Abstract
The safety of operation is a key point to allow the wide use of Lithium-ion batteries. This document gives an ongoing state of the research about the mechanisms of the electrolyte’s degradation of LiPF$_6$ and thermal decomposition of the different cell chemistries involved in the project: LiFePO$_4$/C systems and Cobalt-based/C systems with positive material such as Li(NiCoAl)$_2$O$_4$ and the mixed oxide LiMn$_2$O$_4$-Li(NiCoAl)$_2$O$_4$.

Summary
General objectives
The main objective of this task is to make a review on the chemical runaway mechanism with respect to the different electrode materials involved in this project and integrated into the batteries for finally reporting their behavior under abuse test conditions in term of safety.

Introduction & methodology
Today, several types of positive active material have been developed and each of them has not exactly the same performances in terms of specific energy, cycling life time and safety.

In order to extend the use of the Li-ion batteries from portable electronic devices to hybrid electric vehicles markets, the safety concern becomes one of the most important/essential issues, a general challenge, for the high power and large scale Li-ion cell development especially under abuse conditions.
Several exothermic reactions can occur inside the cell as its temperature increases very quickly and is the reason that thermal stability is a key point for cell safety. When a lithium-ion battery is fully charged, the positive electrode contains a strong oxidizing transition metal oxide (i.e. LiMO$_2$, M = Ni, Co, Mn), while the negative electrode contains lithiated carbon, a very strong reducing material. The non aqueous electrolyte usually constituted of an organic carbonate solvent and a lithium salt tends to be readily oxidized and reduced. Thus, the Li-ion cell itself is thermodynamically unstable and the compatibility of the cell is achieved with the presence of the passivation films on the electrode surface. Therefore, Li-ion batteries are very sensitive to thermal, mechanical and electrical abuse and pose significant fire hazards and possible explosion.

We focus this study on the chemical runaway mechanism occurring under abuse tests conditions already pre-defined in the project: thermal stability, nail penetration, overcharge, overdischarge, short circuit, ARC experiments…

**Starting point: state of the art & reference documentation**

The lithium-ion technology is based on a reversible exchange of the lithium ion between the positive and negative electrodes during the charge/discharges processes. Until intercalation inside the negative electrode, lithium is maintained in the ionic state, preventing any metallic deposit. So, no dendrite can normally establish and grow which could create short circuit between the two electrodes due to penetrations through the polymer separator. This **insertion/reinsertion mechanism** from one electrode to the second one is often called by the term “rocking chair” because the lithium ion is rocked from one electrode to the second one and inversely (Figure 1). During the charge, lithium is de-inserted from the positive electrode and inserted into the negative electrode. The reverse mechanism occurs during the opposite discharge process.
A lithiated transition metal oxide (LiMO$_2$ where M=Co, Ni or manganese spinels LiMn$_2$O$_4$) is generally used as the positive material. Lithium intercalation in such compounds occurs at high potentials, around 4 V vs. Li$^+/\text{Li}^0$. The most commonly and firstly used material is lithium cobalt oxide, because of its good stability, cyclability and its high theoretical capacity of about 160 mAh/g (Table 1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Pr. Cap. (mAh/g)</th>
<th>Density (g/cm$^3$)</th>
<th>En. Dens. (mAh/cm$^3$)</th>
<th>Shape of Discharge Curve</th>
<th>Safety</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>160</td>
<td>5.05</td>
<td>808</td>
<td>Flat</td>
<td>Fair</td>
<td>High</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>110</td>
<td>4.20</td>
<td>462</td>
<td>Flat</td>
<td>Good</td>
<td>Low</td>
</tr>
<tr>
<td>LiCo$<em>{0.2}$Ni$</em>{0.8}$O$_2$</td>
<td>180</td>
<td>4.85</td>
<td>873</td>
<td>Sloping</td>
<td>Fair</td>
<td>Fair</td>
</tr>
<tr>
<td>LiMn$<em>{0.5}$Ni$</em>{0.5}$O$_2$</td>
<td>160</td>
<td>4.70</td>
<td>752</td>
<td>Sloping</td>
<td>Good</td>
<td>Low</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>160</td>
<td>3.70</td>
<td>592</td>
<td>Flat</td>
<td>Good</td>
<td>Low</td>
</tr>
</tbody>
</table>

Table 1: Major commercial lithiated positive material [22]
The LiNi\textsubscript{x}Co\textsubscript{y}O\textsubscript{2} materials offer higher capacity, up to 220 mAh/g for LiNiO\textsubscript{2}, though a lower nominal voltage than LiCoO\textsubscript{2} or LiMn\textsubscript{2}O\textsubscript{4}. LiMn\textsubscript{2}O\textsubscript{4} is also of commercial interest, particularly for applications that are cost sensitive or require exceptional stability upon abuse. It has lower capacity, 110 mAh/g, slightly higher voltage, 3.70 V vs. Li\textsuperscript{+}/Li\textsuperscript{0}, but has higher capacity loss on storage, especially at elevated temperature, relative to cells that use LiCoO\textsubscript{2} or LiNi\textsubscript{x}Co\textsubscript{y}O\textsubscript{2}. Despite its high capacity and low cost, LiNiO\textsubscript{2} is not widely used commercially because of the energy evolved upon decomposition, the relatively low temperature at which self-heating ensues, and the difficulty of preparing the material consistently in quantity.

As a negative electrode, carbon compounds like cokes or graphites are used. The useful capacity of these materials goes from 200 mAh/g for the less graphitized to 372 mAh/g for the highest graphitized compounds (value of the theoretical capacity of LiC\textsubscript{6}). Various types of precursors can be used to produce carbonaceous materials [33]. They reversibly intercalate lithium between 0 and 0.3 V vs. Li\textsuperscript{+}/Li\textsuperscript{0}, which preserves the very low potential of lithium and avoids safety problems associated with the use of metallic lithium in rechargeable batteries.

At first (just after assembly), the lithium ion battery is in its discharged state: all active lithium is stored in LiMO\textsubscript{2}. This material has the advantage of not being reactive on air so that assembly is made easier. The first operation consists of charging the battery, a process during which lithium is de-intercalated from LiMO\textsubscript{2} and intercalated into graphite. In the particular case of graphite, during that first charge, the formation of a passivation film generally identified under the term **SEI for “Solid Electrolyte interface”** is observed for a voltage of about 0.7 V vs. Li\textsuperscript{+}/Li\textsuperscript{0}, related to the electrochemical decomposition of the electrolyte. This passive layer is crucial for the battery stability because it prevents the solvent sphere surrounding the lithium ion from co-inserting into graphite. Without the SEI, the graphite structure would be destroyed by exfoliation [44, 55].

The **electrolyte is made of an aprotic (organic) liquid** because the graphite-lithium electrode is very unstable in presence of labile hydrogen compounds. This is a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and/or diethyl carbonate (DEC), because of their good stability versus graphite. The ionic conductivity is given by the presence of a dissolved lithium salt (LiPF\textsubscript{6} generally) in the electrolyte. Each manufacturer has developed its own electrolyte with or without additives, which are

HELIOS – Review Thermal Runaway Reactions mechanisms - PUBLIC 4/41
precursors to the passivation film and/or play a key role on the thermal stability of the battery.

As announced above, the various electrochemical couples have their own voltage operating window, according to the insertion potential of the electrode materials, and the crystallic structure of the active compounds (Table 2).

<table>
<thead>
<tr>
<th>Positive electrode type (% Negative electrode graphite)</th>
<th>Nominal voltage (V)</th>
<th>Charge voltage threshold (V)</th>
<th>Discharge voltage threshold (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt (layered structure)</td>
<td>3.6</td>
<td>4.2</td>
<td>2.7</td>
</tr>
<tr>
<td>Manganese (spinel structure)</td>
<td>3.7</td>
<td>4.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Phosphate (olivine structure)</td>
<td>3.2</td>
<td>3.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 2: Nominal voltage and charge/discharge voltage threshold for cobalt, manganese, phosphate - based positive electrode (Negative electrode is made of graphitic material)

The respect of these high and low voltage limits guarantees a good operating safety. The charge voltage threshold has to be rigorously controlled because the overcharge leads to a high instability of the over-delithiated positive electrode which becomes additionally more sensitive to the thermal environmental conditions of operating as the report will show. In a battery pack this constraint makes it essential to carry out an equalization of the tension for every cell at the end of charge in order not to produce accidental overcharge leading to an unbalanced state of charge of some cells in the pack.

PRELIMINARY: THE THERMAL STABILITY OF LITHIUM-ION BATTERIES

TGA (Thermogravimetric Analysis), DSC (Differential Scanning Calorimeter) and ARC (Accelerating Rated Calorimeter) are the three widely-used methods to analyze the thermal properties of electrodes and cells. TGA follows the weight loss of samples according to the increase of temperature. DSC is used to measure the heat flow versus the temperature which can indicate the reactions with the specific characteristics (onset
temperature) and the thermal properties (exothermic or endothermic phenomena). ARC creates a near perfect adiabatic environment under specific temperature which provides the thermal stability information under the situation of the worst case. Since the size and morphology of the active material are treated as the important factors to the thermal stability, Scanning Electronic Microscopy (SEM) is applied to compare the size and morphology within variant active material samples. Besides, based on several publications, the SEI (Solid Electrolyte Interface) formation seems to play an important role in the thermal stability [66]. For this reason, the relationship among the SEI formation, electrodes, and electrolytes gain lots of attention as well. However, since there is no quantitative and qualitative measuring way to specify the SEI thicknesses between variant testing samples, the electrochemical impedance spectroscopy (EIS) is used to measure the cell impedance, which can provide the level of SEI formation after equivalent circuits fitting. Generally, the usual experimental parameters are the SOC (State of Charge), types of electrodes, and types of electrolytes in order to understand the thermal stability of commercial batteries. The thermal properties of the lithium ion batteries have thus been investigated a lot in four aspects: electrodes, electrolyte, binder and additives, and cells. Almost all the publications investigated either the individual components, such as electrodes and electrolytes, or the complete cells in order to know where the contribution of self-heating is coming from.

We present below examples of two ARC typical curves (Temperature vs. Time or Self-heating rate (SHS) vs. Temperature) and DSC (Heat flow vs. Temperature) - TGA (Mass loss vs. Temperature) typical curves as often found in publications cited in this report (Figure 2-3).
Figure 2: (A) - Temperature vs. Time. Three regions could be identified: (a) small exothermic chemical reaction, (b) self-heating reaction prior to thermal runaway and (c) thermal runaway region.
(B) Self-heating rate (SHR) vs. temperature. Two temperatures are noted on the curve:
- Onset of chemical reaction preceding thermal runaway (OSCR) (= 123°C)
- Onset of thermal runaway (OSTR) (< 167°C)

Figure 3: DSC (Heat flow vs. Temperature) and TG (Mass loss vs. Temperature) profiles

**Electrodes**

**Positive electrode**

The first experiments led on positive electrodes showed that their thermal stability decreases dramatically with the presence of electrolyte. For example, the positive electrodes (LiNi₀.₈Co₀.₂O₂, LiMn₂O₄) with variant SOC are tested by ARC with and without electrolyte by C. Lampe-Onnerud et al. [77]. As indicated, all of the electrodes show high thermal stability without electrolyte, so that they present no thermal runaway below 300°C. The onset temperatures of the thermal runaway reaction are measured at 225°C for LiCoO₂, 200°C for LiNi₀.₈Co₀.₂O₂, 195°C for LiMn₂O₄, and only 163°C for LiNiO₂ in presence of electrolyte (Figure 4).
By changing the SOC of the electrode LiCoO$_2$ to Li$_{0.5}$CoO$_2$, the results indicate that the batteries of higher SOC possess lower thermal stability, which have lower onset temperature and higher self-heating rate of the thermal runaway reaction.

A recent study of Q. Wang and al. [88] by DSC confirms these results (Figure 5).

By discussing the relationship between the thermal stability and the size of the active material, it is predicted that bigger particles would have better thermal stabilities than the smaller ones [99].
Figure 6: Self-heating rate vs. temperature for the three Li$_{0.5}$CoO$_2$ samples with 1M LiPF$_6$ EC:DEC heated initially at 110°C. (1) Particule size = 0.8 um, $S_{BET} = 0.71$ m$^2$/g, (2) Particule size = 2 mm, $S_{BET} = 0.71$ m$^2$/g, (3) Particule size = 5 mm, $S_{BET} = 0.10$ m$^2$/g [99].

By comparing of the sizes of different materials, the positive electrode made of LiFePO$_4$ possesses higher thermal stability than that with LiCoO$_2$ and Li[Ni$_{0.1}$Co$_{0.8}$Mn$_{0.1}$]O$_2$ [1010].

Figure 7: Comparison of the self-heating rate of LiCoO$_2$, Li(Ni$_{0.1}$Co$_{0.8}$Mn$_{0.1}$)O$_2$, and LiFePO$_4$ in 1M LiPF$_6$ EC:DEC (solid) or 0.8 M LiBoB EC:DEC (dash) electrolytes heated to 110°C (a) LiCoO$_2$: Particule size = 5 mm, $S_{BET} = 0.10$ m$^2$/g, (b) Li(Ni$_{0.1}$Co$_{0.8}$Mn$_{0.1}$)O$_2$: Average primary particule size = 0.2 mm, $S_{BET} = 5.7$ m$^2$/g, (c) LiFePO$_4$: Average primary particule size = 0.2 mm, $S_{BET} = 13.3$ m$^2$/g [1010].
However, the further study by the same group [1111] shows different result from this assumption after using variant particle sizes of LiFePO₄ particles, where the particle size and the surface area only have little effects on the thermal stability for LiFePO₄, indicating that a substantial flexibility for the choice of particle size distribution.

In parallel, several ways for increasing thermal stability are explored. For example, coating the electrode is reported to effectively improve the abuse stability. K.-H. Choi and al. [1212] coat a solid electrolyte film, LiPON (Lithium phosphorous oxynitride) on the surface of a LiCoO₂ composite cathode. Because the thermal stability of the charged electrode coated by LiPON is improved, the LiPON coating layer might be suppressing the exothermic reaction by separating the delithiated LiCoO₂ and the electrolyte solution, thus decreasing the exothermic heat generation. This same group has worked previously on the encapsulation of LiCoO₂ by a new cyano-substituted polyvinylalcohol (cPVA)-based gel polymer electrolyte [1313]. By analyzing with DSC, the heat generating from the encapsulated electrode with electrolyte decreases significantly compared to the normal pristine LiCoO₂ cathode with electrolyte. Similarly this heat-decreasing effect may due to the formation of the complexes between the –CN group of cPCA and the cobalt cations of LiCoO₂ that decreases the contact with electrolyte.

**Negative electrode**

For the negative electrodes, D. D. MacNeil et al. [1414] examine the thermal sensitivities of carbon electrodes with variant surface areas. The surface area is determined by BET (N₂ as adsorbant), the morphology of the material is acquired by SEM, and the thermal stability is determined by ARC. In general, the heating rates increase with the surface area of the electrodes with only one exception which is coke (Figure 8). The explanation of this abnormality is that the N₂ accessible area of the coke is not the same as the electrolyte accessible area, but without sufficient proofs (Figure 9).
From the ARC results, it’s possible to state the peaks to the corresponding reactions, and it is believed that the self-heating process is related to SEI layer. SEI is known to be composed by a stable part (LiF, Li$_2$CO$_3$) and a meta-stable part (lithium-alkyl carbonates) [1515, 1616]. The thermal runaway reaction is first caused by decomposition of the meta-stable part to the stable part. From this point of view, the ability of forming and the ratio of meta-stable/stable SEI layer of different electrolytes becomes the key to determine the thermal stability. As the results show, MCMB anode (synthetic electrode composed by heat-treated mesocarbon microbeam) with electrolyte LiPF$_6$ solubilised into EC (ethylene carbonate) and DEC (diethyl carbonate) form higher thermal stability SEI layer (self-heating begins at 80°C) than with LiBF$_4$ EC:DEC (self-heating begins at 60°C) [1414].

**Electrolyte**

For the commercial Li-ion cells, the most widely used electrolyte is non-aqueous carbonate-based solvents (e.g. EC, DEC, DMC) with Li-based salts, which dominates the unstable thermal properties of the cells. Some studies focus on comparing different types of electrolytes on their thermal stabilities in order to develop cells with higher safety.
LiPF$_6$ is widely used in Li-ion cells, but its thermal stability is not outstanding. J. Jiang et al. [1010] reported that with LiCoO$_2$ as electrode, LiBOB (Lithium bis(oxatliato)borate) possesses worse thermal stability than for LiPF$_6$. However, it is the opposite with LiFePO$_4$ as active material. Besides, J.S. Gnanaraj et al. [1818] investigate several lithium salts for their thermal stabilities: LiPF$_6$, LiClO$_4$, LiN(SO$_2$CF$_2$CF$_3$)$_2$ (named LiBETI) and LiPF$_3$(CF$_2$CF$_3$)$_3$ (named LiFAP). The results show that LiClO$_4$ has least thermal stability and a higher potential of explosion than the others. LiBETI is the most stable one among the all, and the self-heating rate is negligible even at 350°C (Figure 10).

Figure 10: Self-heating rate and pressure developing rate profiles for 1M electrolyte solutions in EC:DEC:DMC (2:1:2): (a) LiPF$_6$, (b) LiFAP, (c) LiClO$_4$, (d) LiBETI and (e) the solvents mixture with no salt added.
Once the solvents evaporate, the gases generated would cause venting and the cell would open. When it comes to the thermal stability of the solvent, EC has the lowest boiling temperature among the three solvents. By decreasing the amount of EC, the safety of the cell would increase.

**Binder and electrolyte additives**

Besides electrodes and electrolyte, the other factors such as binder and additive may also affect the thermal properties of the cells. By using different compositions of binders (mono-polymer, bi-polymer, and tri-polymer) with variant solvents, M.N. Richard and J.R. Dahn [1919, 2020] investigate the effects of binders on thermal stability of the negative electrode. The results show there is no important difference in thermal properties among the electrodes with various binders. The only cause to affect the thermal stability is the existence of plasticizer, which shows lower thermal stability than that without plasticizer.

Some additives to electrolyte are claimed to increase the thermal stability of the cell. The thermal properties of the cell with the vinylene carbonate (VC), γ-butyrolactone (GBL), and trifluoroethyl phosphate (TFP) are investigated [2121]. The addition of VC, which is a well-known additive for film-forming in anode, would increase the onset temperature but cause more violent exothermic reaction at higher temperature. TFP is an excellent oxidation inhibitor, however, the onset temperature of the cell with TFP decreases due to the oxidation of THP itself by the cathode at lower temperature. For GBL, even though the onset temperature has been lowered slightly, the violent exothermic reaction existing without additive can not be suppressed. In conclusion, the binders or additives do not have dramatically effects on the thermal stability of the cells.

**Cells**

The thermal stability of the commercial Li-ion cells has been investigated [2222, 2323, 2424, 2525], more particularly for 18650 types [2626]. However, since the exact components of the commercial cells are usually business secrets, lots of assumptions and uncertainties have been stated to explain the testing results, and only the abuse conditions between the cells from different manufactures can be compared. For the commercial Li-ion batteries, which usually use Li$_x$CoO$_2$ as cathode and carbon-based anode, there is a sequence of thermal events for fully-charged cell [2525, 2722]. First of all, the SEI layer of the anode would decompose at around 100°C (Figure 11). Then, the
interaction between electrolyte and the SEI-free anode would least until about 150°C and form another new SEI layer. From 150°C to 235°C, the decomposition of the cathode occurs and the cathode reacts with the electrolyte. At the end, the anode would react with the binder PVDf (Polyvinylidene fluoride) at around 235°C. However, since the reactions are complex and not really well-defined, the situation would change from case to case.

The successive events are proposed for the heat generation of charged Li-ion cells:

- The chemical decomposition of the passivation film (SEI).
- The chemical reduction of the electrolyte by the lithiated carbonaceous negative electrode.
- The thermal decomposition of the positive electrode.
- The chemical oxidation of the electrolyte by the positive electrode.
- The thermal decomposition of the binder of the composite electrodes.

From the report of S. Al Hallaj et al. [2424], the conditions affect the thermal stabilities of the cells are not just the selections of the materials but also the configurations of the cells, the thickness of the can, the doping of the cathode and so on. However, it seems that there is no related research focused on the comparison of those factors. The thermal stability of cells after ageing under elevated temperature is another
focusing point. In general, there are two phenomena after ageing: the formation of SEI and the self-discharge. The formation of SEI layer is from the decomposition of the electrolyte due to the voltage of anode operating beyond the electrochemical window of the electrolyte. This kind of phenomena happen usually at the first cycle, and is also treated as the important change under ageing conditions. Some publications show that the SEI layer increase under elevated temperature due to the growth or composition change of the SEI layer, which result in the increase of the impedance. Besides, due to the growth of the SEI, the contact loss within anode can cause the capacity fading [66]. As ageing time and temperature increase, the onset temperature of the thermal runaway rises as well due to the protection of the increasing thickness of SEI. Moreover, the self-heating rate of the cell decreases with ageing [2626].

DECOMPOSITION MECHANISMS OF POSITIVE ELECTRODE MATERIALS

**Thermal decomposition mechanism of LiMn_2O_4**

Twenty years ago thanks to the pioneering work of Thackeray et al. [48-49], LiMn_2O_4 spinel was considered (during a long period) as the first and the only possible alternative to LiCoO_2 and this although it's 5-10 % smaller capacity (theoretical capacity of 148 mAh/g) than the layered oxide (160 mAh/g).

LiMn_2O_4 adopts a three-dimensional structure described as a cubic close packing of oxygen atoms with Mn occupying half of the octahedral, and Li an eighth of the tetrahedral sites referring to the 16d and 8a sites ([Li]tet[Mn_2]octO_4), respectively (**Figure 12**). However, this structure is complicated by possible cations mixing between the two types of sites. Lithium extraction from the 8a tetrahedral sites (oxidation of Mn^{3+} to Mn^{4+}) at about 4 V vs. Li^+/Li^0 leads to the defect spinel λ-MnO_2. Lithium insertion (2.96 V vs. Li^+/Li^0) onto Li[Mn_2]O_4 causes a displacement of the Li^+ ions from the 8a (tetrahedral sites) positions onto neighboring interstitial 16c octahedral sites to yield Li_2[Mn_2]O_4 after the insertion of one lithium per spinel unit.
The thermal behaviour of LiMn$_2$O$_4$ has been studied by different groups [51-54] using differential scanning calorimetry or accelerating rate calorimetry but to our knowledge among these works the kinetics of charged LiMn$_2$O$_4$ was few reported.

Combining the results from DSC analysis and X-Ray diffraction, Amarilla et al. [51] have pointed out the relationships between the lattice parameter values, the temperature of the phase transformation and the stoichiometry of different LiMn$_2$O$_4$ samples with nominal Li/Mn molar ratio=1/2 synthesized at 700 and 750°C by the ceramic procedure from Mn$_2$O$_3$ and several lithium sources (Table 3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagents</th>
<th>Synthesis conditions</th>
<th>Lattice parameter</th>
<th>8°Temperature/°C</th>
<th>Enthalpy/100 mg$^{-1}$</th>
<th>Hysteresis width/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Li$_2$CO$_3$+Mn$_2$O$_3$</td>
<td>790/120 700/48</td>
<td>8.238(1)</td>
<td>-8.2</td>
<td>+4.8</td>
<td>-7.2</td>
</tr>
<tr>
<td>H</td>
<td>LiOH.H$_2$O+Mn$_2$O$_3$</td>
<td>790/120 700/48</td>
<td>8.239(1)</td>
<td>-22.1</td>
<td>-11.9</td>
<td>-4.34</td>
</tr>
<tr>
<td>N1</td>
<td>LiNO$_2$+Mn$_2$O$_3$</td>
<td>790/120 700/48</td>
<td>8.2385(8)</td>
<td>-30.3</td>
<td>-21.6</td>
<td>-3.17</td>
</tr>
<tr>
<td>N$_{lm}$</td>
<td>Idem</td>
<td>790/120 700/48</td>
<td>8.2382(6)</td>
<td>-22.6</td>
<td>-15.2</td>
<td>-2.8</td>
</tr>
<tr>
<td>N2</td>
<td>Idem</td>
<td>790/120 700/48</td>
<td>8.238(1)</td>
<td>-15.2</td>
<td>-5.7</td>
<td>5.2</td>
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<tr>
<td>N3</td>
<td>Idem</td>
<td>790/120 700/48</td>
<td>8.241(9)</td>
<td>-2.1</td>
<td>+16.4</td>
<td>-6.8</td>
</tr>
<tr>
<td>N4</td>
<td>Idem</td>
<td>790/120 790/48</td>
<td>8.245(1)</td>
<td>-2.2</td>
<td>+13.1</td>
<td>8.1</td>
</tr>
<tr>
<td>N$_{4h}$</td>
<td>N4 heated at 800°C for 12 h</td>
<td>790/120 790/48</td>
<td>8.2465(8)</td>
<td>-0.3</td>
<td>+19</td>
<td>-7.6</td>
</tr>
<tr>
<td>N$_{4h}$</td>
<td>N4 heated at 850°C for 12 h</td>
<td>790/120 790/48</td>
<td>8.245(1)</td>
<td>+1.2</td>
<td>+27.3</td>
<td>-7.3</td>
</tr>
</tbody>
</table>

Table 3: Reagents, synthesis conditions, lattice parameter, and temperature, enthalpy and hysteresis width for the cubic-orthorhombic phase transformation determined from DSC curves of LiMn$_2$O$_4$ samples (° measured at the apex of the peaks, ° annealing).
By studying the differential scanning calorimetry (DSC), the authors report that the temperatures of the cubic (Fd3m) $\leftrightarrow$ orthorhombic (Fddd) phase transition are spread over a wide range, from -30 to -2°C for the exothermic C$\rightarrow$O phase transition, and from -21 to +13°C for the endothermic O$\rightarrow$C transformation.

From the graph of the lattice parameter vs. the temperature of the endothermic O$\rightarrow$C phase transition ($T_{O\rightarrow C}$) (Figure 13) the authors highlighted that the largest lattice parameter have the highest $T_{C\rightarrow O}$ transition, and hence are the most stoichiometric.

The likeness among the lattice parameter values for samples synthesized at 700°C would indicate that these samples could be considered as identical. Nevertheless, the significant differences among the $T_{O\rightarrow C}$ determined by DSC clearly show that these samples are different.

During their investigation of the reversible and irreversible transformations of the LiMn$_2$O$_4$ spinel undergoes under different atmospheres (air, O$_2$, and N$_2$) when heated up to 1050°C (Figure 14), Massarotti et al. [52] have observed under air and O$_2$, a substantial reversible cation exchange occurs.
Figure 14: Thermogravimetric analysis measurements of LiMn$_2$O$_4$ in air, O$_2$ and N$_2$. Dashed line represents the thermal cycle.

Between 800 and 980°C, a model is suggested in which Mn$^{2+}$ ions substitute Li$^+$ at the tetrahedral (8a) position, and Li$^+$ shifts to interstitial octahedral (16c) site. Charge balance is achieved by a decrease in the Mn$^{3+}$ fraction, which is partially reduced to Mn$^{2+}$ in the regular octahedral (16d) site, according to the charge distribution:

\[(1 + y)\text{LiMn}_2\text{O}_4 \rightarrow (\text{Li}_{1-2y}\text{Mn}_{2y}^{2+})_8[\text{Li}_{3y}^{+}]_{16c}[\text{Mn}_{5y}^{2+}\text{Mn}_{3+5y}^{3+}\text{Mn}_{1}^{4+}]_{16d}\text{O}_4\]

\((y \leq 0.2, y\text{ increases with } T)\)

The average oxidation state of Mn decreases with increasing temperature but, upon cooling the reverse reaction takes place with an O$_2$ uptake which occurs down to 600°C, (thermogravimetrics measurements).

Under N$_2$ flow, a first decomposition occurs between 600 and 800°C and yields Mn$_3$O$_4$, orthorhombic LiMnO$_2$ and O$_2$:

\[3\text{LiMn}_2\text{O}_4 \rightarrow \text{Mn}_3\text{O}_4 + 3\text{LiMnO}_2 + \text{O}_2\]
The second step concerns the transformation of $\alpha$-LiMnO$_2$ into a cubic Li$_x$Mn$_{1-x}$O solid solution ($x \leq 0.5$), consistent with a decrease in the average oxidation state of Mn ions due to the minor O$_2$ release occurs when heating above 900°C:

$$(1-x)\text{LiMnO}_2 \rightarrow \text{Li}_x\text{Mn}_{1-x}\text{O} + 0.5(1-2x)\text{Li}_2\text{O} + 0.25(1-2x)\text{O}_2$$

This cubic phase is stable at high temperature and decomposes upon cooling ($T \leq 800°C$) leaving just the Mn$_3$O$_4$ and $\alpha$-LiMnO$_2$ phases.

The authors supposes that surfaces and grain boundaries are certainly involved along with residual segregated materials in their crystalline or amorphous state while concluding preparation and morphology of the precursor material play a fundamental role in the outcome of the sintering procedure and the final properties (electrochemical or catalytic) of the lithium manganese spinel.

Using accelerating rate calorimetry and X-Ray diffraction, MacNeil and Dahn [53] have reported the thermal decomposition sequence on dry Li$_x$Mn$_2$O$_4$, Li$_x$Mn$_x$O$_4$ in solvent and Li$_x$Mn$_2$O$_4$ in electrolyte, charged to 4.2 V, and compare the results to the corresponding results obtained on Li$_{0.5}$CoO$_2$ [35].

There seem to be two processes occurring during the ARC experiment (Figure 15) and thus for one sample (A), the ARC experiment was terminated at 240°C, where the first decomposition process was believed to be finished. At the termination of both experiments (A and B), and from the XRD profiles (Figure 16) performed on each electrode sample a clear conversion of the $\lambda$-MnO$_2$ structure to the $\beta$-MnO$_2$ structure as samples are heated to 350°C is observed.
The sample that was exposed to higher temperatures (sample B) had a more complete conversion to the $\beta$-MnO$_2$ structure. Thus, dry samples of Li$_x$Mn$_2$O$_4$ charged to 4.2 V transform from the $\lambda$-MnO$_2$ structure to the $\beta$-MnO$_2$ structure with the release of heat starting near 160°C.

Without salt present during the exposure of the charged sample to elevated temperatures there is a solid-state transformation of the $\lambda$-MnO$_2$ structure to the $\beta$-MnO$_2$ structure (beginning 160-170°C), the initial self-heating temperature is the same as that of the $\lambda$ to $\beta$ transition for the sample with no added solvent. The sample with the added solvent demonstrates further self-heating at higher temperatures, resulting in a rapid rise in self-heating rate. This is believed to be due to the solvent oxidation (the combustion of the solvent begins near 200°C and results in a rapid rise in self-heating rate) and reduction of the solid to MnO (Figure 17). The XRD profile of the sample containing the added solvent after the termination of the ARC experiment (Figure 18) reveals that the sample has been reduced primarily to MnO, with small amounts of Mn$_2$O$_3$ and MnCO$_3$ present.
The authors believe that this is due to the combustion of the solvent that releases CO$_2$ and H$_2$O. After the ARC experiment they have moreover noted a severe expansion of the ARC tube due to the generated pressure.

In the presence of LiPF$_6$ salt, a salt-initiated process occurs and is followed first by the solid-state transformation and then by solvent oxidation, coupled with a reduction to MnO. Li-ion cells based on Li$_x$Mn$_2$O$_4$ should be optimized near 0.5 M LiPF$_6$ concentration (Figure 19) in order to have the best thermal tolerance while retaining adequate ionic conductivity.
In the absence of electrolyte salt, the reaction between Li$_{0.5}$CoO$_2$ [35] and solvent initiates (at a SHR greater than 0.02°C/min) at about 130°C, while the reaction between Li$_x$Mn$_2$O$_4$ and solvent initiates at about 200°C under the same conditions. The addition of electrolyte salt tends to make samples of Li$_{0.5}$CoO$_2$ in electrolyte less reactive at low temperatures (for concentrations above 0.75 M), while the opposite is true for Li$_x$Mn$_2$O$_4$ in electrolyte.

MacNeil and Dahn finally suggest that strategies to improve the thermal stability of cells by changing the salt concentration are different for the two electrode materials. For Li$_{0.5}$CoO$_2$, higher salt concentrations, near 1.5 M, are preferred, while for Li$_x$Mn$_2$O$_4$, salt
concentrations near 0.5 M are preferred while the reasons for this difference are not yet well understanding.

More recently, using C80 calorimeter, Wang et al. [54] have studied the thermal kinetics of charged LiMn$_2$O$_4$. At the state of 4.2 V, Li$_x$Mn$_2$O$_4$ starts to release heat at 152°C (Figure 20), and reaches the main peak temperatures at 180, 238 and 266°C with a total heat of reaction −285.9 J/g.

![Figure 20: C80 profiles of charged LiMn$_2$O$_4$ at a heating rate of 0.2°C/min in argon-filled vessel.](image)

The reaction of charged LiMn$_2$O$_4$ is closely accordant on the Arrhenius plots, and then the activation energy is calculated as $E_a = 140.1$ kJ mol$^{-1}$ (assuming the reaction is the first-order reaction and at the initial stage the reactant consumption should be negligible).

Then the authors focus their interest on the thermal behavior of the co-existing system Li$_x$Mn$_2$O$_4$ + LiPF$_6$/EC:DEC (Figure 21).
One mild exothermic process and three exothermic peaks were detected in the coexisting system. Based on these results, the total reaction heat is -1345.8 J/g (based on the mass of LiMn$_2$O$_4$), and the apparent activation energy and frequency factor from the mild exothermic processes of Li$_x$Mn$_2$O$_4$ are $E_a = 71.7$ kJ/mol, $A = 3.11 \times 10^5$ s$^{-1}$, respectively.
**Thermal decomposition mechanism of Li$_x$(Ni,Co,Al)O$_2$**

Until today, the thermal decomposition mechanism of Li$_x$(Ni,Co,Al)O$_2$ has not been particularly studied but some comparison studies have been published [56-57] (Figure 22).

![DSC measurement of cathodes charged at 4.3V](image)

These studies clearly show that the Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ cathode has better thermal stability characteristics than either Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ cathode or its stabilized form Li(Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$)O$_2$. The Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ and Li(Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$)O$_2$ exhibit at least three broad exothermic peaks between 200 and 300°C. Although they start reacting with the electrolyte at the edge of 200°C, the total heat generated by Li(Ni$_{0.8}$Co$_{0.2}$)O$_2$ (2300 J/g) is much greater than that produced by Li(Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$)O$_2$ (1880 J/g). The DSC curve of Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ is different and consists of three sharp exothermic peaks: a pair of two weak peaks centred at 265 and 275°C with an onset temperature of 260°C and a third isolated peak at 305°C with an onset temperature of 300°C. The total heat associated with the three exothermic peaks is estimated at 910 J/g, which is much lower than the heat generated by the Li(Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$)O$_2$.

These results are confirmed by Y. Wang et al. (Figure 23) [57]. In order to draw a fair and scientific comparison between the different active materials, samples were
chosen from industrial production, and their specific surface areas are in the same order of magnitude. In this study, the thermal stability of NMC (LiNi$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$O$_2$), NCA (LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$) and LiCoO$_2$ are compared. These thermal stabilities are assessed by the measurement of the self-heating rate of a mixture between the active material in its charged state and the electrolyte into an ARC Calorimeter [58]. Caution needs to be exercised in the respective amount between the two chemicals.

![Self-heating rate vs. temperature for the charged (4.2V) positive electrode materials](image)

**Figure 23:** Self-heating rate vs. temperature for the charged (4.2V) positive electrode materials (a) LiCoO$_2$ (E-One Moli Energy), (b) and (c) two samples of NCA-01 and -02 Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ (Toda Kogyo Corp. (Japan)), (d) NCM-A Li[Mn$_{0.33}$Ni$_{0.33}$Co$_{0.33}$]O$_2$ (3M Company) reacting with either 30 mg (solid lines) or 100 mg (dashed lines) of 1M LiPF$_6$ EC:DEC. The horizontal long-dashed line indicated a self-heating rate of 0.2°C/min [57]

Although the LiCoO$_2$ sample had the smallest specific surface area of all samples studied, the experiment shows that it is the most reactive of all the samples below 180°C.

HELIOS – Review Thermal Runaway Reactions mechanisms - PUBLIC 26/41
LiCoO$_2$ and NCA reached SHRs of 10°C/min at approximately the same temperature. These results suggest that switching from LiCoO$_2$ to NCA should not lead to significant safety improvements. The NCM samples had the lowest self-heating rates of all the samples, at least below 250°C, suggesting that Li-ion cells with the best safety properties can be made by using NMC. Changing the electrolyte:active material ratio affects the reactivity of both LiCoO$_2$ and NMC positive materials as shown by comparing their SHRs for 30 mg (solid lines) or 100 mg (dashed lines) of 1 M LiPF$_6$ EC:DEC (Figure 29). Obviously, further work is needed to understand the variations of SHR versus temperature with electrolyte:active material ratio.

**Thermal decomposition mechanism of Li$_x$(Ni,Mn,Co)O$_2$**

Thermal stability of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (labelled in the following as NMC) has been studied in detail by a well recognized group in Canada headed by J.R. Dahn. One must first recall that NMC was discovered quite recently, in 2001, by this group and Pr. Ozhuku's one [47]. As described in the previous sections, the development of EV and PHEV applications addresses the problem of safety into which positive electrode has a strong impact. Quite recently (2007) Dahn’s group made an interesting comparison between different layered materials (as reported above within the previous part) and a lot of interesting points can be extracted (Figure 23):

- First, the SHR value of 0.2°/min is reached at lower temperature for NMC then for NCA and finally LiCoO$_2$. NMC appears to be better than NCA and LiCoO$_2$.
- Same tendency observed for a SHR value of 10°C/min.
- It is important to use the value of SHR at 150° for comparison. Indeed this temperature is the fixed temperature applied to a battery when the safety oven test is performed. One can observe that negligible SHR is reached for NMC and NCA with low BET surface area. The SHR value starts to be significant for NCA, with relative high surface area for battery materials (0.47 m$^2$/g), and even more for LiCoO$_2$.
- The behaviour of each material with the amount of electrolyte is unique. For LiCoO$_2$, the self-heating rate at low temperature strongly decreased with the amount of electrolyte. This has been clearly explained by the formation of a protective polymeric film that can prevent the oxygen loss from the positive active
material. For NCA, the quantity of electrolyte has no influence on the self-heating rate whereas, in the case of NMC, the electrolyte quantity has an important role in the heat release. This behaviour has been explained by manganese dissolution that may take place at high temperature and that may be responsible for oxygen loss.

From a safety point of view, we are looking for materials that will have the highest temperature of reactivity with the electrolyte but also materials releasing a limited value of energy. LiCoO₂ is compared with NCA and NMC at different levels of charge (i.e. fully charged at 4.2 V and overcharged at 4.4 V). Surprisingly, all three different samples have their total evolved heat in the reaction between charged cathode and the electrolyte perfectly comparable and equal to 1100 J/(g of positive electrode) (Table 4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔT (°C)</th>
<th>Reaction heat: J/(g positive electrode material)</th>
<th>Literature</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂ – 4.4 V</td>
<td>105</td>
<td>1100 ± 100</td>
<td>1360 ± 100 (Réf. [3737])</td>
<td>1100 ± 250 (Réf. [3838])</td>
</tr>
<tr>
<td>NCA-02 – 4.2 V</td>
<td>&gt; 80</td>
<td>&gt; 850 ± 100</td>
<td>750 to 1050 (Réf. [3939])</td>
<td>1460 (Réf. [4040])</td>
</tr>
<tr>
<td>NCM-A – 4.4 V</td>
<td>105</td>
<td>1100 ± 100</td>
<td>790 (Réf. [4040])</td>
<td>1535 ± 100 (Réf. [3737])</td>
</tr>
<tr>
<td>NCM-C – 4.4 V</td>
<td>100</td>
<td>1050 ± 100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Total evolved heat in the reaction between charged cathode materials and 1 M LiPF₆ EC:DEC electrolyte

In conclusion the thermal stability of NMC is better than these other layered materials but this material strongly reacts at a temperature higher than 180°C. Efforts have been done by many groups, and especially by the Canadian group, to reduce the high temperature stability. First Mg²⁺ has been used as a substitute cation for Ni, Mn or Co in Li[Ni₁/₃Mn₁/₃Co₁/₃]O₂. Whatever the transition metal substituted, there is a linear decrease in the capacity with the amount of Mg, and no improvement has been noticed in terms of capacity or safety [59].
In a second paper [60], the same authors used Al$^{3+}$ as a substitute for cobalt in the lamellar structure. They have demonstrated that high capacity positive electrodes are obtained but more importantly that the safety is dramatically improved (Figure 24).

![Figure 24](https://example.com/figure24.jpg)

*Figure 24: (Color online) Maximum SHR vs Al content, z, for 94 mg de-lithiated Li[Li$_{1/3}$Co$_{1/3}$Al$_z$O$_2$ reacting with 30 mg 1 M LiPF$_6$ EC:DEC with starting temperatures of 70°C (circles for sample charged to 4.3 V and triangles for sample charged to 4.6 V) and 180°C (squares for samples charged to 4.3 V)*

However, the capacity of the Al-doped NMC is, in the end, lower than pure NMC composition. A double substitution (Al$^{3+}$ for Co$^{3+}$ and Ni$^{2+}$ for Co$^{3+}$) has been explored and, as illustrated (Figure 25), good capacity and thermal stability have been reached with this strategy.
Decomposition mechanisms of LiFePO₄

First defined by the pioneering work of Goodenough’s team in 1997 [61], LiFePO₄ (hereafter abbreviated as LFP) has been recognized as one of the most probably interesting alternatives to LiCoO₂ cathode material for lithium rechargeable batteries because of its low cost, environmental compatibility, non-toxicity, high abundance of iron, good electrochemical performance, and high mass specific capacity (170 mAh/g). It gained some market acceptance. Confer to this status behaviour under abusive conditions was investigated by different working groups.

Overcharge/ Overdischarge and Short cut

Kong et al. [62] have compared the gas evolution behavior (GC-MS method) of three different cathode materials (in 18650 batteries) from commercial products (i.e. LiCoO₂: Nippon chemical, LiMn₂O₄: Nippon chemical, and LiFePO₄: Valance) under normal cycling and overcharging to 4.5 V and 5.0 V (Figure 26). They have demonstrated that gas generation behaviors under normal charging condition are not related to the type of cathode materials while under overcharging condition, the amount and the type of gas species are influenced significantly by the oxidation ability of the cathode materials.
In fact, more C\textsubscript{2}H\textsubscript{2} is produced in LFP battery due to its weak oxidation ability and more CO\textsubscript{2} is formed in LiCoO\textsubscript{2} battery because of its strong oxidation ability. Besides, they have underlined that the production of C\textsubscript{2}H\textsubscript{2} can be used as a probe to compare the oxidation ability of the cathode material. The resulting order of the oxidation ability for three cathode materials under overcharging state is LiCoO\textsubscript{2} > LiMn\textsubscript{2}O\textsubscript{4} > LFP. In addition, C\textsubscript{2}H\textsubscript{5}F is also detected as a gas product in all batteries under normal or overcharging condition. It is produced from an electrochemical oxidation reaction from C\textsubscript{2}H\textsubscript{6} with HF.

He et al. [64] have prepared commercial 066094-type liquid state soft pack high power batteries with carbon-coated LFP/graphite electrodes and studied their safety performance and heating mechanism under abusive conditions, such as overcharge, overdischarge, and short current.

During the overcharge, the main reactions to consider are the reaction of electrolyte decomposition, the exothermic reaction between the delithiated cathode and the electrolyte, and the violent reaction between the overcharged anode and the electrolyte at high temperature. In the case of LFP phase it changes into the FePO\textsubscript{4} phase during the
charge process. The FePO₄ phase almost does not react with the electrolyte below 200°C and the heat from the reaction above 200°C is also smaller than that for the fully charged LiCoO₂. The violent exothermic reaction between the lithiated anode and the electrolyte occurs above 240°C, which is initiated by the rapid exothermic reaction between delithiated cathode and the electrolyte. By following the voltage, temperature, and current profiles of high power batteries for 1 C/10 V overcharge test (the overcharge tests were conducted by further charging the batteries with a constant current of 2 A (1 C) using a 10 V power supply (1 C/10 V) after they were fully charged to 4.0 V) (Figure 27a), the authors show that the battery temperature during testing never reaches 240°C, so the violent exothermic reaction between the lithiated anode and the electrolyte almost does not occur which furthermore may explain that no fire and smoke have been detected.

From EIS experiments (after overcharged to 4.8 V) (Figure 27b) the increase in the temperature of the LFP/graphite high power batteries during the overcharge revealed to be related to the reaction of electrolyte decomposition and the Joule heat.

All along the overdischarge test (conditions: the overdischarge test of batteries was conducted by discharging the fully charged batteries to 0 V with a current of 1 C) no distinct temperature increase is observed (Figure 28a). The EIS test (Figure 28b) of the high power batteries before and after overdischarge indicates that the $R_{\text{cell}}$ increases greatly after overdischarge leading to the conclusion that the batteries also generate Joule heat ($Q = i^2 R_{\text{cell}} t$).
He et al. have continued their experiment by reporting the cycling curve of LFP/graphite batteries after overdischarge at 1 C/0 V and with regard to the excellent cycling performance the overdischarge does not really influence the battery performance (Figure 29).

During the short current (the short current tests were conducted by connecting the cathode tab with the anode tab using a low resistance lead (< 5 mΩ) after the batteries were fully charged to 4.0 V. A multimeter was also connected to the cathode and anode tab to measure the voltage of batteries in the short circuit experiment), the battery voltage firstly showed a short plateau at about 1.6 V, and then gradually decreased to 0 V
The batteries were heated rapidly by the irreversible heat generated from the current passing through the electrodes. This rapid heating process produces a steep temperature profile with the highest temperature at the core. At these temperature levels (i.e. < 110°C) the LFP phase is thermally stable in the electrolyte, so the positive decomposition reaction cannot be activated. However, the other exothermic reactions such as the solvent reactions proceed significantly.

**Figure 30:** Voltage and temperature profiles for the short current test of 066094-type liquid state soft pack high power batteries with carbon-coated LFP/graphite.

**ARC**

Dahn’s group have compared the thermal stability of three different charged positive electrode materials: LiFePO₄ (Phostec Lithium), LiCoO₂ (E-one Moli/energy Canada Ltd) and Li[Ni₀.₅Co₀.₈Mn₀.₁]O₂ (synthesized as reported by Jouanneau and Dahn) in two types of electrolytes (LiBoB EC/DEC and LiPF₆ EC/DEC) [1010-1012] (Figure 31-32). These experiments were performed using accelerating rate calorimetry (ARC) measuring the self-heating rate versus temperature of the three samples (mixture of charged positive electrode and electrolyte) with starting temperature of 110°C (Figure 31) and 150°C (Figure 32) using a heating ramp of 5°C/min. The discussion leads to several interesting conclusions:

- LFP has the highest stability among the three materials in LiBoB EC/DEC or in LiPF₆ EC/DEC electrolytes,
LFP in LiBoB EC/DEC exhibit highest stability than LFP in LiPF₆ EC/DEC with no detectable heat released until about 240°C in the two experiments (110°C and 150°C) combined to a large self heating rate (180°C and 190°C for LiPF₆).

Another study of Jiang et al. [1111], based on LFP ARC experiments (starting temperature 110°C), reveals that tuning the particle size (3 µm to 15 µm) and BET specific surface area does not clearly affect the reactivity of LFP in electrolyte samples (LFP in LiBoB EC/DEC and LFP in LiPF₆ EC/DEC) and confer a certain flexibility for electrode designers in the choice of particle size distribution to use from a safety point of view. Exothermic reaction is observed between 190°C and 235°C in LiPF₆ versus 240°C and 290°C in LiBoB joining last results.

Zaghib et al. [65] have compared different cathode materials in (LiFSI)-EC/PC/DMC electrolyte and a fully charged state. The temperature at which thermal runaway is initiated increases in the following order:

LiNiₓCoₙAl₂O₂ > LiCoO₂ > LiFePO₄ (Phostec) for which a small heat effect contribution is observed at 290°C.
**NAIL AND CRUSH**

Nail penetration (2.5 mm diam.) and crush test (semicircular edge of a 16 mm thick iron plate) were carried out by Takahashi *et al.* [66] on a prismatic cell (H = 47 mm, W = 34 mm, Thick = 11 mm, weight = 40 g; similar to commercial available prismatic cells) of LFP based material. Before each test, the cell was charged galvanostatically to 4.0 V at 200 mA, followed by constant voltage charging at 4.0 V during 8 hours. These abuse tests have no effect on such cells: no smoke, no fire and no explosion were observed.

**HIGH TEMPERATURE**

In order to understand the thermal abuse behavior of high capacity and large power lithium-ion batteries for electric vehicle application, Guo *et al.* [67] have recently developed a three-dimensional thermal finite element modeling of lithium-ion in thermal abuse application. In their study, the model predictions are compared to oven tests results for VLP 50/62/100S-Fe (3.2 V/55Ah). Cathodes and anodes were respectively coated on aluminum and copper foils and both electrodes used PVDF and NMP binder. The separator was made of tri-layers of polypropylene, polyethylene and polypropylene (PP/PE/PP). The electrolyte consisted of 1M LiPF$_6$ in ethylene carbonate-dimethyl carbonate-ethyl methyl carbonate (EC/DMC/EMC) solvent with mass ratio 1:1:1.

The cell was initially at a normal operating temperature (25°C) and was charged first in galvanostatic mode at 1 C rate with a voltage cut-off limit of 4.2V and then in a potentiostatic mode until the current dropped to 1000 mA. After 2 h stewing, the cell was then suddenly placed in an oven that was preheated to the required test constant temperature ranging from 140°C to 160°C. The cells used in the oven test were charged at C/3 and discharged at 1 C rate.

Their study lead to several observations:

- The cells placed in the 140°C and 150°C oven test do not go into thermal runaway contrary to the cell heated in the oven at 155°C and 160°C.
- For this last cells and while the cell heats up, the temperature profile is highest at the can surface and decreases toward the core. For example with the experiment conducted at 155°C oven, at 1200 s, as the exothermic reactions are activated and start to release heat, the core temperature of the cell increases, and the temperature reaches a maximum at the center *(Figure 33a).* At about 3600 s the
cell undergoes thermal runaway and the highest temperature reaches above 246°C at the cell center (Figure 33b).

Besides, they have followed the evolution of the cell voltage during the experiment (Figure 34) and noted that around 1200 s the cell voltage dropped quickly to 1.3V and then suddenly moved back to 3.6 V.

After the cell voltage had recovered, it remained at an almost constant value during the remaining heating period of the test until the voltage sharply decreased to 0 V once more caused by internal short-circuit induced and the thermal runaway may occur.

The results indicate that the LiFePO₄ active material is more thermally stable under oxidation potential than LiCoO₂.

Furthermore, the shutdown mechanism of the separators can improve cell safety during abuse test, so addition of the ceramic coating should contribute to the strength and
resistance to melting and shrinking of the separator. Moreover, it was found that there is
hardly any temperature gradient (between center and surface) in both longitudinal and
transversal directions inside the cell geometry when placed in 150°C oven test, while the
maximum of the temperature gradient along thickness. The small temperature gradient
suggests that the relatively large thermal conductivity along the Y and Z directions allows
heat produced to be removed from the cell.

About thermal abuse test and from INERIS’s experiments, it’s necessary to take
also in consideration the influence of the packaging, for example: the stick used in a
coffee bag that can be destroyed upper 120°C leading to the runaway of the battery.

CONCLUSIONS

It is a long-term goal to find safer positive electrode materials and also to
understand the reasons sustaining improved safety performance. The studies by
Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA)
indicated that oxygen release from charged cathode materials plays a significant role in
the safety performance of lithium-ion batteries. According to the literature, charged NCM
has better thermal properties, in other words better safety characteristics, than that of
conventional NCA, since NCM has limited oxygen release potential [4444]. Their onset
temperature has been evaluated through ARC calorimetry studies. A difference of more
than 100°C has been measured compared with the other layered materials like NCA.
However, the total evolved heat is in the same order of magnitude as the other layered
materials. Both Al³⁺ and Ni²⁺ substitutions for Co³⁺ seem to be the ideal strategy that
leads to high energy density and good thermal stability altogether.

However, at the time the analysed paper was published, NCA and NCM materials
with low specific surface area were not readily available, as they are today.

Description of the results

The document shows obviously that the thermal behaviour of the electrode materials
are strongly depending on:

(i) the nature of the material,
(ii) the nature of the electrolyte (salt, solvents, additives),
(iii) the state of charge and state of health of the accumulator and,
(iv) the origin of the increase of temperature which can be related to an operation at high discharge current for example, to not well controlled environmental conditions, to an accidental overcharge (default of equalizing) or to an internal or external short-circuit.

Today, a comparative study of active materials thermal stability inside electrolyte but not integrated inside a battery container is available to classify materials from the most thermically stable to the less thermically stable. The classification is only valid for similar electrolyte/active mass ratios and similar capacity stored inside the material. This thermal behaviour of electrode materials (self-heating rate) can be described by determining two temperatures from adiabatic calorimetry experiments:

(i) Onset of chemical reaction preceding thermal runaway and,

(v) Onset of thermal runaway. We expect that the speed of increase of temperature during this thermal runaway could be an informative parameter too.

However, this classification is not so easy to make when the materials are included inside a real commercial cell, because other parameters influence the self-heating rate of the accumulator such as: shape, internal design and connexion, thermal fuse. As indicated, because the first exothermic phenomenon leading to the self-heating of the cell is relative to the passivation film decomposition on the surface of the carbon negative electrode, the nature of the carbonaceous material used has an influence that must be taken into account.

References