the Li-ion battery has for origin three resistive phenomena: ohmic resistivity, resistivity of transfer of matter, and resistivity due to charge transfer [11]. These last two resistors of electrochemical origins require specialized techniques to dissociate them (electrochemical impedance spectroscopy for example). They are often combined in a heat source. Resistance is also related to the maximum power available while the capacity defines that of the maximum energy that can be used.

3.7.6. State of Charge

The state of charge is one of the most used estimators when talking about the battery. More rigorously, the state of charge of the accumulator which we will designate below by the acronym SOC (“State of Charge”) represents the ratio of the number of electric charges accumulated by the accumulator and of the number of electric charges that it is capable of storing, C_{init} (in Ah). It is defined

by [15]:

$$\text{SOC} = \text{SOC}_0 - \frac{\int I_{\text{batt}} dt}{C_{\text{init}}} \quad (4)$$

It is usually expressed in %. Thus, a 100% state of charge (SOC₀) refers to an accumulator with a maximum amount of stored electricity. Conversely, a state of 0% charge refers to an “empty” battery.

3.7.7. Health

The state of health indicator (SOH) is a quantity that quantifies the loss of performance due to battery degradation [15] [16]. It is used in the case of the study of aging and is used to compare the total instantaneous capacity and the maximum capacity obtained when the battery is new. However, a correct assessment of the state of health of a battery must also take into account the increase in its internal resistance, especially in the case of aging [17].

4. Electrothermal Behavior of Li-Ion Batteries

Like all types of electrochemical systems, the temperature strongly influences the Li-ion battery electrochemistry. The performance of a lithium-ion cell is sensitive to temperature, resulting at high or low temperatures in a reduction capacity and available power [2] [3] [18]. It is therefore essential to take into account this parameter.

4.1. Influence of High Temperature

While using the battery, the temperature of the battery may increase by several tens of degrees. Indeed, there persists within the battery thermal losses which increase the temperature of the battery. In the literature of the last two decades, it is described that at high temperatures, operation can cause performance issues and sometimes even security issues [19]. Indeed, Li-ion batteries can present risks of thermal runaway with increasing temperature [19]. When the cell temperature increases, the rate of electrochemical reactions is augmented, sometimes interpreted exponentially (according to Arrhenius' law). The thermal power generated by the cell also evolves according to the same law. Yes, the evacuation of losses does not match this evolution of power generation, the melting of the separator and therefore an internal short circuit will lead to the destruction of the cell with a risk of ignition and explosion.

At the same time, LiCoO₂ technology also presents major risks at high temperatures that are unacceptable for possible use in electric vehicles. At high temperatures and potentials, oxygen outgassing may occur, but in a less significant. As these have low boiling temperatures and voltage-high saturation vapor, they suddenly evaporate and increase the internal pressure until the battery case explodes.

From a more physical-chemical point of view, the temperature also intervenes in the energy balance. Indeed, the internal resistance varies inversely propor-

tional to the temperature in the current operating range of a vehicle (**Figure 3**). A high temperature favors the electrochemical reaction from a point of view of thermodynamics, which is why the internal resistance is lower.

To a lesser extent, temperature affects the thermodynamic performance of the cell by varying the open circuit potential (OCV). This also implies, if the accumulator is not stressed, that if the OCV varies, then the equilibrium potential of the two electrodes will move towards a new equilibrium value, which will also lead to a variation in the state of charge of the accumulator or battery [19].

Finally, from a vehicle point of view, to limit the risk of thermal runaway of the Li-ion battery and to preserve the performance of the cells, if the battery temperature reaches the critical value, the maximum current from the pack to the electric motor is reduced to prevent thermal runaway, resulting in lower vehicle performance. For a hybrid vehicle, the unavailability of the battery implies a mandatory change to thermal mode, which increases the consumption of fuel and CO₂ and polluting particles.

4.2. Influence of Low Temperature

According to current literature [20]-[28] the performance of Li-ion batteries is relatively low at low temperatures. They are qualified as inefficient where a general decrease in the performance of the accumulator is observed. This decrease relies on the temperature dependence of three main parameters.

First, there is a voltage drop at low temperatures. The potential of reference of the accumulator, which corresponds to its potential at thermodynamic equilibrium indeed depends on the temperature. For electrochemists, this potential is described in particular by Nernst's law:

$$E = E_0 + \frac{RT}{nF} + \ln \frac{a(\text{ox})}{a(\text{red})} \quad (5)$$

With a_i = the activity of the species in solutions, R = the ideal gas constant, T = the temperature of the medium, E = the cell voltage, and E_0 = the standard potential at equilibrium.

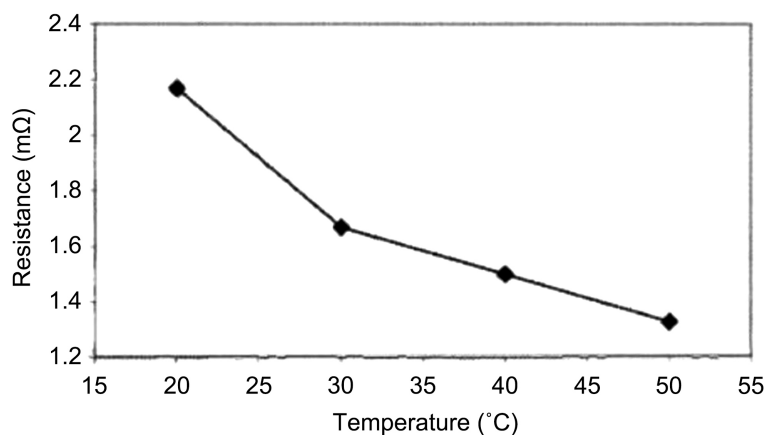


Figure 3. Evolution of internal resistance as a function of temperature [18].

Force to note that the tension parameter of the Nernst equation (Equation (5)) is temperature dependent. Thus, the lower the temperature, the more the potential will undergo polarization [24].

Then the capacity of the cell reports a decrease in storable capacity. Robinson reported a marked reduction in the voltage and capacity of a Li-ion cell when the temperature drops from 20 °C to -10 °C [25]. Zhang [22] also showed for a selection of Li-ion cells that at -20 °C the available capacity is 60% of the capacity initially measured (Figure 4). However, when the temperature drops to -30 °C or -40 °C, the capacity loss becomes much greater. In particular, at -40 °C, the capacitance can be reduced to 30% of its initial capacity.

It seems that this decrease in capacity is due to slowdowns in mechanisms internal to the cell such as the diffusion of cyclable species (Li^+) preventing these species responsible for circulating and therefore delivering the stored electricity [23]. However, as we mentioned in the previous section, the reaction kinetics works in both directions, in the sense that if a cold battery is heated, the circulation of charged species becomes possible again and the capacity is first “hidden” by winter conditions becomes available again.

In addition, the performance limitations of Li-ion batteries are also due to the global increase of the third parameter: the internal resistance.

Indeed, at lower temperatures, the electrolyte tends to gel [26] [27], which creates a strong resistance to ion transport [28]. This is why the internal resistance and, in particular, the ohmic resistivity increases sharply for winter temperatures. In addition, according to some authors, this increase is the consequence of increasing the load transfer resistance. Indeed, at the interface electrode/electrolyte, when an oxidation/reduction reaction takes place, the transfer of load occurs. The latter, whose reaction sites are on the surface of the electrode, is described by an exponential relationship called the Butler-Volmer equation:

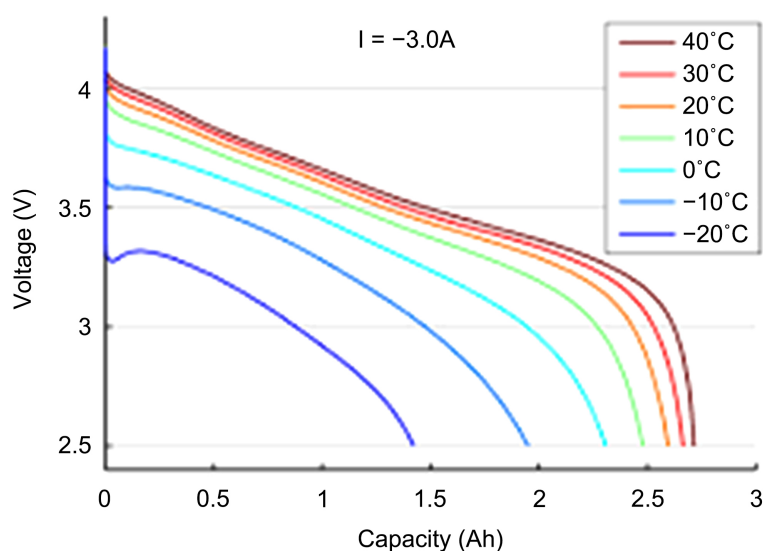


Figure 4. Influence of cold temperature on the capacity of a Li-ion cell [20].

$$i = i_0 \left[\exp\left(\frac{\alpha_a F}{RT} \eta\right) - \exp\left(\frac{\alpha_c F}{RT} \eta\right) \right] \quad (6)$$

With i , the surge current (A), i_0 , the exchange current (A), the surge, F , the Faraday's constant (C/mol), α_a and α_c are the anodic charge transfer coefficients and cathodic, respectively. Analogously to Equation (6), there is also a correlation between temperature and charge transfer coefficients. The drop in temperature causes a drop in the kinetics at the interface, and therefore a reduction in the number of Li^+ ions exchanged. For the sake of simplification, the Butler-Volmer relation is often linearized, which will allow the charge transfer impedance to be expressed as a resistance. As an indication, the decrease in charge transfer kinetics increases the impedance.

To conclude, Nagasubramanian and al. [27] seem to confirm the hypothesis that on a temperature range between -20°C and 25°C , the purely ohmic resistance varies little, while at the interface between the electrolyte and the electrode a resistance to charge transfer increases when the temperature decreases, thus causing, a general increase in internal impedance in winter conditions.

5. Aging of Li-Ion Batteries

Aging is the evolution, over time and/or use, of the properties of a system. A Li-ion battery is a complex multi-electrochemical system component, and each of these components will age. The aging of an accumulator manifests primarily through loss of capacity and increased internal resistance. The estimate of the lifetime is therefore a crucial piece of data in the step thermal management of the pack.

Indeed, a good understanding of aging phenomena at low temperatures gives a prerequisite for defining experimental protocols. However, the aging phenomena involved in a battery are complex and interdependent. Thus, thereafter, the electrochemical analysis of our results will remain summary.

5.1. Types of Aging

Firstly, it is necessary to distinguish between two forms of aging for Li-ion accumulators: calendar aging [28] and cycling [29].

5.1.1. Aging by Calendar

The calendar aging mode corresponds to the degradation of performance in function of time when the battery is not electrically stressed, that is to say when it is only constrained by the slow and irremediable mechanisms [30]. This aging is imputed by different factors.

At rest, the voltage (or by extension the state of charge) at which the battery is stored is an important factor [31]. The continuous reduction of the solvent at the electrode interface of carbon/electrolyte seems to be the main cause of aging [32]. A state of high charge can therefore promote the electrolyte reduction reaction and contribute to greatly accelerating the aging of some batteries [33]. As-

sociate support in tension during storage (“floating”), can itself contribute to the acceleration of the aging (Figure 5) [34]. High temperatures also accelerate the degradation of the cell but low temperatures can be unfavorable [35].

5.1.2. Aging by Cycling

This mode of aging is more severe than the previous one since it incorporates other degradation parameters such as charge/discharge currents and the amount of charge exchanged [32]. When an accumulator undergoes aging by cycling, it is said that this one is cycled. Its final number of cycles is an end-of-life criterion and represents the number of cycles achievable by a battery subjected to repeated cycles, generally, the number of cycles is evaluated when the cell has lost 20% of its capacity initially. In this type of degradation, aging ‘is a function of the number of cycles’ and not of time, but also of the state of charge (~SOC) window, of the depth of discharge (DOD) [36], etc. The temperature also remains a factor determining the number of cycles achievable. Raising the temperature speeds up the insertion of lithium causing accelerated aging. The low temperature also influences this number because of the presence of another electrochemical mechanism called lithium plating presented in more detail later in the report.

Finally, Figure 6 shows the evolution of the capacity for the two types of aging. Due to the use of the cell, aging by cycling is more brutal than calendar aging. However, among the four stages, (A, B, C, and D) that make up this evolution, the first three stages A, B, and C achieve rather the same trend than calendar aging and may correspond to a regression exponential with the number of cycles (or storage time).

5.2. Mechanism of Degradation

As mentioned previously, the degradation is indeed the result of several mechanisms that can interact with each other, which complicates the study of aging. That degradation results in a loss of capacity depending on the cycles or the time of storage as well as an increase in impedance. Battery damage Li-ion cannot be attributed to a single and unique factor or mechanism but to a great number of phenomena that interact distinctly at the anode and the cathode.

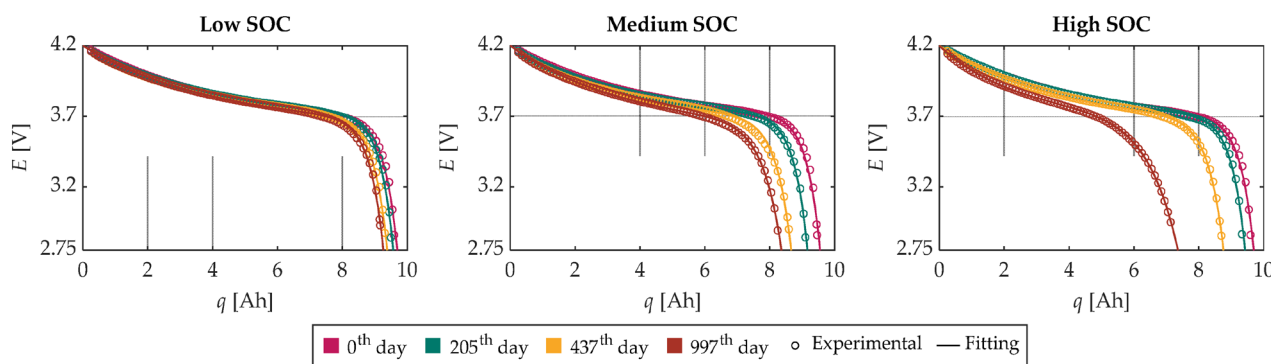


Figure 5. Discharge profiles after 6 calendar months for a voltage maintained or an open circuit [35].

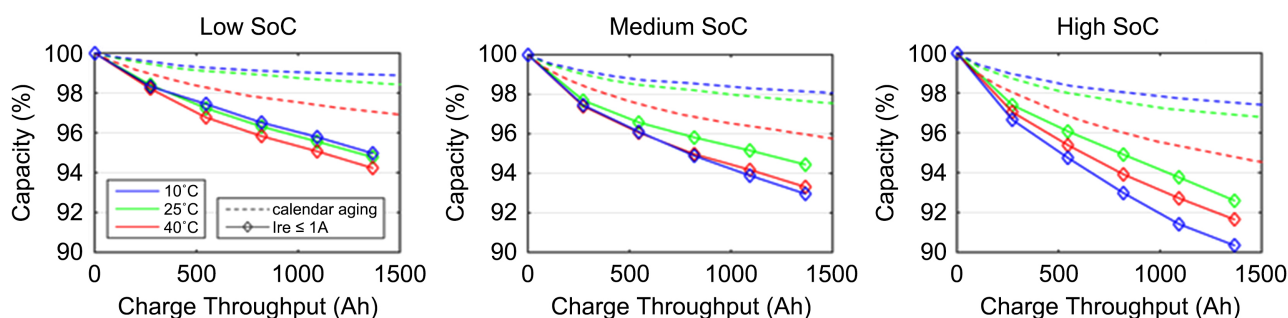


Figure 6. The general evolution of the capacity for aging by cycling or calendar aging [37].

5.2.1. Mechanism Affecting the Negative Electrode

The majority of Li-ion batteries today use a type of electrode graphite. Therefore, we will focus here exclusively on the aging of this type of electrode. The aging of these negative electrodes mainly affects the formation and growth of solid-electrolyte interface (SEI), cyclable lithium loss, and changes within the active material [38].

Although it is considered the main source of anode aging in graphite, SEI first plays a key role in the proper functioning of the cell.

Its role consists first of all of a role of passivation and protection of the active material. It results from the reaction of the anode with the electrolyte during the formation stage [39].

Indeed, carbon electrodes have the particularity of working at voltages outside the window of stability of the electrolytes used which favors the reactions of reduction of the electrolyte with the anode.

In fact, because of this window of potential, the formation of the SEI occurs throughout long battery life as long as the electrolyte comes into contact with the graphite. The oxidation of the electrode induces a consumption of lithium on the surface of the anode as well as an increase in the internal resistance due to the growth of the SEI layer [40]. It also leads to the increase in transfer resistance of load, and clogging of the graphite anode pores [41] [42]. The formation of this surface is therefore a predominant source of Li⁺ loss.

The integrity of the electrolyte itself can also be questioned. Indeed, the Irreversible consumption of Li⁺ ions in the electrolyte is due to two factors [40]:

- 1) The formation of the SEI layer through the decomposition of the electrolyte during the training stage.
- 2) The reaction of lithium-ion with the entities of the decomposed electrolyte and water present in it during battery operation.

Finally, some mechanisms contribute to the performance degradation of the graphite negative electrode by mechanical fatigue. When inserting/reinserting the Li⁺ ions within the graphite, it will change in volume by about 10%. These processes will therefore have little effect on the material itself [43].

However, these expansions and repeated contractions can lead to rupture of the SEI, due to the dilation of the electrode materials, exposing new graphite surfaces to the electrolyte. That surface will then undergo a new passivation

which will reduce the specific capacity and increase the impedance.

5.2.2. Mechanism Affecting the Positive Electrode

In [44], the authors gave a detailed analysis of the problems of aging of the cathode formed from oxides of lithiated metals. These can be very different depending on whether the active material is mainly made up of LCO, LFP, or even of LMO. These problems can be summarized as the loss of the active ingredient, and the interaction of cathode elements dissolved in the electrolyte at the anode.

Figure 7 summarizes the mechanisms apparent at the positive electrode.

According to Vetter *et al.* [45], the aging of cathodes based on transition metals would be mainly due to the dissolution of the main metal of the cathode. Indeed, in most cases, the active material is partially dissolved in the electrolyte at the interface solid/cathode electrolyte. For materials based on manganese (Mn), this dissolution generates the presence of transition metal ions in the electrolyte—typically Mn^{2+} . In the case of LFP, it has been experimentally demonstrated that the speed degradation of these cells is intimately linked to the presence of iron dissolved in the electrolyte [46].

In addition, it appears that this disproportionation reaction causes the migration of ions dissolved metals towards negative potentials to recombine with other species to increase the growth of negative SEI [43] [47]. This contamination is moreover very present in the case of manganese-based electrodes [43].

Also, the insertion and disinsertion of Li^+ ions lead to a change in the volume molar of the materials, which can cause mechanical stresses for the particles of the oxides and therefore for the cathode too. Unfortunately, these changes in molar volumes can induce fractures and stresses in the active material and therefore lead to electrode decohesion. For LFP cathodes, Pahdi and al [48]

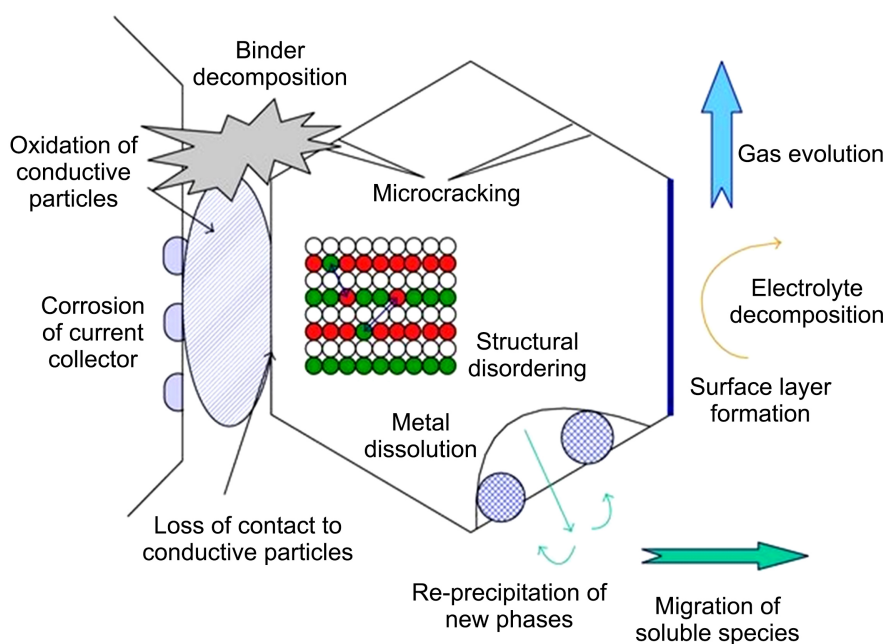


Figure 7. Aging mechanisms of cathode materials [43].

showed that the iron phosphate was subject to an expansion of 6.81% of its volume during the lithiating process. Analogously to graphite, LFP can therefore be altered by the succession of these cycles of use.

5.2.3. Review of Aging Mechanisms

The aging of a lithium-ion battery is therefore something very complex and aging phenomena are numerous and strongly depend on the materials used.

In addition, today there are several parameters whose influence on this phenomenon has been identified. The state of charge is known for its impact on the evolution of the properties of the SEI [49]. Indeed, the distribution of potentials intervenes with the thermodynamic stability of certain compounds, the reactivity of the electrolyte but also in the change in the crystal structure of some cathode materials.

Temperature is also identified as an important factor in aging. However, as the subject of the thesis concerns the effect of the thermal gradient on the Li-ion accumulators, it is important to devote the next part to the influence of the temperature over the lifetime.

5.3. Influence of Temperature

The previous part highlighted the role of temperature on the behavior electro-thermal of the Li-ion accumulator, with a general drop in performance.

That said, battery performance is also known to decline over the course of time and their use due to wear and tear. Temperature is one of those factors which can lead to the accelerated aging of Li-ion batteries. Let's look first at the effect of high temperature.

5.3.1. Influence of High Temperature

As a general rule, the temperature conditions the kinetics of all the reactions involved in a battery, in particular the secondary reactions such as the reactions corrosion [50]. When the battery operates at high temperatures, these reactions secondary are precipitated. For example, at the anode, the growth of SEI is accelerated and can dissolve to form chemically more stable inorganic compounds whose ionic conductivity for lithium is very low, which induces a decline in battery performance [47] [51]. At high temperatures, the SEI layer can dissolve to re-precipitate in the form of more stable lithium salts than the SEI.

This new layer is less permeable to Li^+ ions and therefore increases the impedance of the anode. In addition, this layer can be catalyzed by the incorporation of metal ions resulting from the dissolution of the materials of the positive electrode. Indeed, at the cathode, the strong temperatures favor the phenomena of dissolution of the main metal and accelerate the degradation of cathodic materials [41] [42].

5.3.2. Influence of Low Temperature

If the kinetics is accelerated at high temperatures, conversely, at cold temperatures, it is slowed down. Thus, at low temperatures, the mechanisms previously

presented are assumed to be disadvantaged because the temperature considerably limits the kinetics of insertion/disinsertion mechanisms in anodic reaction sites as well as diffusion phenomena within the electrolyte [28]. However, low temperatures may have a detrimental effect on graphite electrodes.

Indeed, for calendar aging, at low temperatures, problems of solubility of parasitic species (LiF, PF₅, Li₂CO₃, CH₃OCO₂Li, etc.) may appear at the anode/electrolyte interface. This non-solubility of the species is compromising since the SEI layer continues to grow even when the cell is not stressed. What's more, these species are highly reactive and can interact with other elements of the cell (solvent, current collectors, etc.).

Regarding the use of a Li-ion cell, because the electrode potential is close to that of the Li/Li⁺ couple [52] (Figure 8) and that for low temperatures the diffusion of lithium within the graphite and the SEI is reduced, the formation of a metallic lithium layer can take place [53]. This phenomenon is commonly referred to such as covering the electrode with lithium ("lithium plating"). It is very favored when the rate of reduction of the Li⁺ ions, directly imposed by the current that traverses the electrode (high charges, for example), exceeds the kinetics of the mechanisms of intercalation within the active material.

Thus, the local agglomeration of matter tends to favor the deposition of a fine metallic lithium film, comparable to that deposited during an electro-deposition process [54]. Thereafter, the metallic lithium is very reactive, the interactions that can intervene between this layer of lithium and the electrolyte can accelerate the electrolyte deterioration process and the growth of SEI [55].

Studies have shown that these overruns of operating temperatures, that is to say, use at low temperatures, accelerate the degradation of the cell [56]. Indeed, this process degrades the performance of the battery and decreases its safety due to obstruction of reaction sites by metallic lithium. And what is more, in the long term the dendrite formation causing internal shorts can damage the cell [54].

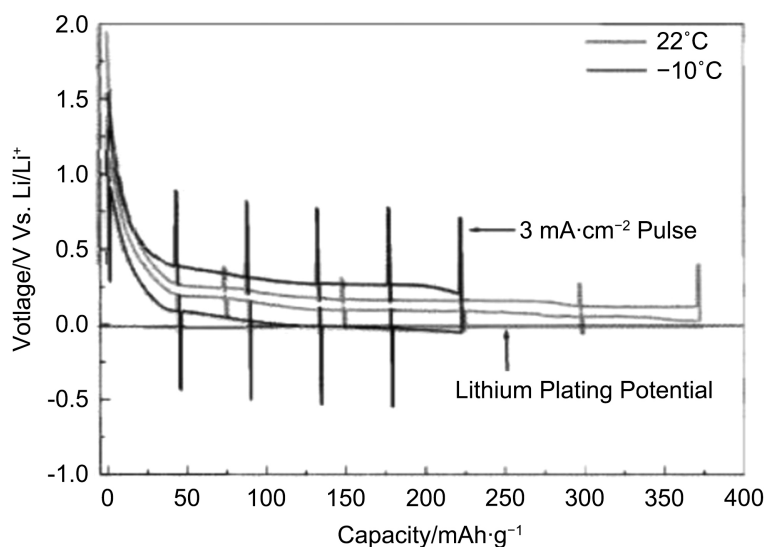


Figure 8. Potential of the negative electrode as a function of temperature [52].

These temperature-related mechanisms are therefore in interaction with each other.

Attempts to overcome these mechanisms exist. For example, when starting at cold, or the use of the vehicle in extreme climatic conditions, thermal pre-conditioning and possibly thermal heating are required. The next part lists the different thermal managements listed for today's electrified vehicles.

6. Thermal Management of a Pack

The thermal management of a battery pack is an essential aspect of our thesis. The role of the temperature management system is to keep the battery pack within a range of ideal operating temperatures. To understand the interest and the difficulties that reside around thermal management, it is first necessary to situate its context.

6.1. Context

In a conventional vehicle, the management of the temperature of the internal combustion engine is simple to set up. In winter, the engine is generally little constrained by the cold temperatures thanks to the wide operating temperature range of gasoline up to -60°C [57], which allows it to maintain its operation, even at very low temperatures. In summer, a cooling system is integrated into the vehicle to maintain engine temperature [58].

In the case of a hybrid vehicle, the thermal management process is more complex. Indeed, Li-ion cells are more affected by the operating temperature. It is necessary to cool the pack in summer and warm it in winter. Unfortunately, at these same periods, simple cooling by ambient air is unnecessary since the air is at the same temperature as the environment (cold in winter, hot in summer).

Thus, configurations requiring the installation of several additional equipments (often bulky) are required, which complicates the problem of thermal management. Moreover, in a cell pack, it is important to manage the thermal imbalances between cells [59].

Cells in the center of the pack are often warmer. The performance of different cells is therefore different, as well as their aging.

Given the difficulty associated with the thermal management of a pack, a complex system thermal management is necessary to control the proper functioning of the pack. This battery management system is commonly called BMS (Battery Management System"). It is an electronic system that controls the entire pack. He supervises also the temperature of the battery pack components. Thermal management is a function of the BMS, it prevents any overheating of the pack which proves to be a damaging factor and limits the life of the batteries at high temperatures by using cooling systems.

In contrast, at low temperatures, the battery pack must be warmed up to guarantee its proper functioning. But operation at low temperatures may also cause premature aging of batteries through phenomena irreversible and some-

times even security problems. In the literature [60] [61] [62], there are several types of thermal management, they can be classified according to the technique used: by air, by liquid, and by phase change material.

6.2. Air Management

6.2.1. Definition

An air coil heating/cooling system is simply the use of air to cool or heat the cell pack. Whether it's for a cooling or heating system, in thermal management by air, the latter can be taken from one of the following 2 sources: the outside air or the air taken directly from the air-conditioned/heated cabin. In the first case, the airflow withdrawn can take advantage of the forward speed of the vehicle to increase its flow and reduce fan power. However, the use of outside air requires very often pre-conditioning because the ambient air varies according to geography and climate (cf.7.1).

In the second case, the air conditioning from the cabin offers a limited flow and a certain cost in energy, but allows to have a control on the temperature of the air. However, in the case of pack heating in winter, the use of cabin air presents a dilemma of choice. Indeed, the energy of the pack is already limited by the conditions of winter, warming up the passenger compartment, and consequently, the pack would lead to exhaustion total energy contained in the cells. In addition, problems related to acoustics may affect the comfort of the driver and passengers in the passenger compartment.

Air cooling/heating has the advantage of being light and having a cost low (exchangers, fans, etc.). Air cooling systems are also preferred in the case where the cell packs are less voluminous and therefore easier to thermally regulate. Generally, in this category, ambient air or the air in the passenger compartment is propelled using a fan in a system predisposed to this effect.

When the required cooling or heating power is large enough, battery cells can also be cooled via plate metals which are then cooled/heated by forced convection in a pipe of air. Such a system is certainly more effective but also more restrictive. Indeed, the required elements add weight and clutter to the overall system.

To conclude on management by air, it is generally difficult to maintain a good temperature homogeneity within the battery due to the low heat capacity of the air. The studies carried out by Pesaran [61] show that it is difficult to maintain a temperature gradient below 5° within the air pack, where liquid management would be perfect.

6.2.2. Examples of Air Heating Systems

At low temperatures, the battery pack must be warmed up to ensure its good functioning. At first glance, the use of ambient air seems quite inadequate.

Indeed, in winter conditions, the outside air is generally as "cold" as the pack of batteries. Thus, convection by outside air seems to be compromised. Also, the energy of the pack to heat the passenger compartment and the cells require

energy which is already rendered unavailable by the extreme conditions. However, there is in the literature thermal air heating strategies. A first solution presented by Ji and al, [63], was to use heating pads combined with an air source (fan) powered by an external system, *i.e.*, a source other than the battery pack, to even out the heat flow. The solution seems a little elaborate in the sense that many additional bulky systems are required, in any case, the principle used remains interesting. In particular, this system is found in the current electric vehicle (Nissan Leaf, [64] with thermal management and the use of heat exchangers to warm up the battery pack.

6.3. Liquid Management

6.3.1. Definition

According to Pesaran [61], liquid cooling systems are more efficient than air but are more complex to adapt to electric vehicles. Indeed, although this type of cooling requires the installation of an additional water loop in addition to pipes between the battery cells, water has a calorific value far greater than air [50]. This superiority therefore gives it increased use in electrified vehicles.

Liquid cooling/heating can be done in two ways which differ by the nature of the liquid used: by water or by refrigerant. In the case of the use of water, the water loop is made up of exchangers and a pump. Air ambient powered by a fan cools/heats the exchangers. Thus, water leaving the battery passes through the heat exchangers allowing it to be cooled (and possibly reheated in winter) before being pumped back into the battery (Figure 9).

Refrigerant cooling, on the other hand, requires more installation substantial than water (Figure 10).

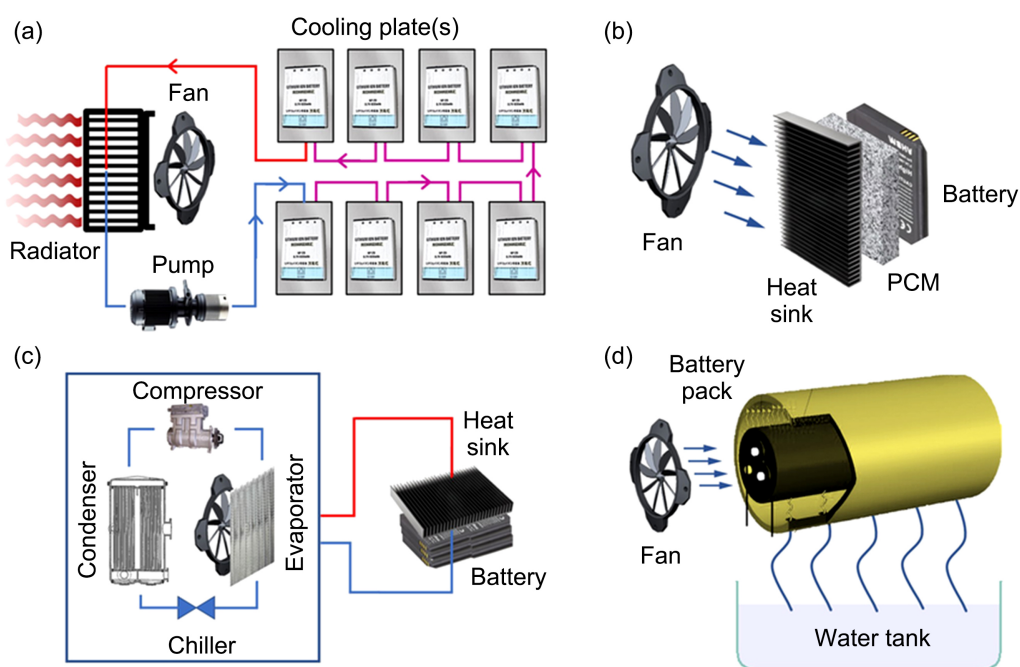


Figure 9. Liquid thermal management [65] [66].

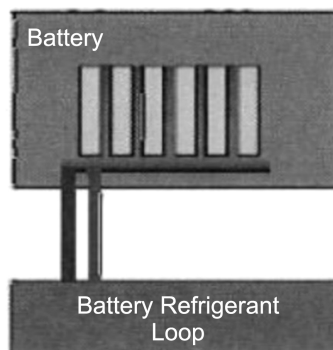


Figure 10. Refrigeration loop associated with a battery pack [68].

Indeed, we find the principle of cooling everyday items such as a refrigerator. Installing a loop refrigerant therefore requires the integration of a loop made up of 4 main elements which are: the evaporator, the compressor, the condenser, and the expander. As in any refrigeration system, evaporation of the liquid causes absorption of calories from the external medium (here, the cell pack). The refrigerant is then pumped by the compressor to the condenser where it restores the absorbed power and returns to the state liquid [67].

6.3.2. Examples of Liquid Heating Systems

This time again, one would think that heating by liquid route would be unthinkable due to the fairly rapid solidification of water or glycol at low temperatures.

However, looking at the user manuals of the five vehicles best-selling electric and hybrid vehicles in Canada (Nissan Leaf, Chevrolet Volt, Tesla S, Ford Fusion Energy BMW i3 according to the EV Sales blog), we can see that the management liquid thermal is the most used for four of them, even during winter conditions (Figure 11). Indeed, the advantage is to use the refrigerant loop.

The latter is heated using high-voltage heating resistors powered either by internal or external sources. Thus, paradoxically the refrigerant circulating between each cell warms them.

Unlike air cooling/heating, liquid cooling generally helps to avoid noise pollution. However, it requires the installation of several additional elements which are imposing heavy which increases the energy consumption; the weight and therefore the cost of the overall system.

6.4. External/Internal System

Alongside the thermal management differentiated by the fluid used, we also find a differentiation according to the origin of the supply to the heating system. An internal system will therefore be a theory where the cooling/heating is supplied by the source main vehicle: the battery pack [61] [62]. On the other side, we find an external system where power is supplied from a source external to the system traction [61] [62]. Often in hybrid systems, the MCI plays this role and sometimes even engine gases can heat the battery pack.

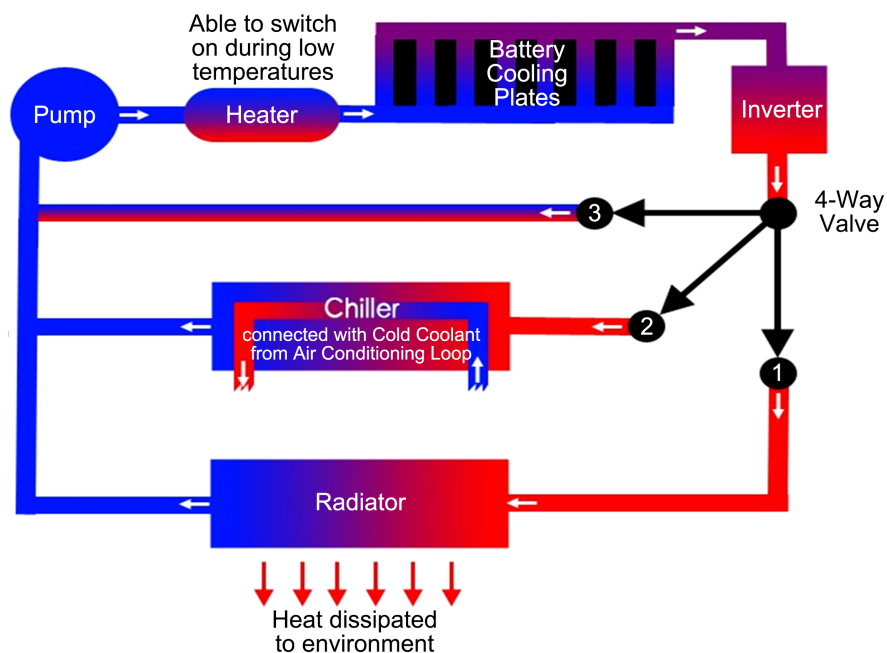


Figure 11. Using coolant to heat the pack [69].

6.5. Phase Change Materials

The development of phase change materials (PCM) for housing is beginning to have some impact in the field of batteries (Figure 12). This guy of material has the interesting property of having its mass capacity modified according to the temperature at which it is [35]. This mixture thus makes it possible to absorb and store the thermal fluxes generated by the battery in operation and in particular when the pack temperature is in the phase transformation area of the PCM. When the element temperature exceeds the phase change equilibrium temperature, the thermal capacity of the PCM decreases sharply and allows excess heat to be dissipated outwards. Often used at high temperatures, a study in the early 2000s conducted by and al [70] used this calorific value for batteries at low temperatures. If the temperature of the battery pack is below the set point PCM phase change, the heat stored by the PCM will be released to the pack of batteries. Thus, regardless of the temperature of the pack (hot or cold), the PCM would provide a major advantage for automotive applications.

However, the use of PCM implies an increase in mass and total cost of the battery component. The geometry of the batteries that can be used in PCMs is also a constraint that limits the development of PCM battery cooling solutions. Indeed, PCM matrices are better suited to cylindrical cells, or in current vehicles, prismatic geometry is predominant thanks to its gain of space.

6.6. Heating by Alternating Current

Along with external heating, another method has been established for the conditioning of batteries at low temperatures: internal heating by current alternating (AC). Indeed, the installation of an external heating often requires the addition

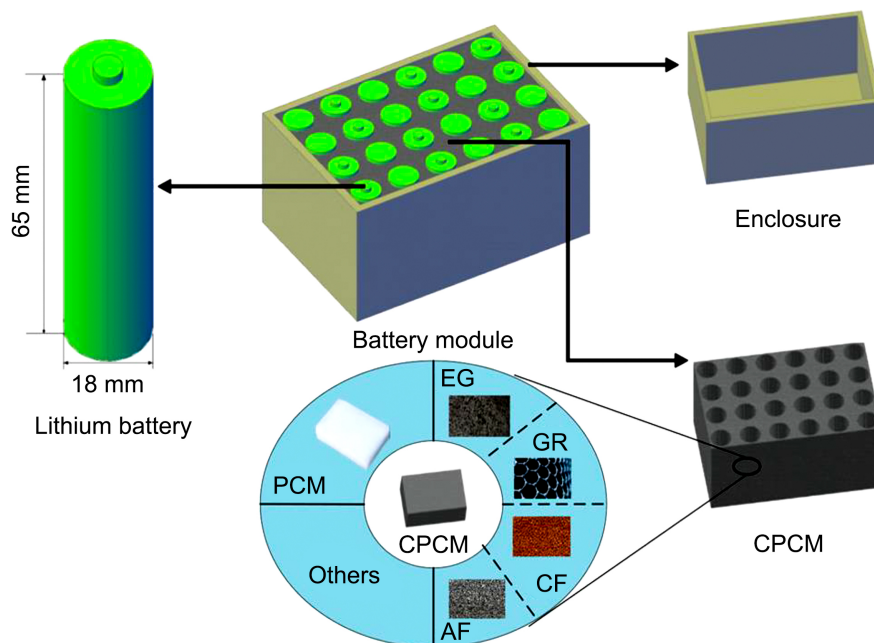


Figure 12. Commercialization of phase change materials.

of elements that are large, and heavy, and increase energy consumption. In 2004; Stuart *et al.* [63] presented a method for heating lead/acid batteries directly with the application of an AC instead of heating pads. The interest of this method is to rely on the joule losses to heat the batteries without having to resort to an external heater.

Their experimental tests showed that currents of amplitudes warmed the battery very quickly and with a uniform temperature in the cell.

In the same register, Jin and al [71] with a more recent battery technology (Li-ion), showed that the internal heating in a Li-ion cell pack could bring a uniformity of the temperature within a pack, with a very low thermal difference between each cell.

Unfortunately, a major drawback appears immediately when it comes to heating internally. The use of an AC for the conditioning of the batteries generates damage due to battery cycling (see 1.6.1.2) since a current is applied directly to the cell. This cost in degradation by cycling, non-existent for external heating, can slow down integrating AC heating into an automotive system.

Heating by AC, which is easy to set up, therefore provides uniformity and speed of execution but causes damage due to cell cycling. So, if this solution has a future in the automobile, batteries resistant to degradation by cycling should be considered.

7. Conclusions

This thesis was devoted to a bibliographic study concerning lithium-ion batteries for automotive applications. First, we presented their introduction to the automotive world. After stating their magnitude characteristics, we explained their

principle of operation, to end with the different packaging. Then, the aging of lithium batteries was discussed in the interest of the behavior of each constituent element of the cell. Finally, the various thermal managements associated with a pack have been mentioned.

The major conclusion is that Li-ion technology is a mature technology for use in large series in the field of automotive traction chains. Nevertheless, progress still needs to be completed to ensure their effective operation. It is essential to maintain efforts to understand the thermal strategies currently used in winter conditions. Indeed, current strategies remain primitive in the sense that few of them deal with the combination of the thermal aspect at low temperatures and its impact on aging. Therefore, it seems necessary to increase the energy efficiency and lifespan of Li-ion batteries during winter.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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Abbreviations

SOC: State of Charge

DOD: Depth of Discharge

SEI: Solid Electrolyte Interface

LCO: Lithium Cobalt Oxide

LFP: Lithium Iron Phosphate

LMO: Lithium Manganese Oxide

OCV: Open Circuit Voltage

LTO: Lithium Titanate Oxide

LFMP: Lithium Ferrous Manganese Phosphate

Mn: Manganese