Lithium Ion Battery Failures and the Formation of Thermite Reactions

Rodney LaFollette and Michael D. Eskra

Eskra Technical Products, Inc.
Saukville, WI 53080

Abstract

It is often observed that some runaway Li-ion cells with layered cathode materials, become much hotter internally than existing thermal runaway models predict, Further, metals originally in the positive active material (such as Co, Ni, and Mn) are often found in cells whose temperatures became very high. It has been postulated that the formation of metals can be attributed to reduction of rock salt species (MO, where M is the metal), or the reaction of lithiated active material ($LiMO_2$) with CO_2. We propose an alternate explanation for formation of metals, that also results in very high cell temperatures, namely thermite reactions between the Al positive electrode current collector, and the positive active material. These reactions are highly exothermic, in contrast with the reactions of MO and $LiMO_2$ mentioned. In this paper the chemistry of thermite reactions is presented. Incorporating thermite reactions in runaway models will likely improve temperature prediction of Li-ion cells in thermal runaway.

Introduction

Numerous mathematical models have been developed to better understand thermal and chemical process that take place, including those involved in thermal runaway in troubled Li-ion cells (1,2,3,4,5,6,7,8). These models include chemical and thermal effects of solid-electrolyte interface (SEI) decomposition; reactions between the exposed anode and the electrolyte; melting of the polymer-based separator; reactions between the cathode material and electrolyte, and electrolyte evaporation.

Evidence from autopsied runaway cells often show that internal temperatures probably exceeded those predicted from such models. It is our view that in models that deal with very high temperature reactions, inclusion of thermite reactions would allow more accuratele predict of cell temperatures. Thermite reactions take place at elevated temperatures (usually > 300 C). A thermite reaction is similar to a typical redox type reaction, involving a metal and an oxide of a different metal. The basic reaction is

$$M^1 + M^2_y O_x \rightarrow M^1\, O_x + yM^2 \qquad (1)$$

Where M^1 and M^2 are dissimilar metals. Thermite reactions can be highly exothermic. In the case of Li-ion cells, we consider that the most common thermite reaction would take place between an aluminum current collector and the positive metal oxide active material. In principle though, it could also involve reaction of other metals in the cell, such as the copper foil current collector used in most negative electrodes. In this paper reaction between Al and the positive active material will be considered.

The standard accepted processes that take place in thermal runaway of Li-ion cells, are first presented, as a context for later discussion of thermite reactions. For the most part thermal runaway models treat the following sequence (1). **Initial heating** takes place, due to either external heat or internally generated heat usually from an internal short. This is the initiation of temperature rise in the cell.

A solvent-electrolyte layer (SEI) layer exists on the surface of the negative active material. **SEI decomposition** begins at around 85 - 135 C. The metastable species $(CH_2OCO_2Li)_2$ reacts, according to

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_2 + CO_2 + 0.5O_2$$
$$2Li + (CH_2OCO_2Li)_2 \rightarrow 2Li_2CO_3 + C_2H_2 \qquad (2)$$

The above reactions are mildly exothermic (-20 kJ/mol C). The C_2H_2 and O_2 that are generated can later react in additional exothermic reactions.

The **separator melts** at 130 – 150 C, depending on its composition. While this is an endothermic process, it often leads to internal shorting from softening of the polymer, which accelerates heat generation.

Oxidation of the polymer separator also can take place, depending on the availability of oxygen or other reducing species. Separators are usually a composite of polymers such as polyethylene and polypropylene. For polyethylene, the reactions are

$$[C_2H_4]_n + 3O_2 \rightarrow 2H_2O + 2CO_2$$
$$[C_2H_4]_n + 2O_2 \rightarrow 2H_2O + 2CO \qquad (3)$$

with heats of reaction of -44.6 and -31.1 kJ/g polymer, respectively. These reactions also lead to a pressure increase in volume-constrained cells. Oxidation of the separator usually competes with oxidation of the electrolyte solvent(s). The presence of reductants such as O_2 or CO will determine the oxidation rate.

At 165 – 220 C, the (exposed) **anode reacts with the electrolyte solvent**. Most electrolytes use mixed solvents. Ethylene carbonate (EC) is often chosen to model the effective electrolyte reactions (9). The EC reactions are

$$C_3H_4O_3 + Li^+ + e^- \rightarrow 0.5(CH_2OCO_2Li)_2 + C_2H_4$$
$$C_3H_4O_3 + Li \rightarrow Li_2CO_3 + C_2H_4 \qquad (4)$$

these reactions are exothermic (-28 – 114 kJ/mol C).

In cells using layered cathode active materials, **decomposition of the active material** begins at 180 – 200 C. There are many different reactions of a layered material ($LiMO_2$). Shurtz and Hewson (9) have provided an accounting of the various reactions, which are of the form

$$LiMO_2 \rightarrow \begin{array}{l} LiMn_2O_4 \\ MO_2 \\ MO \\ M_3O_4 \end{array} + O_2 \qquad (5)$$

The above reactions are characteristic of most layered oxides (where M = Co, Ni, Mn, Al). Exception are found with Ni and Al, where not all of the reactions take place.

Shurtz and Newson used the following notation for the most important degradation reactions (Equations 5):

R1: $2MO_2 \rightarrow 2MO + O_2$
R2: $3MO_2 \rightarrow M_3O_4 + O_2$
R3: $2M_3O_4 \rightarrow 6MO + O_2$
R4: $LiMO_2 + MO_2 \rightarrow LiM_2O_4$
R5: $3LiM_2O_4 \rightarrow 3LiMO_2 + M_3O_4 + O_2$
R6: $2LiM_2O_4 \rightarrow 2LiMO_2 + 2MO + O_2$ (6)

R1 is an overall reaction, and does not likely occur directly; rather it is the result of several successive reactions (9).

Shurtz and Hewson do not include reactions involving M_2O_3. There are a number of models that do include it (10). It is likely an intermediate in the formation of spinel species (M_3O_4) from MO_2.

The heats of reaction for Reactions R1 – R5 are given in Table 1. It should be noted that Reactions 3 and 5 are always endothermic, and in the case of Reaction 3, strongly so. Reaction 4 is always exothermic.

Table 1. Heats of Reactions for Metal Layered Oxides.

		ΔH_R	kJ/molar basis		
Reaction	1	2	3	4	5
molar basis	MO_2	MO_2	M_3O_4	LiM_2O_4	$LiMn_2O_4$
Co	47.7	-20.6	205.1	-73.9	53.3
Ni	-3.2	NA	NA	-29.9	NA
Mn	134.8	58.5	228.9	-22.2	80.7
Al	467.8	18.4	1348.2	-73	91.4

There are two important assumptions of in the thermodynamic development of Shurtz and Hewson, both of which appear to be quite reasonable. The first is that partially discharged positive active material (Li_xMO_2) is treated as a solution of two separate phases,

$$Li_xMO_2 \rightarrow xLiMO_2 + (1-x)MO_2 \qquad (7)$$

The other is that mixed metal oxides (NCA, NMC, etc.) can be treated as an ideal mixture of the individual metal oxides. As an example, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ would be

$$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 = 0.8LiNiO_2 + 0.15LiCoO_2 + 0.05LiAlO_2 \qquad (8)$$

The outgrowth of this latter assumption is that thermodynamic properties (such as heats of reaction) of mixed metal oxides can be treated as the sum of the contributions of the single metal materials. These authors compared their predictions of properties for several mixed metal oxides to measured values, and found agreement to be quite good. This powerful assumption allows modelers to perform calculations for mixed metal layered oxides where thermodynamic properties are not available.

Oxidation of electrolyte solvents usually takes place as cathode degradation begins. This is due to the availability of oxygen which is a byproduct of these reactions. Table 2 shows heats of oxidation for three common electrolyte solvents, EC, propylene carbonate (PC), and dimethyl carbonate (DMC), full and partial oxidation,

Table 2. Heats of Reaction for Solvent Oxidation.

Reaction	ΔH_R (kJ/mol O_2)
EC: $C_3H_4O_3 + 2.5O_2 \rightarrow 2H_2O + 3CO_2$	-472.2
PC: $C_4H_6O_3 + 4\ O_2 \rightarrow 3H_2O + 4CO_2$	-454.3
DMC: $C_3H_6O_3 + 3\ O_2 \rightarrow 3H_2O + 3CO_2$	-476.4
EC: $C_3H_4O_3 + 1.5O_2 \rightarrow 2H_2O + 3CO$	-86.0
PC: $C_4H_6O_3 + 2\ O_2 \rightarrow 3H_2O + 4CO$	-110.9
DMC: $C_3H_6O_3 + 1.5O_2 \rightarrow 3H_2O + 3CO$	-11.6

Full oxidation of solvents is highly exothermic. Their oxidation results not only in increased temperatures, but pressure rise due to generation of CO_2 and CO. Many reactions are possible beyond those shown in Table 2 (11).

There are other thermal runaway reactions that are often considered in runaway models. One is the interaction of the electrolyte salt (often $LiPF_6$). Another is reaction involving the electrolyte binder (usually polyvinylidene fluoride; PVDF). Both of these reactions release HF, which participates in and enables other runaway processes.

Thermite Reactions. Shurtz and Hewson observed that on occasion metal products (initially present in the cathode material), have been found in autopsied runaway cells (9). They postulate that the reduction of the active material to metals, is the result of either reduction of MO to form the metal and oxygen, or the reaction of $LiMO_2$ with CO_2, to form Li_2CO_3, metal and gaseous oxygen. They note that both of these processes are highly endothermic.

We propose that it is quite reasonable that metal formation is due to thermite reactions, which are exothermic. In these reactions no gaseous oxygen is formed; rather oxygen removed from the metal oxide, shows up in reaction products such as Al_2O_3.

A thermite reaction is essentially a redox-type reaction between a pure metal and the oxide of another metal (see Reaction 1). The initially pure metal is oxidized, and the metal in the initial oxide is reduced. In our present interest (runaway Li-ion cells), we confine discussion of thermite reactions largely to Al and the layered metal oxides.

There have been a number of reports of thermite reactions in Li-ion cells or related conditions. Jiaxing et al. (10) performed DSC/TGA experiments with MnO_2, with and without Al present. They determined that the degradation reaction is not a simple redox reaction, but involves reduction of MnO_2, resulting in oxygen loss and formation of Mn_2O_3 and Mn_3O_4. They found that when stoichiometric amounts of Al were present (inert atmosphere), reaction products included Al_2O_3, but no Al. Exothermic peaks in the DSC/TGA data, with Al present, could explain by thermite reactions. There was also metallic Mn present in reaction products. Thermite reactions of both Mn_3O_4 and MnO_2 with Al are highly exothermic, and more than compensated for the endothermic formation of Mn_2O_3 and Mn_3O_4, as well as melting of Al metal. Thermite reactions take place in parallel with the decomposition reactions of MnO_2 (in the absence of Al).

Inouye and Mukai also studied various cathode materials (NCA, NMC, $LiCoO_2$) using DSC/TGA. They also examined the heating behavior of full cells, including electrodes, electrolyte (EC/DEC, 1 M $LiPF_6$), both with and without current collectors. They observed many exotherms typical of the reactions with the materials described. Cells with Al current collectors though showed a very strong exotherm as the temperature approached 480 C, not present when no Al was not in the cell. Unfortunately, their instruments did not go above 480 C. Even so, their measured peak (which they state could only be due to a thermite reaction), was as large or larger than the exotherms observed when no Al was present. They calculated that had the instrument worked through a higher temperatures, the energy released would have been ~ 3200 J/g active material (compared to 1116 J/g and 1792 J/g for the two large exothermic peaks).

Wu et al. did DSC/TGA (and other) analysis of NMC 811, with and without Al (12). They also observed exothermic peaks with Al, that they attributed to thermite reactions.

Wu et al. also did XRD measurements of material at different placed in the electrode thickness. They found that in general the extent of their “thermite-type” reaction was limited by the available contact with Al, as the thermite products were largely limited to the Al/active material interface at the back of the electrodes.

It is normal to consider the delithiated material (MO_2; see Reaction 7) as participating in a thermite reaction, as it is less stable than the lithiated species ($LiMO_2$). Possible reactions are

$$\begin{aligned} &\text{T1: } 3\,MO + 2Al \rightarrow 3M + Al_2O_3 \\ &\text{T2: } 3\,M_3O_4 + 8Al \rightarrow 9M + 4Al_2O_3 \\ &\text{T3: } M_2O_3 + 2Al \rightarrow 2M + Al_2O_3 \\ &\text{T4: } 3\,MO_2 + 4Al \rightarrow 3M + 2Al_2O_3 \end{aligned} \qquad (9)$$

Calculated heats of reaction are shown in

Table 3. The reactions are highly exothermic. Table 4 shows the change in Gibbs free energy. Contrasting the heat of reaction with the Gibbs free energy, one can see that there is only a small difference between the two. Since G = H – TS, it can be deduced that the enthalpy term is dominant, and reactions are not hindered by the entropy change.

Table 3. Heats of Thermite Reactions, Positive Electrode.

		△H (kJ/mole MO_x)		
Reaction	**T1**	**T2**	**T3**	**T4**
Co	-320.8	-1324.2	-1098.2	-1117.1
Ni	-318.0	-1275.2	-1186.2	-881.0
Mn	-173.7	-846.5	-718.8	-597.0
Fe	-286.5	-1113.4	-850.2	

Table 4. Gibbs Free Energy of Thermite Reactions, Positive Electrode.

		△G (kJ/mole MO_x)		
Reaction	**T1**	**T2**	**T3**	**T4**
Co	-313.2	-1314.7	-1004.8	
Ni	-315.7			
Mn	-164.5	-826.5	-701.1	-589.7
Fe	-276.0	-1058.1	-838.8	

Thermite reactions can only proceed if Al comes into intimate contact with the metal oxides found in the positive electrode. This is not necessarily a given, as molten Al is quite mobile within a cell experiencing runaway. However, when the materials do meet, release of large amounts of energy can raise the internal cell temperatures beyond those predicted from “normal” runaway reactions.

The presence of metals in autopsy results of runaway cell has been presented as possible evidence of the reduction of metal oxides (MO, $LiMO_2$), to produce metal and gaseous oxygen, in endothermic reactions. We feel it is more likely that the presence of metals (originally in the cathode active material) are due to thermite reactions

Thermite reactions compete with other active material degradation reactions. To illustrate this the degradation steps proposed by Shurtz and Hewson will be described for $LiCoO_2$ (9). The partially discharged active material ($LixCoO_2$) is present as two comingled phases as posited earlier (Figure 1). The less stable delithiated species (CoO_2) reacts to form the spinel species, Co_3O_4, which in turn (and eventually) will form the rock salt CoO. Oxygen is produced in these reactions. The lithiated species ($LiCoO_2$), though more stable, can react with CO_2 if available in the cell. The reaction would produce the delithiated CoO_2, along with the rock salt and Li_2CO_3. The Co_2O_3 species might appear in the normal (non-thermite) degradation process, as an intermediate species in the reduction of CoO_2 to form the spinel species (Co_3O_4).

Figure 2 shows the same processes with consideration for thermite reactions. At every stage of degradation, a thermite reaction potentially competes with the non-thermite reaction. In fact, there is an extra possible thermite reaction not matched with a comparable non-thermite reaction, namely the reduction of the CoO to Co.

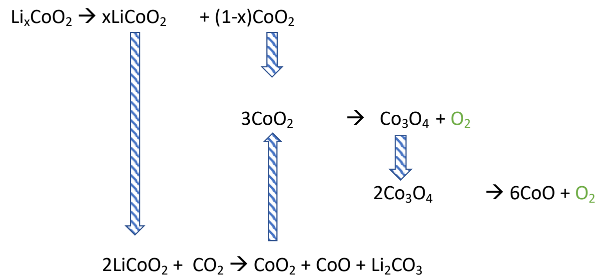

Figure 1. $LiCoO_2$ Degradation Based on Thermodynamic Analysis of Shurtz and Hewson (9).

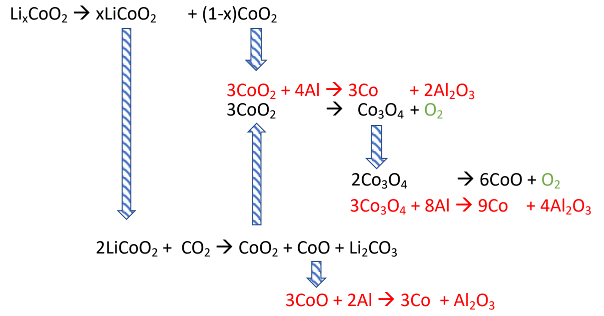

Figure 2. $LiCoO_2$ Degradation Processes with Thermite Reactions Considered. Thermite Reactions in Red.

Thermite reactions start to take place at higher temperatures. This could play a role in determining which of the reaction in Figure 2 are favored, and the fraction of the degradation processes due to thermite reactions. The very rapid temperature rise in many runaway cells could allow thermite reactions to compete successfully.

Observations and Conclusions

Anecdotal experiences of many researchers after autopsies of runaway Li-ion, have led many to believe that thermite reactions not only take place but are an important contributor to the heat generation within the cell. Support for this is provided by several studies using DSC and TGA. In these studies, exotherms where observed, along with mass loss measurements, whose only plausible explanation would be thermite reactions. Those exotherms did not take place when Al was not present. The formation of metallic species originally in the cathode active material, provided further evidence of thermite reactions.

Thermite reactions depend on intimate contact between Al and the cathode material. Experience has shown that Al can move within a cell as the temperature rises. Still, accurate predictions of cell temperatures can require consideration of this important class of reactions, so that model predictions can more closely reflect physical reality.

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