

# THERMAL STABILITY OF CHEMICALS USED IN LITHIUM-ION BATTERIES

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## **List of symbols and abbreviations**

**LIB** Lithium Ion Battery

**PC** Propylene carbonate

**EC** Ethylene carbonate

**DEC** Diethyl carbonate

**DMC** Dimethyl carbonate

**PVDF** Polyvinylidene fluoride

**SEI** Solid electrolyte interphase

**ARC** Accelerating rate calorimetry

**DSC** Differential scanning calorimetry

**Dendrite** Growth of metallic lithium on an electrode

**LiTFSI** Bis(trifluoromethane)sulfonimide lithium salt

**PEO** Polyethylene oxide

**SOC** State of charge

## **Acknowledgments**

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## **1. Introduction**

Lithium-ion batteries (LIBs) have high operating voltage and good cyclability, but their safety problems have been known for a long time. LIBs have a propensity to undergo thermal runaway if subjected to impact, high temperatures or overcharge. The current rechargeable LIBs are mostly established in use and their composition is usually very similar. The threat of accidents caused by thermal runaway has led to strict safety guidelines in use, transportation and disposal of LIBs.

On top of the problems in the current commercial LIBs, research aims for ever higher energy densities to allow for smaller electronics and to reduce the weight of battery packs. Especially the commercialization of electric vehicles demands battery solutions where the power and charge life time is significantly increased, if these new vehicles are to have the kind of performance consumers are used to in modern vehicles. Changing battery chemistry or voltage to increase energy density leads to batteries having more volatile chemistry and increases the potential for violent exothermal reactions.

It is important to be aware how changes in the battery composition affect their safety features, and also important to find battery solutions that are not susceptible to thermal runaway. This thesis is meant to highlight the importance of safety considerations in rechargeable lithium-ion batteries.

## 2. Rechargeable lithium-ion batteries

### 2.1 General

Lithium-ion batteries (LIBs) are the most common type of rechargeable batteries. They are used in small scale battery applications such as mobile phones and laptops, and in larger scale applications such as electric vehicles. The popularity of lithium ion batteries is explained by the fact that they currently have the best performance of commercially viable solutions. LIBs have higher operating voltage (3,6-3,7 V) and better energy density ( $\sim 500 \text{ Wh/dm}^3$ ) than rechargeable batteries based on alternative chemistries, such as Ni-Cd battery. <sup>1</sup>

For a long time (since invention by Sony in 1991) most of the commercial lithium ion batteries have been made with the “usual” set of components:  $\text{LiCoO}_2$  as the cathode material, graphite as the anode, polyvinylidene fluoride (PVDF) as binder and electrolyte based on lithium salt ( $\text{LiPF}_6$ ) in some mixture of propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC).<sup>1-3</sup> This first generation of rechargeable lithium ion batteries is slowly being replaced by the next generation of materials, such as manganese dioxide cathode,<sup>4</sup> multi-metal oxide cathode, gel electrolyte and tin based anode<sup>5</sup> or iron phosphate cathode<sup>6</sup>. Research is constantly done to develop batteries with higher energy density, faster charge rate and longer life time. Other considerations such as cost and safety of chemicals have also led to studies of alternative materials to use.<sup>2</sup> There are many good reviews about the history and development of rechargeable lithium ion batteries, for example Goodenough et al.<sup>7</sup>

### 2.1.1 Chemistry

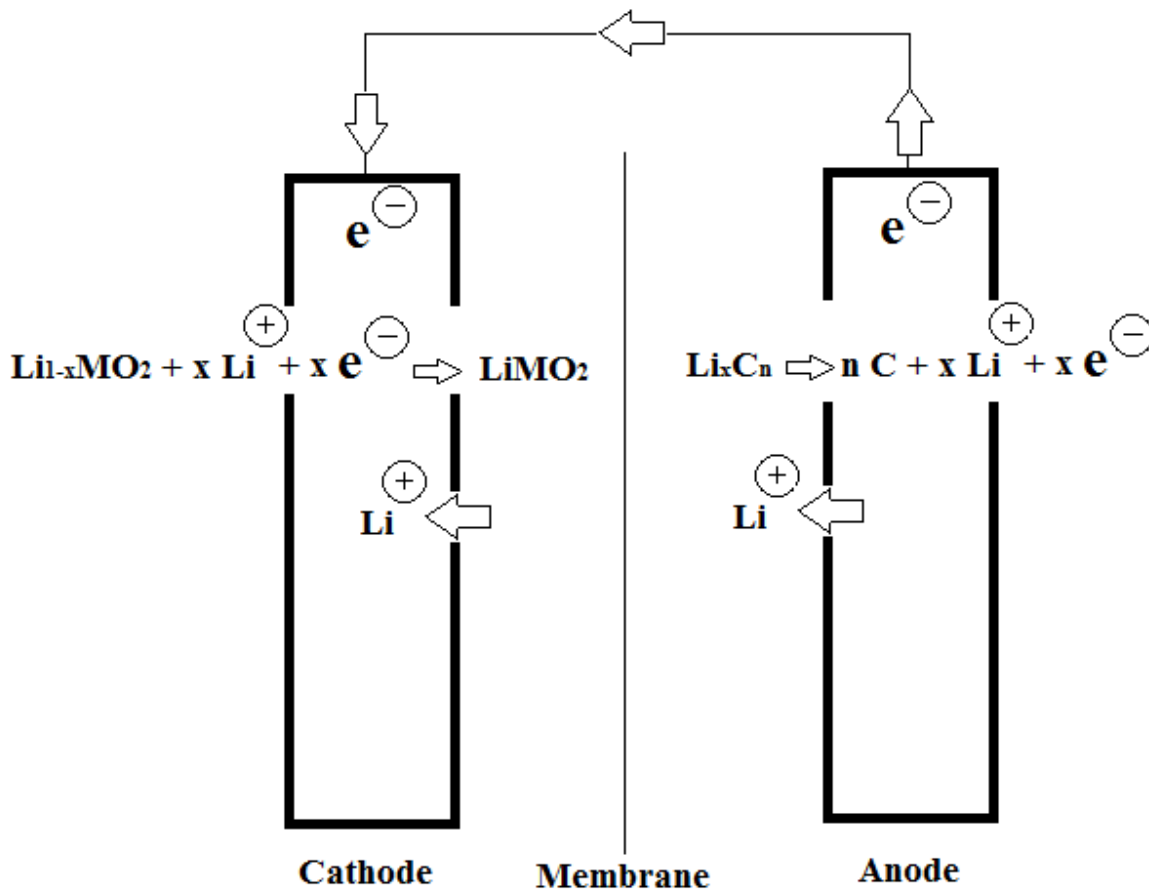
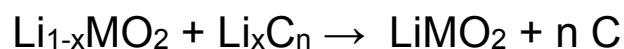


Figure 1 Operation principle of rechargeable lithium-ion battery cell with a transition metal oxide cathode and graphite anode (adopted from Goodenough et al.<sup>2</sup>)

A lithium-ion battery is based on the movement of lithium ions between the anode and the cathode. The anode and cathode are both made out of so called intercalation compounds, i.e. compounds that can reversibly receive and release lithium ions to or from their structure in a chemical (red-ox) reaction. As can be seen in Figure 1, both an electron and a lithium ion are released in the reaction on the anode, and an electron and a lithium ion are consumed in the reaction on the cathode. Electrons are forced to travel through the metal wires connecting the two electrodes while lithium ions travel straight through the electrolyte from one electrode to the other.

The full cell reaction during discharge (in a battery using a transition metal oxide cathode and a graphite anode) is<sup>8</sup>:



This reaction is spontaneous and the cell provides energy when lithium ions move from the anode to the cathode. Since this reaction is reversible, it can be reversed by applying electric current (charging the battery).

While the reaction is in theory 100 % reversible, in practice the battery capacity fades every time it is charged and discharged because of various side reactions. The cyclability and life time of a battery depend on how close to 100 % the reversibility of the cell reaction is.

### 2.1.2 Components

To function, a lithium ion battery needs a cathode, an anode, a separator and electrolyte. A cell has a single anode-cathode pair. A battery can consist of multiple cells.

**Positive electrode**, which is the cathode in galvanic cell, consists of active material (which is the intercalation compound), binder and conducting carbon. Cathode active material is commonly a lithium transition metal oxide. **Negative electrode**, which is the anode in galvanic cell, consists similarly of active material, conducting carbon and binder. The active material in anode is usually graphite. **Binder** is a polymer, commonly polyvinylidene fluoride (PVDF), that is used to make the electrode into a film (instead of a loose powder) on a current collector. Conducting carbon is added to the electrodes in order to make their internal electron conductivity better. **Separator** is a plastic membrane that keeps the anode and cathode from touching each other and the battery from short circuiting.

**Electrolyte** is usually a solution of a lithium salt ( $\text{LiPF}_6$ ) in an organic solvent mixture (some variation of PC/EC/DEC/DMC).  $\text{LiPF}_6$  is used as the salt because it is "less dangerous and poisonous than other possible suitable salts".<sup>9</sup> Electrolyte is the medium which delivers lithium ions from one electrode to the other. The lithium ions are nominally generated in the cell reaction, but in actuality they are given or received by the lithium salt in the electrolyte. Electrolyte also has to function as an electron insulator, so that the electrons are forced to travel through the wires connected to the battery and do work, instead of moving directly from electrode to electrode in a short circuit. Preventing electron movement through the cell requires that potential of the anode has to be higher than the HOMO of the electrolyte to prevent oxidation of electrolyte on the anode, and the potential of the cathode has to be lower than the LUMO of the electrolyte to prevent reduction on



the cathode. Because of this the electrode potentials (and therefore the energy of the battery) are limited by the HOMO-LUMO gap of the electrolyte (Figure 2).<sup>10</sup>

This limitation can be circumvented by kinetic control. This means that the battery is knowingly designed in such a way that the potential of the anode is too low to be stable. During the first (carefully controlled) charging of the battery, the electrolyte is reduced on the anode, but the break-down products created during the reaction form a passivating layer around the anode and prevent any further reduction happening during following cycles. This formed layer is called solid electrolyte interphase (SEI). If the SEI layer is damaged, the electrolyte decomposition will begin again and lead to rapid heat and pressure rise. A stable SEI layer is therefore needed for a safe battery, especially because the most common anode material, graphite, has a potential that is too low (1.1 V vs. Li) for any organic solvent based electrolyte to operate without a SEI layer. Most cathode materials are within the electrochemical window (~4 V vs Li) of the organic solvent based electrolytes, so their functioning does not require SEI layer in the same way the anode does. SEI layer composition depends on the identity of the lithium salt and the solvent in the electrolyte, and a stable SEI layer needs additives, such as EC, in the electrolyte to form.<sup>11</sup>

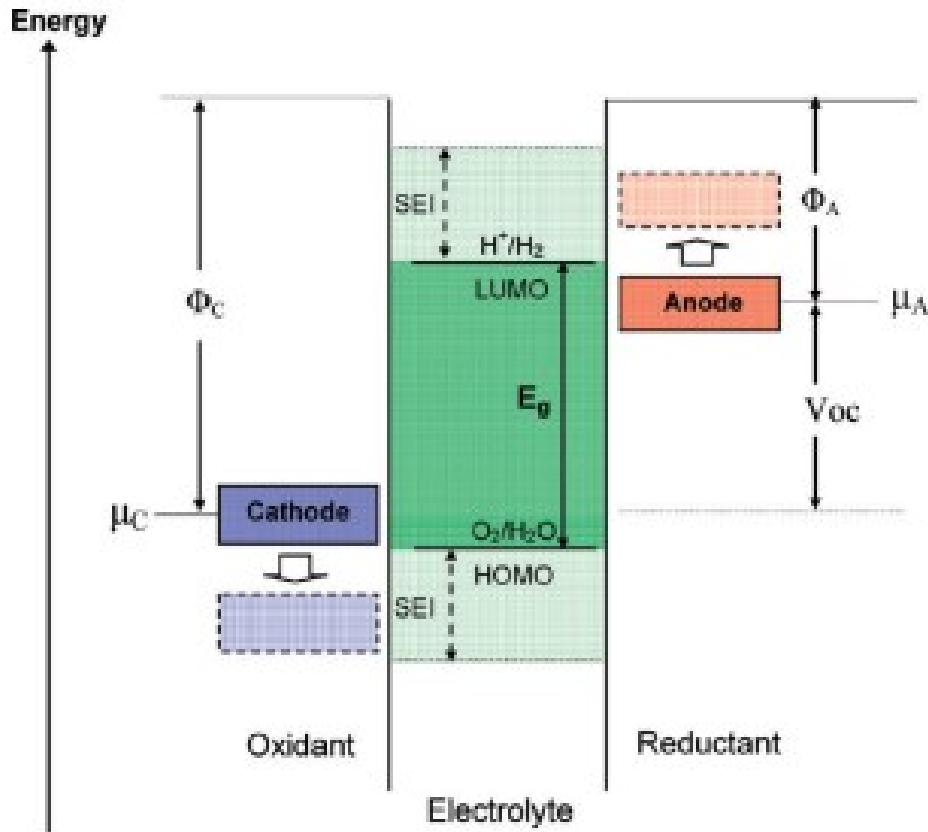


Figure 2 Energy diagram of an aqueous electrolyte from Godenough and Kim.<sup>2</sup>  $\Phi_C$  and  $\Phi_A$  are cathode and anode work functions.  $V_{OC}$  is the open circuit voltage of the cell.  $E_g$  is the stable potential window for electrolyte. The faded areas show where kinetic control is needed for battery to function.

### 2.1.3 Characteristics

The characteristics that are commonly used to define battery performance are voltage, capacity, energy density, power and charge/discharge rate.

**Voltage** of a lithium ion battery is more complicated to calculate than that of a simple two metal electrochemical pair. The open-circuit voltage  $V_{OC}$  of a lithium ion cell is given by the difference in the lithium chemical potential between the cathode ( $\mu_{Li(cathode)}$ ) and anode ( $\mu_{Li(anode)}$ )<sup>10</sup>:

$$V_{OC} = \frac{\mu_{Li(cathode)} - \mu_{Li(anode)}}{F}$$

where  $F$  is the faraday constant. Both the electron transfer and the lithium ion transfer are factors that affect the  $V_{OC}$ . The energy required to transfer electrons to and from the electrode material is defined by its work function,  $\phi$ . The energy required to transfer

lithium ions to and from the electrode material structure is determined by the structure and geometry of the binding sites that the lithium ions attach to.<sup>10</sup>

In order to have a high  $V_{OC}$ , the chemical potential of lithium in the cathode should be high, and the chemical potential in the anode should be low. The chemical potential is determined by the binding sites that are available to lithium ions in the active material structure. From graphite, the lithium ions are easily removed (low potential), from transition metal oxides lithium ions are more difficult to remove (high potential). In transition metal oxides, the binding sites and chemical potential of lithium are determined by the oxidation numbers of the metal ions in the compound. To maximize the voltage, transition metal ions should have a high oxidation number. There might also be multiple different binding sites with different potentials, which means that the lithium ions are removed or added in several steps.<sup>10</sup>

The actual voltage of a battery in use is not the same as a calculated theoretical voltage. Output voltage drops quickly to a lower voltage and then over time slowly falls below the cut-off voltage, where the battery is considered empty (Figure 3). The nominal operating voltage that is given to consumers is the midpoint between the initial output and cut-off voltages. The discharge curve of a battery should ideally be as flat as possible so that the variation in the voltage is small as the battery charge is used.<sup>12</sup>

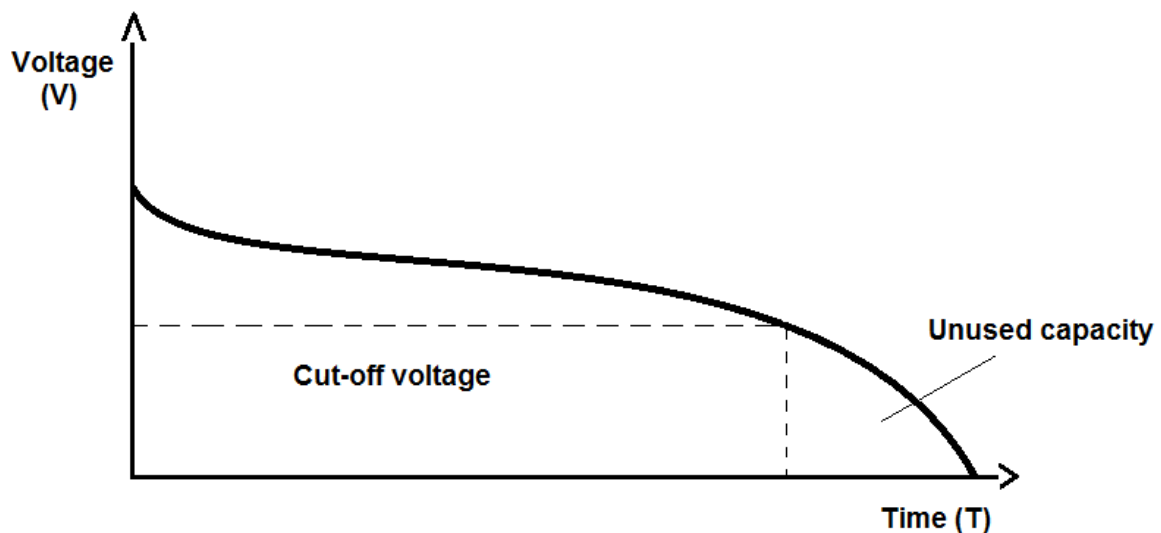


Figure 3 Example of a discharge curve for a lithium ion battery.

**Capacity** of a battery is measured in Ah or mAh/kg. A battery with a capacity of 10 Ah can sustain a current of 1 A for 10 h or a current of 10 A for 1 h. Capacity of an active material is determined by the amount of reversibly intercalated lithium ions. There is only a limited amount of lithium ions that can be inserted in to the structure of an intercalation compound before the structure is forced to change in order to accommodate the incoming lithium ions. This leads to increase in the volume of the electrode, which usually stops the battery from functioning. Similarly there is also a limit to how large portion of lithium ions can be removed from a material structure before it collapses. The number of reversible binding sites available for lithium ions therefore limits directly the capacity of the battery. A material that has a large amount of Li-binding sites can hold more lithium and therefore holds more charge.<sup>10</sup> At the moment, anode materials such as graphite can hold a larger amount of lithium ions than is possible to insert in to any cathode material of the same volume. This means that the amount of cathode material in a battery needs to be disproportionately larger. **Energy density** (specific energy) is calculated as capacity (mAh/kg) times voltage (V) and is given per unit of mass or volume (Wh/kg or Wh/L). For an electrode material, energy density is calculated with theoretical capacity and given per mass (or volume) of the material. For a whole battery, the energy density is calculated with measured capacity and given per mass of the battery.

**The charge-discharge rate** determines how fast the battery can be charged and also how fast it can be discharged. Discharge rate determines the **momentary power** that can be obtained from the battery. The charge-discharge rate of a battery depends on the rate of lithium ion diffusion within the active material (and in the electrolyte) and therefore the structure of the intercalation compound. The more freely the lithium ions can move, the faster is the diffusion rate. For example layered structure allows 2D movement, spinel structure allows 3D movement and olivine-structured  $\text{LiFePO}_4$  allows lithium ion movement in only one direction.<sup>13</sup>

The structure of the intercalation compound can be layered such as with transition metal oxides ( $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ), where the lithium, metal and oxide are in separate layers that alternate, or graphite where the lithium ions and graphite layers alternate. Intercalation compounds can also have a more complicated structure. Some common ones are presented in Figure 4 Crystal structures of some active materials for lithium-ion batteries adopted from Islam et al.<sup>13</sup>Figure 4.

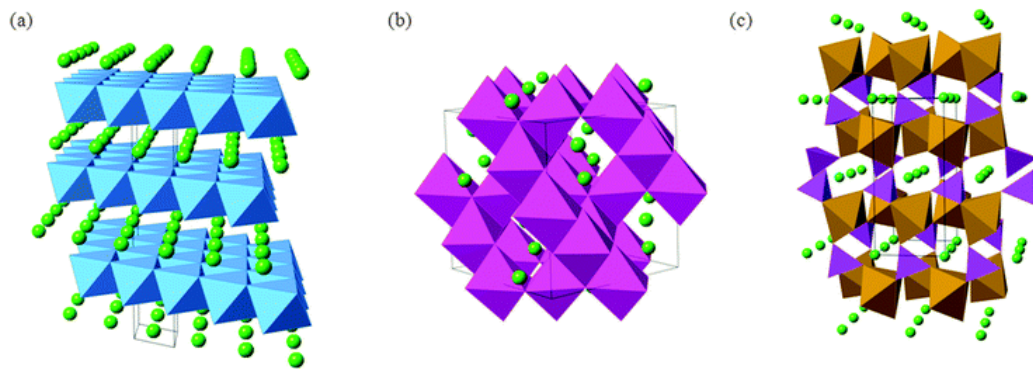


Figure 4 Crystal structures of some active materials for lithium-ion batteries adopted from Islam et al.<sup>13</sup> a) layered structure b) cubic  $\text{LiMn}_2\text{O}_4$  spinel c) olivine structured  $\text{LiFePO}_4$ . Green spheres represent lithium.

### 3. Thermal runaway

In a normally functioning battery, the only reactions that should be occurring are the half-cell reactions on the electrodes and the lithium ion transport between the electrodes and the electrolyte. In a failure state, other chemical reactions will occur. Some of these reactions degrade battery performance over time. The dangerous reactions are ones that generate heat rapidly. In a Li-ion battery that is built from the most commonly used components (described in the previous chapter), there is a danger of chain reaction where one exothermic reaction, once begun, will generate enough heat to launch another exothermic reaction and so forth, until the battery will eventually catch fire or even explode. This phenomenon is known as the thermal runaway process. It has led to several accidents where lithium ion battery systems were the cause of a fire<sup>14</sup> and cargo fires while lithium ion batteries were transported<sup>15</sup>.

#### 3.1 Progression of reactions

The progression of reactions under thermal runaway is dependent on all the components and also the design of the battery pack itself. Heat generating reactions that are possible in abuse conditions (according to Spotnitz et al.)<sup>16</sup>:

- Heat production due to entropy changes, resistance or overpotential. This can produce dangerous amounts of heat (~100 °C temperature rise) because lithium ion cells tend to have very high internal resistance compared to other cell types
- SEI decomposition on anode
- Lithium anode reacting with fluorinated binder
- Intercalated lithium reacting with electrolyte on the anode after SEI layer is gone (producing  $\text{Li}_2\text{CO}_3$  and flammable gas)
- Intercalated lithium reacting with fluorinated binder on anode
- Electrolyte decomposition due to temperature or self-reaction (producing flammable gas)
- Cathode material decomposition (producing oxygen if the cathode is a transition metal oxide)
- Formation of metallic lithium due to overcharge, which can further react with electrolyte or binder.

Accelerating rate calorimetry (ARC) simulations done by Spotnitz et al.<sup>16</sup> put the reactions in order as stated in Table 1. In addition to these reactions if there is moisture or alcohol present,  $\text{LiPF}_6$  salt may react to form HF, which is a highly toxic gas.<sup>17</sup>

The insight to the reactions occurring in a battery cell during thermal runaway was provided mostly by differential scanning calorimetry (DSC) studies. Early study done by Zhang et al.<sup>18</sup> using  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  cathodes, mesocarbon microbead anode and 1 M  $\text{LiPF}_6$  EC/DMC electrolyte gave several important results.

- Two reactions were observed on anode: a reaction with onset of 130 °C only released about 120 J/g of heat, was only observed in the presence of electrolyte and was unaffected by lithiation degree. Another reaction, with onset of 230 °C was affected by lithiation (heat increased with lithium content on anode, though the heat was at a maximum only 360 J/g) and was attributed to PVDF reacting with Li.
- When heating the cathode, a clear reaction was only observed when the cathode was wet with electrolyte.
- The salt concentration of the electrolyte had an effect on the cathode reaction.
- The onset temperatures for the cathode reactions were affected by the lithiation degree (charge of the battery).

**Table 1.** Order of reactions in Accelerating Rate Calorimetry simulations of thermal runaway according to Spotnitz et al.<sup>16</sup>

No.	Reaction	Onset temperature	Products	Notes
1	SEI decomposition	~70 °C		Small temperature rise <2°C
2	Li/solvent reaction	~85 °C	Produces Li <sub>2</sub> CO <sub>3</sub> and flammable gas	If using lithium metal anode
3	Li <sub>x</sub> C <sub>6</sub> /solvent reaction	~110 °C	Produces Li <sub>2</sub> CO <sub>3</sub> and flammable gas	If using carbon based anode Temperature rise up to 100 °C
4	Intercalated Li/binder reaction	~160 °C	Produces LiF and flammable gas	Only occurs if there is anode material left to react from the previous. Actually occurs around 230 – 250 °C if binder is PVDF <sup>18-21</sup> Reaction happens via dehydrofluorination <sup>22</sup>
5	NiCoO <sub>2</sub> decomposition	~170 °C	Produces oxygen	Rises fast to be the dominating reaction
6	Solvent decomposition	~180 °C	Produces flammable gas	
6	Li/binder reaction	~180 °C	Produces LiF and flammable gas	If using lithium metal anode
7	Mn <sub>2</sub> O <sub>4</sub> decomposition	~190 °C	Produces oxygen	

Similar DSC studies done by other researchers<sup>19, 20, 22</sup> confirm that thermal runaway begins when the SEI layer on anode breaks down. Biensan et al.<sup>20</sup> put the onset temperatures of anode reactions at roughly 120°C and 250°C (negative electrode being graphite bound with PVDF and electrolyte PC/EC/DMC (1:1:3) + 1 M LiPF<sub>6</sub>). The first reaction was only detected when electrolyte is present with the negative electrode. When the salt was changed from LiPF<sub>6</sub> to LiBF<sub>4</sub> or LiTFSI, the onset and heat released by this reaction were affected, indicating that it is the breaking of the passivating layer on the



anode. The second peak was confirmed to be anode/PVDF reaction, because it was dependent on the amount and nature of the binder. This reaction was determined to be the most violent and exothermic one out of all the possible ones by kinetic studies done with DSC.<sup>20</sup>

Another large heat spike in the thermal runaway is caused by cathode decomposition, which releases oxygen from the transition metal oxide active material and leads to oxidation of electrolyte solvent, although reactions on the anode also produce a noticeable amount of heat and partially overlap the cathode reactions around 200 – 300 °C.<sup>19</sup>

A DSC study done by Maleki et al.<sup>21</sup> with LiCoO<sub>2</sub> cathode, graphite anode and 1 M LiPF<sub>6</sub> EC-MEC electrolyte, shows well the comparative heats released in the different reactions. In Figure 5 are results from three DSC measurements that were done separately with anode material with electrolyte, cathode material with electrolyte and then with a "battery", where separator, cathode foil, separator and anode foil were stacked together in one crucible with added electrolyte. There are clearly two main reactions that generate heat. The first one is attributed to the decomposition of LiCoO<sub>2</sub> cathode and the combustion of electrolyte that follows at about 167 °C. The second is the anode/PVDF reaction at about 225 °C. It is worth mentioning that the measurement has been made in an aluminium crucible, which allows electrolyte to evaporate during measurement. Therefore, there is plenty of unreacted anode material left to react with the binder.

The binder material has very little effect on the reactions below the temperatures where the anode/PVDF reaction begins (230 - 250 °C). Any difference is attributed to the fact that some binder materials absorb more electrolyte, and therefore the reactions produce more heat.<sup>23</sup>

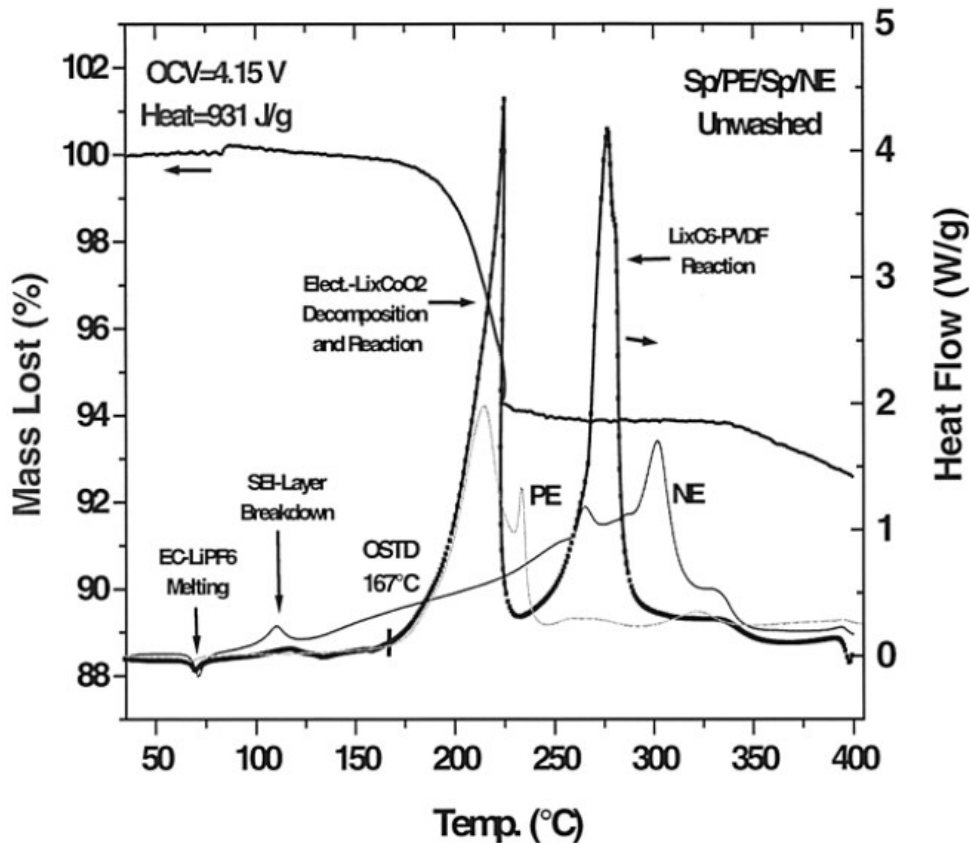


Figure 5. Picture from Maleki et al.<sup>21</sup> Dotted line marked with PE is result of measurement of  $\text{LiCoO}_2$  cathode material with electrolyte. Line marked NE is result from  $\text{Li}_x\text{C}_6$  anode with electrolyte. The thick black line is result from stacked separator, cathode foil, separator, anode foil in the same crucible with electrolyte.

Importance of the cathode reaction and the anode/PVDF reaction were confirmed by Biensan et al.<sup>20</sup> in a series of tests where whole battery cells, charged to 3,5 – 4,5 V, were pierced with a nail to make them intentionally short circuit. A voltage was defined as safe for the battery if no venting of gas, fire or explosion occurred. When the cells were composed with a non-fluorinated binder, a significantly higher safe voltage was observed than with cells made with PVDF. Changing the particle size of carbon on the anode so that the reaction kinetics of the anode/PVDF reaction were slower led to significantly higher safe voltage. A higher safe voltage was also obtained when the cathode material was  $\text{LiCoO}_2$  instead of  $\text{LiNiO}_2$ , just as was expected from DSC studies where  $\text{LiCoO}_2$  showed higher stability and less dependence on charge than  $\text{LiNiO}_2$ .

Combined DSC and XRD studies by MacNeil and Dahn<sup>24</sup> indicate that the cathode decomposition is not an isolated reaction, but is affected by the electrolyte. At least when using  $\text{LiCoO}_2$  as cathode active material and electrolyte with EC solvent, the organic solvent of the electrolyte reduces the active material, lowering the decomposition temperature significantly. (Which is why cathode material stability should always be

studied in the presence of the electrolyte.) When  $\text{LiCoO}_2$  was heated with added solvent (EC:DEC 33:67, no salt) the onset of the exothermic reaction was 130 °C. Onset of the decomposition with dry  $\text{LiCoO}_2$  was 240 °C.

In addition to the electrolyte solvent, the salt also appears to have an effect on the reactions.  $\text{LiCoO}_2$  cathode with electrolyte (same solvent but with  $\text{LiPF}_6$  salt), showed a much slower reaction and the onset was close to 240 °C.<sup>25</sup> Increasing the concentration of the  $\text{LiPF}_6$  salt inhibits  $\text{LiCoO}_2$ /electrolyte reaction but it has the exact opposite effect when cathode material is  $\text{LiMn}_2\text{O}_4$ .<sup>26</sup> The amount of the electrolyte has different effects on different cathode materials, though generally higher electrolyte/cathode mass ratio means more heat is released (because the cathode material releases more oxygen than is used by the electrolyte combustion).<sup>27, 28</sup> The identity of the salt also has effect on the onset of the electrolyte/cathode reaction.<sup>29</sup>

Zhang et al.<sup>30</sup> showed that charge has a significant effect on the heat released during the cathode/electrolyte reaction. Released heat ( $\Delta H$ ) grows proportionally to the charge of the cell. Röder et al.<sup>31</sup> showed that the charge of the cathode has an effect on the onset ( $T_0$ ) of the cathode/electrolyte reaction, when the voltage is in a range where the active material is undergoing a phase change. This is because charging the cell involves removing lithium ions from the cathode structure, making it more and more unstable and eventually forcing the structure to reorganize (order-disorder transition) to accommodate for the lost lithium ions. When the cathode is charged over such a point, the active material structure will be different and will have a different decomposition temperature (or several different decomposition steps).<sup>32</sup> Such changes should also be visible in the charging curve of the cell.<sup>33</sup> Stability and safety of a battery is generally better the smaller the capacity (amount of lithium initially on the anode)<sup>22</sup> and charge (amount of lithium on cathode) are.<sup>2</sup> ARC study by Wang et al.<sup>28</sup> also indicates that a slow self-heating reaction, before the sharp onset of cathode decomposition and electrolyte combustion, begins at a lower temperature the higher the charge is.

Events during thermal runaway may vary depending on how the thermal runaway is triggered, for example some active materials are more resistant to overcharge than others. In  $\text{LiCoO}_2$  cathodes charged to 100 % SOC (4,2 V) the reaction most responsible for the thermal runaway was the cathode/electrolyte reaction. When the cell was charged over 100 % SOC, the reaction most responsible for thermal runaway was anode/electrolyte

reaction (onset dropped to  $\sim 80$  °C), likely because metallic lithium was formed on the anode.<sup>16, 34</sup>

If metallic lithium is used as anode, it is very likely that the lithium ions don't deposit as a regular layer on the anode surface. Instead, branch-like growths of metallic lithium begin to form on the anode surface. These branches of lithium, called dendrites, slowly grow with every charge/recharge cycle towards the cathode and eventually lead to an internal short circuit. Metallic lithium is widely considered too dangerous to be used in consumer products. (It is still used for research purposes as a reference electrode). High charge/discharge rates may lead to dendrite formation even in graphite anodes.<sup>35</sup>

In conclusion, the reactions and their order in thermal runaway process are affected by all the components in the battery system. The process begins usually by a failure on the anode, such as the break-down of the SEI layer or dendrite formation. The resulting decomposition of the electrolyte generates heat and flammable organic gasses, and finally the decomposition of the cathode generates oxygen and heat and results to combustion of the flammable gasses. Intercalated lithium reacting with PVDF on the anode provides further heat. The reactions are overlapping and their order and whether they trigger at all depends on charge of the battery, anode and cathode active materials, electrolyte solvent and salt concentration, binder material and marginally its weight percent. Capacity of the battery also affects the reactions of the battery cell. Small and thin batteries dissipate heat faster than large and bulky designs. Therefore it is also a safety matter if an active material has a bad capacity and requires large and thick electrodes.<sup>16</sup>

### **3.2 Battery safety tests**

Battery safety is most often studied in terms of the temperature resistance of the battery: how high (or low) temperature is needed to kick-start the thermal runaway process. High temperatures are not however the only means of abuse by which a runaway reaction can begin. Some recognized test standards are designed by Underwriters Laboratories (UL-1642 or SU-2054), United Nations (UN) for transportation and International Electrotechnical Commission (IEC-project) and Japan Storage Battery Association (JBA).<sup>20, 36</sup> Safety tests include: <sup>16, 20, 37</sup>

- Thermal tests such as oven test, where a battery is heated to high temperatures ( $>130$  °C), sometimes left to sit for a long periods of time in elevated temperatures ( $\sim 80$  °C). Thermal tests tell how batteries react to high temperatures that might be generated during charge/discharge or improper storage.

- Mechanical tests such as crush test (battery is crushed) and needle test (battery is punctured with a metal needle, sometimes at once, sometimes slowly). Mechanical test shows how the battery reacts to mechanical damage and internal short circuit.
- Electrical test such as overcharge test (battery is charged over intended voltage limit). Overcharge test simulates failure of charging. Lithium ion batteries must be charged with constant voltage chargers, not constant current chargers, because charging over the intended operating voltage of the battery leads to decomposition of the electrode materials and the electrolyte and can lead to thermal runaway.<sup>12</sup>
- Additional tests include simulating conditions that can occur during cargo shipping or storage (pressure, vibration etc.).

## 4. Preventing thermal runaway

The trouble with thermal runaway is that the exothermic reactions are chained, triggering one after the other. Ways to prevent the reactions from ending in a fire or explosion are:

- More thermally stable components
- Inflammable components
- Mechanical means (heat dissipation, pressure valves, shut-down separators)

The following chapter investigates means to improve battery safety by replacing the currently used electrode chemicals with ones that possess better thermal stability, and replacing the electrolyte with non-flammable alternatives. The binder material is not further discussed in this work.

### 4.1 Thermal stability of anode

Improving the safety of the anode can be done by using an anode with a potential that does not require the formation of a SEI layer or by reducing the surface area of the anode in contact with electrolyte.

Lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) anode has higher potential than graphite (1,5 V vs. Li) and sits within the electrochemical window of the organic solvent based electrolytes.<sup>35</sup> This means that it will not reduce the electrolyte and no SEI layer formation is necessary. It is used commercially as a safe alternative for graphite anode.<sup>38</sup> The higher voltage of the anode also means that the cell will have lower potential (2,5 V if  $\text{LiCoO}_2$  cathode is used), and lithium titanate has theoretical capacity of 175 mAh (for graphite 330 mAh/g)<sup>16</sup>. On the other hand, lithium titanate has a flat discharge curve and a very clear end point for cut of voltage, meaning that the cycling is easy to keep in bounds that don't deteriorate the anode structure.<sup>35</sup>

Mesocarbon micro fibres or beads have better safety than graphite, possibly because they have slower reaction kinetics for the anode/binder reaction. In DSC measurements lithiated graphite had a heat value of 1220 J/g when MCMF had a heat value of 648 J/g.<sup>21</sup>

### 4.2 Thermal stability of electrolyte

Improving safety of a conventional organic solvent based electrolyte can be done by improving the stability of the SEI layer that forms as a product of its breakdown products. Solid electrolyte interface (SEI) layer is an interface that forms on the surface of the anode from the reaction products of electrolyte reduction. This interface prevents fresh electrolyte from coming to contact with the anode and the reaction stops (or slows down to a

manageable rate). This is the only reason why lithium can be used as an anode. Same phenomenon happens when lithiated carbon is used as an anode. Stable SEI is therefore a prerequisite for a good battery. Not only does it affect the safety (SEI break down allows the very exothermic reduction reaction to begin again) but it defines the voltage that the battery is capable of. Chemically modifying the SEI to be as stable as possible improves the safety of batteries that use organic solvent based electrolytes.<sup>39</sup> The intricacies of SEI modification are not further explained in this work.

Some of the organic solvent based electrolytes are less volatile than others, but they are all still flammable and susceptible to thermal runaway. A big problem is that EC, one of the more volatile solvents is also an additive that is used to form a stable SEI layer.<sup>40</sup>

Another way of improving safety is to replace the organic solvent based electrolyte entirely with a non-flammable option. Quite a lot of attention is given to different non-flammable electrolyte candidates here, because replacing the flammable organic solvent based electrolytes makes most sense from a safety point of view.

In addition to better safety, alternative electrolytes may provide other beneficial properties, such as higher stable operational voltage (>5 V) which would be too high for organic solvents, compatibility with the “dream” batteries (Li/O<sub>2</sub> and Li/S), that have very high theoretical capacity (conversion chemistry instead of intercalation chemistry).<sup>41</sup> Solid electrolytes allow the use of some cathode materials that cycle poorly with liquid electrolyte (such as sulphur, which dissolves in organic solvents).<sup>42</sup> Solid electrolytes also allows for the use of lithium metal as anode, because they inhibit dendrite growth, and liquid<sup>43</sup> or gas<sup>44</sup> as cathode.

#### 4.2.1 *Ionic liquids*

Ionic liquids are salt melts of organic salts. Several cation and anion combinations have been studied and shown some promise, some of the most studied being ionic liquids based on imidazolium cations.<sup>45</sup>

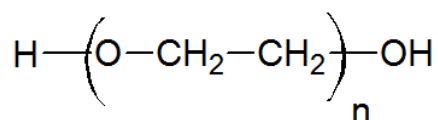
Ionic liquids are liquids at room temperature, have good lithium ion conductivity, are non-flammable, non-toxic and have wider electrochemical window than organic solvent based electrolytes. Because of their low vapor pressure, they can be used in applications such as Li/air batteries.<sup>46</sup> However, most studied ionic liquids are not chemically stable below the voltage 1,1 V, and do not form a SEI layer, so they can't be used with carbon or lithium anode. Because of this, they are usually mixed with organic solvents (EC), to

create a SEI layer or used in combination with solid inorganic or polymer electrolytes. Although recently ionic liquid consisting of pyrrolidinium cation and bis(fluorosulfonyl)imide (FSI) anion showed good cyclability with Li/LiCoO<sub>2</sub> cell without additives, meaning that it forms a SEI layer on its own.<sup>47</sup> Ionic liquids are also quite expensive due to the small production amounts.<sup>2</sup>

#### 4.2.2 Solid polymer electrolytes

Polymer electrolytes are polymers that can dissolve alkali metal salts, and can therefore conduct Li-ions. Polymer electrolyte simultaneously acts as a conductor of Li-ions and a separator between cathode and anode. Good properties of polymer electrolytes are that they are flexible enough to remain in contact with the electrodes, even if the volume of the electrodes varies with charge. Polymers, with strong enough mechanical properties to apply pressure on the anode, can inhibit dendrite growth and therefore make use of Li metal as anode safe.<sup>48</sup> Because of dendrite growth inhibition and the greater chemical stability of the solid electrolyte compared to organic solvent based electrolytes, very energy dense systems, such as Li/O<sub>2</sub> may become viable.<sup>44</sup>

The most common polymer used is polyethylene oxide (PEO), also known as polyethylene glycol, containing a lithium salt (LiPF<sub>6</sub> or LiAsF<sub>6</sub>). PEO is cheap and non-toxic.<sup>2, 48</sup>



PEO dissolves lithium salts by complexing the positive metal ion with the oxygen atoms in the chain. The anion from the salt remains in a cluster with the cation (this type of polymer electrolyte is called ion-coupled system). The polymer conducts lithium ions because the complexed lithium ions are able to move between coordination sites. This mobility is affected by two things, the mobility of the polymer chain so that lithium ions can come in to contact with new coordination sites, and the formation and breaking of the Li-O bonds in the complex. Which one of these two is the rate limiting reaction depends on temperature.<sup>48</sup>

Above 40 °C, the rate limiting factor is the formation and breaking of the bonds in the complexes. In this case the solvating group (the chain oxygen atom is attached to) affects the ion conductivity. At high temperatures some polymers have sufficient ion conductivity



to rival liquid electrolytes.<sup>48</sup> At room temperature however the limiting factor is the mobility of the polymer. Mobility of the chain can be improved by using comb structured polymers and (for example PEO/PPO copolymer) instead of a straight chain polymer, and prohibiting crystallization of the polymer with either additives (e.g., Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, or ZrO<sub>2</sub>), plasticizers or polymer chain design (PEO-PMMA, which has ionic conductivity as good as 10<sup>-5</sup> S/cm, 10<sup>-1</sup> S/cm for typical liquids).<sup>49</sup> Despite this, no purely polymer electrolyte system (with or without additives) has yet been created that has sufficient Li-ion conductivity to function properly at below 40 °C.<sup>48</sup>

Polymer electrolytes also undergo the same kind of side reactions at electrolyte interfaces as organic liquid electrolytes do, and therefore a SEI layer is formed, which changes the transport properties of the polymer compared to bulk. Movement of Li-ions between the electrode and the polymer electrolyte is also slowed by spatial obstructions (the polymer can not move freely at the interface). This leads to “Interfacial impedance”, which further limits the current density that can be obtained.

Because the ion mobility is much slower in polymer electrolyte than in liquid electrolytes, persistent concentration gradients for the salt anion and Li-ion can form near electrode surfaces, which may lead to salt precipitation or lowered glass transition temperature (and therefore poor mobility and Li-ion conductivity) on one electrode, and salt depletion on the other. Over all, strong concentration gradients can lead to poor recyclability. This has been countered by developing single ion systems, where the anions of the salt are locked immobile in the polymer chains, and therefore can not form concentration gradients.

The greatest challenges of solid polymer electrolytes are the interfacial behavior and poor ion conductivity at room temperature. Of course the cost of these polymer electrolyte systems climbs the more intricate the design has to be, and it is difficult to find polymer systems that have all the desired properties. For now, the problems are usually solved by using hybrid electrolyte systems.

#### 4.2.3 *Inorganic solid electrolytes*

Inorganic solid electrolytes are glass or ceramic compounds that contain lithium in their structure. One of the simplest is lithium oxide glass. Solid inorganic electrolytes conduct lithium ions by allowing them to move between sites in the structure. There are vast

amounts of different inorganic lithium ion conductors and the transportation mechanisms differ. Some are amorphous and some are crystalline in structure.<sup>42</sup>

Crystalline type include garnet (e.g.  $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ , where M varies) and perovskite (e.g.  $(\text{ABO}_3)$ -type lithium lanthanum titanate (LLTO)) structure and LISICON (e.g.  $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$  where Zn and Ge might be different metals) type structures and their variations. The types are arranged according to structure, so a LISICON membrane may have different metal atoms instead of Zn and Ge, but the structure stays the same.<sup>50</sup>

Amorphous type include lithium oxide glasses and LiPON (phosphorous oxynitride glass) and their variations. Also there are composite type inorganic solid electrolytes that are doped with for example mesoporous alumina to make the structure more porous, improving its Li-ion conductivity.<sup>50</sup>

Inorganic solid electrolytes can stand higher voltages than organic solvent based electrolytes. Some of them are so resistant that they don't decompose at all while the cell is operating, and therefore don't form SEI layer, so the resistivity in the interface is lower. Solid inorganic electrolyte allows use of Li metal as anode and liquid as cathode<sup>43</sup> such as lithium-bromine flow-through battery (4 V open circuit voltage and high capacity (335 mAh/g)) which allows greater voltages and capacities to be obtained. The best of these inorganic solid electrolytes (such as LLTO) have a lithium ion conductivity that is comparable to organic polymer electrolytes ( $10^{-3}$  -  $10^{-6}$  S/cm),<sup>50</sup> but their conductivity is still several orders of magnitude lower than with liquid electrolytes ( $10^{-1}$  S/cm).

Biggest flaw in inorganic solid electrolytes is that they are not flexible enough to remain in contact with the electrodes if their volume changes during charge/recharge cycle. This means that inorganic solid electrolytes can only be used in thin film battery applications, where the thickness of the separator is less than 1  $\mu\text{m}$ .<sup>42</sup> Also the slow manufacturing process of the thin films is mostly too slow to be practical commercially. The manufacturing process is very important, because it affects the composition and structure and therefore properties of the electrolyte.<sup>42</sup>

LiPON is used in manufacturing thin film and micro batteries, although not in commercial use. It has sufficient electronic resistivity and chemical stability to retain its charge in storage (~1 year) when using Li metal as anode. Li ion conductivity is still quite low  $\sim 10^{-6}$ .<sup>42</sup> LISICON<sup>®</sup> membranes are available commercially and a patent<sup>51</sup> exists, that incorporates a LISICON type solid electrolyte in to a Li/sulphur rechargeable battery.

#### 4.2.4 Hybrid electrolyte system

Hybrid electrolyte systems are a blend of polymer and inorganic solid electrolytes, ionic liquids and organic solvent electrolytes. They are attempts to optimize the good properties and get rid of the unwanted ones that each electrolyte type has. Most promising are gel polymer systems, where a polymer electrolyte matrix contains conventional organic solvent based electrolyte.<sup>42</sup>

Gel polymer systems are promising, because they have about the same lithium ion conductivity as liquid electrolyte systems, but because the organic solvent is contained within a polymer, the thermal runaway reaction is inhibited and safety of the battery is improved. Often also solid inorganic electrolyte powder (or some other additive) is added as filler particles to improve mechanical properties and inhibit dendrite growth, which is still one of the most serious threats in lithium ion batteries. Gel polymer systems still use flammable organic solvents though, and require a SEI layer to function, so thermal runaway is not impossible.<sup>52</sup>

Gel polymers can be manufactured in continuous tape laminate of cathode, polymer and anode, so they are easier to manufacture in large quantities. The commercial gel electrolyte batteries (also called plastic rechargeable Li-ion batteries) initially developed by Bellcore in 1996 consisting of graphite/LiMn<sub>2</sub>O<sub>4</sub> where the polymer electrolyte consists of a copolymer of vinylidene fluoride with hexafluoropropylene (PVDF-HFP) swollen with EC-DMC-1M LiPF<sub>6</sub><sup>53</sup> has the same performance as a battery of similar electrodes with a liquid electrolyte would have.<sup>54</sup>

There seems to be lack of commercial gel electrolyte batteries currently available for consumers.

### 4.3 Thermal stability of cathode

Cathode safety can be improved by using materials that decompose in higher temperatures or using materials that don't release oxygen when they decompose. Safety can be improved also by limiting the heat released during the cathode decomposition, though it is arguably of lesser importance than preventing the reaction from happening entirely by rising the onset temperature as high as possible. Heat value is also not entirely dependent on the cathode material, because it is coupled with exothermal electrolyte oxidation and increases with increasing charge. Heat released during cathode/electrolyte reaction is commonly 500 - 1000 J/g,<sup>18, 31</sup> so minor reductions to this heat value are not

really significant. Like with anode, larger cathode particle size leads to lower reaction heat and very small particle size can lower the onset temperature.<sup>55</sup>

Differences in thermal stability between different transition metal oxide cathode candidates (such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$ ) are likely caused by the differences in oxidation potential that the different metal atoms have, which in turn dictates how easily the reorganization of the active material structure happens.<sup>7,32</sup> Using  $\text{LiCoO}_2$ , the cathode decomposition/electrolyte oxidation reaction begins around 180 – 200 °C.<sup>18</sup>

$\text{LiMn}_2\text{O}_4$  is one of the candidates that shows better stability in DSC studies than  $\text{LiCoO}_2$ , beginning its cathode/electrolyte reaction at about 225 °C.<sup>18</sup>  $\text{LiMn}_2\text{O}_4$  is also cheaper than the cobalt containing compound.  $\text{LiMn}_2\text{O}_4$  has spinel structure instead of layer structure, which allows faster charge/discharge. Unfortunately the structure undergoes Jahn-Teller distortion with charge and discharge, so the volume changes quite significantly and makes  $\text{LiMn}_2\text{O}_4$  difficult to use as an electrode material. Manganese containing compounds also have a problem with some of the manganese dissolving in to the electrolyte and deteriorating the battery performance.<sup>7</sup>

Mixed metal oxides, such as  $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.3})\text{O}_2$  and similar materials with different Ni/Co/Mn ratios also show improved thermal stability in DSC studies, beginning their cathode/electrolyte reaction around 250 - 310 °C.<sup>31, 56</sup> They also contain less cobalt, so are cheaper than pure  $\text{LiCoO}_2$  and do not have the same volume distortion and manganese dissolution problems that pure  $\text{LiMn}_2\text{O}_4$  has.<sup>7</sup>  $\text{Li}_x(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$  showed similar thermal stability as  $\text{LiCoO}_2$  in the presence of electrolyte.<sup>57, 58</sup>

Olivine type  $\text{LiFePO}_4$  does not release oxygen in the same way that the transition metal oxides do. The decomposition reaction begins around 250 °C and has heat value of only 240 J/g.<sup>59</sup> It is the safest of cathode materials currently in commercial use, though the improved safety comes with lower cell potential (3,2 V) than  $\text{LiCoO}_2$  cathode batteries (4,2 V). Surprisingly  $\text{LiMnPO}_4$  does decompose releasing oxygen and shows worse thermal stability than  $\text{LiCoO}_2$ .<sup>59</sup>  $\text{Li}_0\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$  also releases oxygen while decomposing around 250 °C, but the amount of heat the cathode/electrolyte reaction generates is still very low, 148 J/g (same study gives heat value of 92 J/g for  $\text{LiFePO}_4$ ).<sup>60</sup>

## 5. Thermal analysis for evaluating battery chemicals

The safety of a battery can be evaluated according to standardized tests mentioned in chapter 3. But, for battery research purposes, it is crucial to separate individual contributions of each battery chemical in thermal runaway process. Battery manufacturers also have need to compare the intrinsic safety properties of different cathode or anode materials. The easiest way to accomplish these things is to use thermal analysis techniques such as differential scanning calorimetry (DSC) or accelerating rate calorimetry (ARC). In this thesis only DSC technique is further considered.

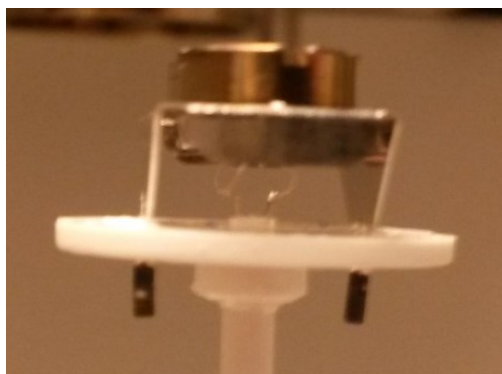
### 5.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique that is widely used for its simplicity and fast results. In DSC measurements, the sample is heated in a crucible and the temperature difference between the sample and an empty reference crucible or a crucible containing inert sample is followed. Heating programs are usually simple ramps, for example 5 °C/min to 350 °C. Sample size in DSC is very small (~5-20 mg).

DSC devices can be roughly divided in to two groups based on their operating principle: power compensation and heat flux. In power compensation device the sample and the reference have separate heating systems and their temperature is followed individually. When there is a difference in temperature between the sample and reference, the temperature difference is then corrected by heating the sample more (or less) as needed to maintain the temperature dictated by the heating program. The energy needed to correct the temperature tells the reaction enthalpy.<sup>61</sup> Power compensation devices are not discussed in this work in greater detail.

In heat flux devices the sample and reference are both heated identically, and the temperature difference between the sample and reference crucible is followed with thermocouples. Thermocouple (Figure 6) consists of two conductors of different materials in contact with each other. When there is a temperature difference between the different materials, a voltage is produced in to the circuit (thermo electric effect), which turns in to an electrical signal. The signal received is the temperature difference between the sample and the reference (in  $\mu\text{V}$ ), hence the name differential scanning calorimetry.

The temperature difference can be converted in to difference in the thermal power that is needed to heat the sample and the reference ( $d\Delta q/dT$  e.g. how much more power per a degrees rise in temperature does the sample demand). This allows for example calculating the specific heat  $C_p$  of a sample.



*Figure 6 Thermocouples under the DSC/TG sample holder of a heat flux DSC device. The signal that is received from the device is the difference in temperature between two crucibles.*

The greatest benefit from measuring temperature difference in thermal power is that it is possible to observe reactions that happen in the sample regardless of whether or not they have effect on the mass of the sample, and to calculate the enthalpy of the observed chemical or physical transformation. Other possible quantitative measurements done with DSC include reaction kinetics study, purity of substance, thermal conductivity and vapor pressure.<sup>61</sup>

Often DSC devices are also capable of thermogravimetric measurements (TG), in which case the sample holder is connected to a scale machinery below the furnace. The method is then called simultaneous thermal analysis (STA) technique. The scale requires a separate cooling system so that its signal does not drift overly much while the sample is heated. It should be noted that DSC measurements and TG measurements can interfere with each other because loss of mass is seen also in the DSC curve (vaporizing the sample takes energy). If accurate DSC curves for calculating enthalpy of reaction are needed, then a crucible with a lid should be used to stop the sample from losing mass.

The furnace of the DSC device is usually filled with purge gas that can be a static atmosphere or flow through the furnace. The gas composition and flow speed need to be well known, so that the heat conductivity is known. The gas can be inert if it is needed to protect the sample and the device components or oxidizing/reducing to observe a chemical reaction in the sample. DSC can also be connected to mass spectrometer, in which case it can be used to map out the thermal behaviour of a fairly unknown samples (how much mass in percentage does it lose, at what temperature, in how many stages and what is the gas produced).

There are different types of configurations for calorimeters, and the design choices of the device are mostly based on what purpose the manufacturer intended it for. Some allow for higher temperatures, some for oxidizing/reducing gasses, measurements in vacuum

and so forth. High temperature DSC devices can heat the sample up to around 2000 degrees of Celsius and are mostly used to study metal samples.<sup>62</sup> Low temperature DSC devices are designed to heat or cool the sample somewhere between -200 and 900 degrees of Celsius, and are used to study organic samples, polymers, or various chemical reactions.<sup>63</sup> Some devices can also be fitted with automatic sample changers for routine analysis in, for example, quality control.

## 5.2 Use of DSC measurements in thermal runaway analysis

DSC is one of the applications that is commonly used to evaluate thermal stability of battery chemicals. DSC is reasonably fast and easy method for these kinds of measurements, especially when the temperatures used are quite low (around 300 – 400 degrees). Because the reactions that are studied are chemical reactions, they have a certain speed with which they can happen. Scan speed of the heating program needs to be small (2-5 °C/min) to allow time for the reaction to happen. DSC is not capable of recognizing reactions (such as differentiating whether peak is caused by presence of Ni<sup>2+</sup>/Ni<sup>3+</sup> or Ni<sup>3+</sup>/Ni<sup>4+</sup> red-ox pair), or even capable of separating simultaneous reactions. When recognition of reactions is needed, DSC is used in conjunction with XRD or XPS measurements. Analysis of DSC peak shape is often not necessary for this exact reason. The properties most of interest in DSC measurements while investigating battery chemicals are onset temperature and heat released during the reactions.

**Onset temperature ( $T_0$ )** is the temperature where reaction peak begins. Onset temperature is calculated by drawing tangents from the background line and the peak incline and the onset temperature is the point where these two lines cross. The device thermal analysis program uses derivatives of the signal to calculate the tangents, and onset is easy to calculate when the peak is sharp. With chemical reactions, the peaks are often rounded or rise very slowly. In such cases the calculated onset temperature is not the temperature where the heat generation begins, and can lead to incorrect conclusions. For example, for the reaction of LiFePO<sub>4</sub> with electrolyte, onset temperatures of 268, 270 and 277 °C have been measured.<sup>59</sup>

**Enthalpy ( $\Delta H$ )** is more correctly called released heat when talking about multiple simultaneous chemical reactions. Enthalpy measurements for physical transformations can be measured very accurately, but absolute value for heat released during a chemical reaction is almost impossible to measure with DSC. The value that is received from the measurement depends on how the device is calibrated, how accurately the mass of the

sample is inputted in to the device program, how the integration points are chosen from the DSC curve, and in the case of the cathode decomposition/electrolyte oxidation reaction the heat also depends on the amount and type of electrolyte that is added. For example, for the reaction of  $\text{LiFePO}_4$  with electrolyte, heat values of 147 J/g, 204 J/g, 260 J/g and 268 J/g have been measured.<sup>59</sup>

In Figure 7 is a typical table that can be formed from DSC measurement results for easy comparison of different cathode or anode materials and their behavior in different charge states. Comparing the  $T_0$  values it can be seen, for example that  $\text{Li}(\text{Ni}_{3/8}\text{Co}_{1/4}\text{Mn}_{3/8})$  begins cathode decomposition/electrolyte combustion reaction in higher temperature than all the other studied cathode materials, and this is true in almost all of the voltages studied. This implies that in a battery under thermal runaway, this cathode material would endure greatest amount of heat generated from anode reactions without triggering cathode decomposition. Of course, the table values should not be accepted blindly. It is imperative that the thermal stabilities of cathode and anode are studied in the presence of the electrolyte, because electrolyte participates in the reactions that occur inside actual battery cell. Variables of the cathode or anode (identified in the previous chapters) that are important to know when interpreting the results are:

- Charge
- Surface area or particle size
- Crucible type (especially if it is sealed or not)
- Electrolyte amount and type



Voltage	Cap. (mAh/g)	$T_o^a$ (°C)	$T_p^b$ (°C)	$P_p^c$ (W/g)	$H_{tot}^d$ (J/g)	Surface area (m <sup>2</sup> /g)
4.0 V						
LiCoO <sub>2</sub>	247	175	232	3.5	1700	0.1
LiNiO <sub>2</sub>	250	187	216	31.2	1200	0.7
LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	275	192	212	2.0	1200	0.3
LiMn <sub>2</sub> O <sub>4</sub>	–	–	–	–	–	0.6
FMC	233	173	250	5.8	1600	0.8
Li[Ni <sub>3/8</sub> Co <sub>1/4</sub> Mn <sub>3/8</sub> ]O <sub>2</sub>	246	230	282	2.8	660	5.9
4.2 V						
LiCoO <sub>2</sub>	224	180	231	4.0	760	
LiNiO <sub>2</sub>	237	184	214	23.9	1600	
LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	250	193	213	2.5	1200	
LiMn <sub>2</sub> O <sub>4</sub>	123	207	289	0.7	990	
FMC	223	169	231	3.1	1200	
Li[Ni <sub>3/8</sub> Co <sub>1/4</sub> Mn <sub>3/8</sub> ]O <sub>2</sub>	219	252 (1)		1.0	400	
		300 (2)		1.0		
4.4 V						
LiCoO <sub>2</sub>	170	181	256	3.8	1100	
LiNiO <sub>2</sub>	234	182	209	30.5	1300	
LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	221	197	228	3.1	1600	
LiMn <sub>2</sub> O <sub>4</sub>	123	209	280	0.8	860	
FMC	190	175	220	0.9	1600	
Li[Ni <sub>3/8</sub> Co <sub>1/4</sub> Mn <sub>3/8</sub> ]O <sub>2</sub>	185	270	297	4.3	290	
LiFePO <sub>4</sub>	160 (3.8 V)	221	252	0.3	520	15.2
4.6 V						
LiCoO <sub>2</sub>	140	190	236	3.4	990	
LiNiO <sub>2</sub>	194	181	209	0.8	1200	
LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	198	194	234	5.7	1300	
LiMn <sub>2</sub> O <sub>4</sub>	110	216	281	0.8	890	
FMC	180	180	231	0.9	1200	
Li[Ni <sub>3/8</sub> Co <sub>1/4</sub> Mn <sub>3/8</sub> ]O <sub>2</sub>	158	245	295	5.2	310	
4.8 V						
LiCoO <sub>2</sub>	90	219	254	1.8	760	
LiNiO <sub>2</sub>	145	174	247	0.8	1300	
LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	165	193	267	2.5	1400	
LiMn <sub>2</sub> O <sub>4</sub>	20	254	267	0.8	310	
FMC	140	236	255	1.6	720	
Li[Ni <sub>3/8</sub> Co <sub>1/4</sub> Mn <sub>3/8</sub> ]O <sub>2</sub>						

<sup>a</sup> Onset temperature.

<sup>b</sup> Peak temperature.

<sup>c</sup> Peak power.

<sup>d</sup> Total evolved heat.

Figure 7. Parameters obtained from DSC measurements can be used to compare the thermal stabilities of different cathode materials in table form. Table is taken from MacNeil et al.<sup>64</sup>

## 6. Conclusions

This thesis describes the reasons and reactions which lead to thermal runaway in rechargeable lithium ion batteries. The introduction points out the danger of thermal runaway involved in LIB usage, shipping and storage, and also the dangers potentially created by increasing the energy density of LIBs. Second chapter describes the basic concepts of rechargeable lithium ion batteries and the chemistry that is most common in commercially produced LIBs. Third chapter identifies ways in which individual cell components participate during thermal runaway and the variables of the battery that influence the thermal runaway process. Fourth chapter lists several ways to prevent thermal runaway in LIBs, paying special attention to non-flammable electrolytes. Last chapter highlights the usefulness of thermal analysis techniques in determining the potential danger of specific chemicals used in LIBs.

As mentioned in the introduction, LIB research aims to provide batteries with high energy density. One of the things that holds back the development of batteries with higher energy density is the fact that LIBs are susceptible to thermal runaway. In chapter two it is noted that the susceptibility of LIBs to thermal runaway is caused mostly by the combination of graphite anode with organic solvent based electrolyte. This combination is used in most commercial LIBs. The potential of carbon anodes is too low to fit in the electrochemical stability window of organic solvent based electrolytes, and the electrolyte can decompose on the anode.

Chapter three concluded that thermal runaway usually begins on the anode, when the anode SEI layer is damaged or because of dendrite growth. The order of reactions may differ depending whether thermal runaway was caused by heat, physical impact or overcharge. Most notable reactions contributing to the heat generated during thermal runaway were found to be the electrolyte decomposition on anode, intercalated lithium reacting with PVDF binder on the anode and cathode material decomposition, which releases oxygen and leads to electrolyte combustion. Electrolyte, both the salt and solvents used, was found to be an important variable when investigating thermal runaway, because it does not only decompose on the anode and combust when given oxygen, but actively participates by reducing the cathode material, thereby lowering the cathode material's thermal decomposition temperature. Charge of the battery has to be considered in several different ways when investigating thermal runaway. Overcharge can cause generation of metallic lithium on the anode, lowering the onset of thermal runaway.

Cathode structure can be destabilized by charging the battery to a too high voltage, causing the cathode decomposition reaction to trigger in much lower temperatures and lowering the onset temperature of thermal runaway. Charge of the battery is usually directly proportional to the heat released in the thermal runaway reactions. Lower charge generally leads to a safer battery.

Chapter four lists several alternative chemical components that have either been studied or are in commercial use to create LIBs that are not susceptible to thermal runaway. Most interesting among them are the non-flammable alternatives for organic solvent based electrolytes. Non-flammable electrolytes with higher electrochemical stability window would open the possibility of designing batteries with higher charge (> 5 V). However, all of the non-flammable electrolytes were found to have their own drawbacks and none are commercially viable at the moment. There is at least one safe anode material alternative for carbon in commercial use. Lithium titanate has potential which fits in to the electrochemical stability window of the organic solvent based electrolytes, and no electrolyte decomposition occurs. Some cathode materials also showed improved safety when compared to  $\text{LiCoO}_2$ . Mixed metal oxides, particularly  $\text{Li}(\text{Ni}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.3})\text{O}_2$  and its variations, show the most potential as new cathode materials. Their high thermal decomposition temperature gives a chance for heat generated on the anode to dissipate from the battery cell without triggering the cathode decomposition, and their voltage potential, cyclability and other characteristics are in most cases found to be equal or better to  $\text{LiCoO}_2$ .  $\text{LiFePO}_4$  is a safer cathode material alternative to  $\text{LiCoO}_2$  that is already in commercial use. Its improved safety is based on the fact that  $\text{LiFePO}_4$  does not release oxygen during decomposition, but  $\text{LiFePO}_4$  has lower cell potential than a carbon/ $\text{LiCoO}_2$  battery would have. Lastly, the theory behind differential scanning calorimetry has been explained and some considerations about its use in investigating the thermal stability of battery chemicals has been discussed in chapter five.

In conclusion, there is potential for LIBs that are not prone to thermal runaway. Some are already commercially produced. Such arrangements however often sacrifice energy density for better safety. It is the nature of a battery to have a volatile chemistry. There are hardly any materials that have the electrochemical stability to stand contact with as low potential as carbon anode and even fewer that can stand metallic lithium. At the moment the potential of cathodes does not pose a safety problem, but if the potential of batteries is to be raised over 5 V, similar phenomena can be expected on the cathode as well. This leads to a situation where kinetic control is the only way to ensure proper battery operation

and, as has been shown in this work, kinetic control can fail under abuse conditions. As long as there is no “perfect” battery arrangement, where the electrochemical stability windows of all components are arranged in a way that leaves no possibility for side reactions, it is very important to be aware of thermal behavior of each battery chemical and their combinations. With this knowledge LIBs can at least be designed to be more resistant to failure and be safer when some of them inevitably fail.

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