Experimental investigation of thermal behaviors of the components of high nickel lithium-ion batteries under various states of charge

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Abstract

The main safety issue that hinders the utilization of Lithium – ion batteries (LIBs) on a large scale pertains to the thermal runaway (TR) phenomenon, which is one of the main causes of the failure of the lithium-ion battery. In the present study, two high-Nickel Lithium-ion battery samples: NCA 88 and NCA 91 Nickel Cobalt Aluminum: Li[Ni$_{1-x-y}$ Co$_x$ Al$_y$]O$_2$ with 88% and 91% Nickel content (%wt) as cathode and Silicon-Carbon Nanocomposite (SCN) as anode at five different states of charge (SOCs) are examined. The thermal analysis was performed using the Differential Scanning Calorimetry (DSC) technique. It is observed that increase in Nickel content adversely affects the thermal stability of the battery. This is due to the increase in the evolved oxygen with relation to the Nickel content, which aids in triggering the TR phenomenon. On increasing the Nickel content, the onset temperature of the TR phenomenon decreases. It was also observed that for SOCs greater than 50%, the probability for thermal runaway increases and the triggering reaction is identified to be the decomposition of the Solid Electrolyte Interphase (SEI) layer. It was also observed that the probability of the thermal runaway phenomenon is the greatest for SOCs ranging from 75% to 100% for both battery samples.

Keywords: High-nickel Lithium-ion batteries; Thermal Runaway; Thermal analysis; Differential Scanning Calorimetry

1 Introduction

Lithium-ion batteries have become one of the most important energy storage because of their high specific energy densities and stable cyclic performance [1]. They have been used in various portable devices such as laptops, cameras, mobile phones, etc. Moreover, for the past few decades, the Lithium-ion battery technology is being used extensively for electric vehicles (EV). They are also used for manufacturing large and medium sized energy storage systems (ESS) which includes battery packs for EVs, backup power for communication networks, and military reserve power [2]. Thermal runaway is a phenomenon which occurs when a lithium ion battery undergoes thermal, mechanical or electrical abuse, such as external heating, internal short circuit etc. which can trigger a series of chain redox reactions which lead to considerable heat generation. The temperature of the battery rises dramatically, leading to the ejection of flammable gases. As the temperature of the battery rises, the internal structure of the battery will destabilize, leading to fire and explosion [3]. The most common commercialized cathode materials for Li-ion batteries include layered oxides: LiMO$_2$ (M = MN, Co, Al) and olivine phosphates LiMPO$_4$ (M = Fe, Mn, Co and Ni). The Layered oxide cathode materials in their charged states are metastable under ambient conditions, but at elevated temperatures (> 200 ℃) they start to decompose and release oxygen because of the high effective oxygen partial pressure[3]. Nickel-rich metal layered oxides like NCA Li[Ni$_{1-x-y}$ Co$_x$ Al$_y$]O$_2$ and NMC, (Li[Ni$_{1-x-y}$ Co$_y$ Mn$_z$]O$_2$) (x+y≤4) have caught the attention of researchers for the development of next generation Lithium-ion batteries. This is due to their higher capacity and cost effectiveness when compared to other low Nickel and conventional cathode materials [4]. However, Nickel-rich cathode materials have still not become popular because of operational problems including performance degradation and safety hazards, particularly due to storage or operation near fully delithiated states or/and at higher temperatures.

NCA is a commercially successful cathode material, however due to the poor thermal stability of this material, the NCA cathode has not been used to its full potential. This is a very important issue which needs to be addressed [6]. It is reported that at highly delithiated (charged) state, the reduction of Ni^{4+} to Ni^{2+} during the heating releases oxygen, which can lead to severe thermal runaway by reacting with the highly flammable electrolyte material leading to catastrophic failure of the LIB [6]. This is the main reason why it is necessary to study the thermal behavior of High-Nickel NCA cathode to understand its characteristics and gauge its safety parameters. Despite providing high energy capacity, the oxygen release safety concern is one of the major drawbacks in the use of Ni-rich cathode materials.

Recently, the research interest has shifted to charging Nickel-rich layered oxides like NCA and NMC to even higher voltage capacities to develop cathode materials with very high practical capacity. However, it is observed that by increasing the Ni content, there is an increase in the tendency to both surface and bulk transformations, particularly at higher states of charge (SOCs) or elevated temperatures [7]. This ultimately stops kinetics of Lithium diffusion and increases the impedance of the cell, which ultimately leads to the practical capacity loss. When the charged High-Nickel oxides are heated, phase transformations occur which result in the release of oxygen. The released oxygen further reacts with the electrolyte which is a highly exothermic reaction. The cathode is further degraded as the exothermic reaction creates a positive feedback loop, leading to the ultimate failure and thermal runaway of the cell. This is a major safety concern [8]. On increasing the Nickel content of the cathode, the onset temperature of the phase transformation and oxygen release lowers even further [9]. Thus, increasing the Nickel percentage in the cathode further leads to the increased instability of the entire Lithium-ion battery.

In a study by Golubkov et al.[10] it was shown that delithiated Li$_x$(Ni$_{0.80}$ CO$_{0.15}$ Al$_{0.05}$)O$_2$ cathode material undergoes complex phase transformations along with the release of oxygen in the temperature range of 175℃-600℃. This is dependent on the state of lithiation as:

$$Li_x(Ni_{0.80} CO_{0.15} Al_{0.05})O_2 \rightarrow \\ Li_x(Ni_{0.80} CO_{0.15} Al_{0.05})O_{1+x} + 0.5(1+x)O_2 \quad (1)$$
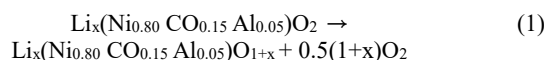
Lithiation state x can be calculated as:

$$x = 1 - \frac{n_{Li}^{irr} + n_{Li}^{res} + \frac{1}{F} \text{ SOC } C^{norm}}{n_{NCA}^a} \quad (2)$$

The amount of liberated O$_2$:

$$n_{O_2}^a = \frac{1-x}{2} n_{NCA}^a \qquad (3)$$

Here C^{nom} is typical cell capacity in Ah, F is the Faraday Constant (F= 96485 A s mol^{-1}), n_{NCA}^a is the amount of NCA units in the cathode. n_{Li}^{irr} is the amount of irreversibly trapped Li in the anode caused by initial cell formation (mol) and n_{Li}^{res} is the amount of residual Li in the anode of a cell which is discharged to V_{min} (mol).

In a study by Bang et al.[11], a four-step mechanism was suggested where the evolution of oxygen from the decomposition of the high-Nickel NCA cathode material reacted with the flammable electrolyte compounds. This creates a highly exothermic reaction that further degrades the cathode and finally, leads to the catastrophic thermal runaway of the Lithium-ion battery.

Step 1: Partial structural decomposition due to continuous lithiation and delithiation of the $Li_xNi_{0.80}Co_{0.15}Al_{0.05}O_2$ into disordered oxide (spinel-like structure) leads to liberation of small amount of lattice oxygen.

Step 2: Oxygen released reacts with the electrolyte component Ethylene Carbonate (EC) due to the lower flash point of 150℃.

$$C_3H_4O_3 + 2.5O_2 \rightarrow 3CO_2 + 2H_2O \qquad (4)$$
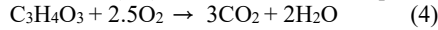
Step 3: Heat released in the above reaction further accelerates structural decomposition of the cathode leading to the release of more oxygen and finally, the total collapse of the layered oxide

$$Li_{036}Ni_{0.80}Co_{0.15}Al_{0.05}O_2 \rightarrow 0.18Li_2O + 0.80NiO + 0.05Co_3O_4 + 0.025Al_2O_3 + 0.373O_2 \qquad (5)$$
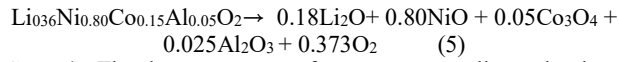
Step 4: The large amount of oxygen as well as the heat produced helps in the combustion of the remaining electrolyte components (EC, EMC LiPF$_6$) leading to a highly exothermic reaction. This creates a positive feedback loop which result in thermal runaway of the entire Lithium-ion battery if the reaction is not controlled.

$$C_3H_4O_3 + 2.5O_2 \rightarrow 3CO_2 + 2H_2O \qquad (6)$$
$$C_3H_8O_3 + 2.5O_2 \rightarrow 3CO_2 + 2H_2O \qquad (7)$$
$$LiPF_6 \leftrightarrow LiF + PF_5 \qquad (8)$$

The aim of the present study is to highlight the effect of the Nickel content and oxygen generation on the thermal runaway characteristics of NCA based Li-ion batteries under five different States of Charge (SOC) levels 0%, 25%, 50%, 75%, and 100%). Two high-Nickel Lithium-ion battery samples, (i) NCA 88 (88% Ni) and (ii) NCA 91 (91% Ni) are considered for investigation. For observing the thermal behavior of the given battery samples, Differential Scanning Calorimetry (DSC) technique is applied.

2 Experimental

2.1 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermal analysis technique where the heat flow into or out of a sample is measured as a function of temperature or time, while the sample is exposed to a controlled temperature program by means of a commercially used setup. Thermal analysis using DSC technique was applied to investigate the side reaction sequence at three different heating rates of 5˚C/min, 10˚C/min and 15˚C/min. This study utilized the NCA 88 Li [Ni$_{1-x-y}$Co$_x$Al$_y$] O$_2$ cathode and NCA 91 Cathode. The anode is a silicon-carbon nanocomposite (SCN), the electrolyte used is 1.15M LiPF$_6$ (Lithium Hexaflurophosphate) with EC (Ethylene Carbonate), EMC (Ethyl Methyl Carbonate), DMC (Dimethyl Carbonate), VE (Vinylene Carbonate) and VEC (Vinyl Ethylene Carbonate) and PA517 as additives. The various side reactions employed in this study include 'Anode+Electrolyte', 'Cathode+Electrolyte' and 'Cathode+Anode+Electrolyte+Separator' for the NCA 91 and NCA 88 LIBs. The samples used for the DSC analysis are summarized in table 1

Table 1: Details of the samples used for DSC measurements

Sample	Sample Weight (mg)	Temperature Range (˚C)	Heating Rates (˚C/min)
Cathode+Electrolyte	5~6	30~640	5,10,15
Anode+ Electrolyte	5-6	30~640	5, 10, 15
Anode+ Cathode+ Ele. + Separator	7~10	30~640	5, 10, 15

3 Results and Discussion

3.1 NCA 88

Figure 1 shows the DSC results of NCA 88 at 10˚C/min and 15˚C/min. For the heating rate of 5˚C/min, the individual side reactions (anode+electrolyte and cathode+electrolyte) are not highly exthermic. However, the full cell (anode+cathode+electrolyte+separator) is highly exothermic, especially for SOC greater than 50%. However, it is to be noted that the cell does not undergo thermal runaway phenomenon. Therefore, it is not included in the present results. As observed in Fig. 1 (a), at 10˚C/min heating rate, TR phenomenon is observed for 100% SOC while the heat of reaction (ΔH) increases progressively with increasing SOC. On observing the DSC data, it is observed that between 200°C- 300°C, the maximum heat flow for SOC 100% goes up to 12 W/g, indicating an aggressive exothermic reaction. As observed from Fig. 1 (b), at 15˚C/min, highly exothermic, TR phenomenon is observed for the full cell in the temperature ranges of 180°C-350°C. The maximum heat flow for SOC 100% goes up to 20 W/g, indicating an aggressive exothermic reaction, indicative of the thermal runaway of the cell. The reaction for all the cases begins at around 60°C with the decomposition of the Solid Electrolyte Interphase (SEI) at the anode. At around 200°C, the exothermic reactions observed for different SOCs occurs at the cathode and is attributed to the decomposition of the cathode material and the reaction of the evolved oxygen with the components of the electrolyte. A significant observation for all the three heating rates shows that the trigger reaction occurs at 60°C is not observed for SOCs below 50%. Therefore, it can be concluded that the cell is thermally stable up to SOC 50% and cannot trigger the TR phenomenon.
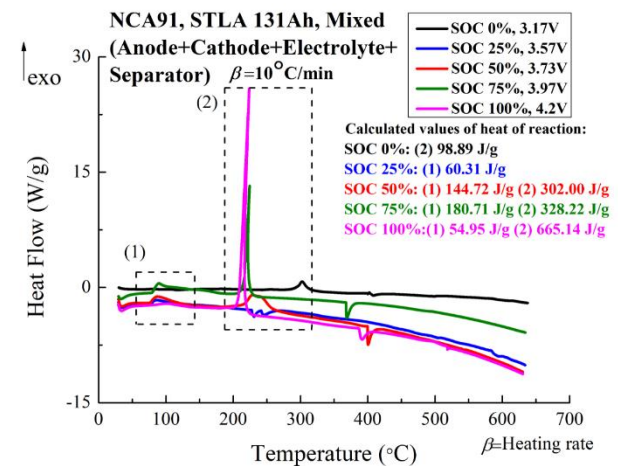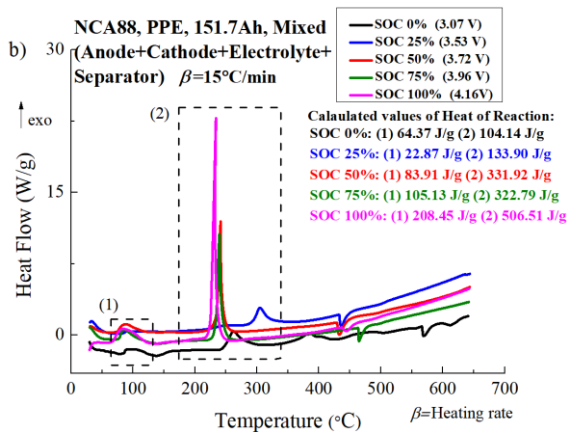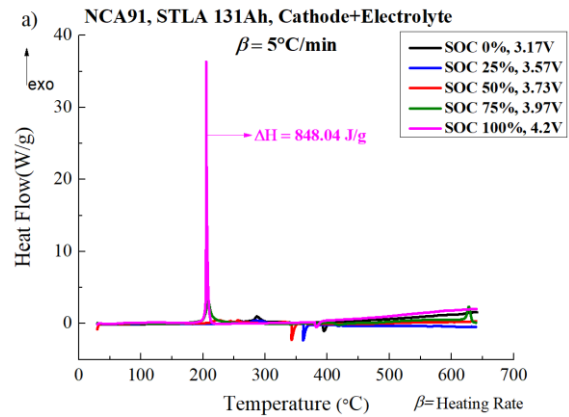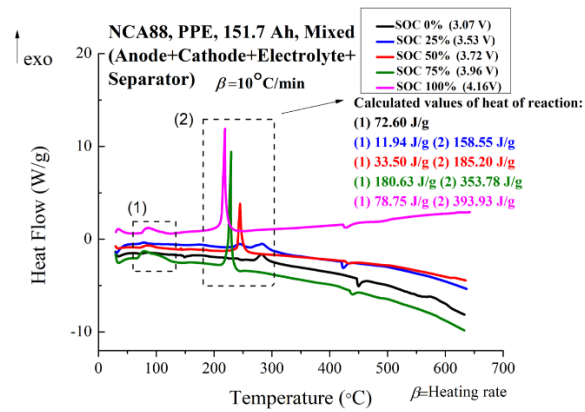
Figure 1: DSC results for NCA 88 showing full cell TR phenomenon. a) At 10˚C/min, b) at 15˚C/min. The TR phenomenon increases with increasing the heating rate as well as the SOC.

3.2 NCA 91

Figure 2 shows the DSC results for NCA 91 at different heating rate for five SOCs, on increasing the Nickel percentage to 91%, unique results are observed. In Fig. 2 (a), at 5˚C/min heating rate, the side reaction cathode+electrolyte is highly exothermic, showing TR phenomenon at around 200˚C for SOC 100%. The maximum heat flow for this side reaction at 100% SOC is observed to be around 30W/g, indicating an aggressive exothermic reaction. This shows catastrophic failure of the cathode material if the battery is heated for a very long time. In Fig. 2 (b), (c), for both 10˚C/min and 15˚C/min, the TR phenomenon is observed in the full cell (anode+cathode+electrolyte+separator) between 200˚C-350˚C. Here too, the TR phenomenon is only observed for SOCs above 50% and is prominent when SOC is 75% and 100%.

At heating rate of 10˚C/min, the NCA91 full cell shows maximum heat flow for SOC 100% to be around 25W/g. For the 75% SOC, the maximum heat flow is around 48W/g indicating aggressive thermal runaway phenomenon in the cell. Similar results are obtained for 15˚C/min, SOC 100% case is more aggressively exothermic with maximum heat flow to be around 30 W/g while the SOC 75% case shows a maximum heat flow of around 12 W/g. These results show that in the temperature range of 200˚C-350˚C, thermal runaway phenomenon is observed which becomes progressively exothermic as the heating rate and the nickel content is increased.
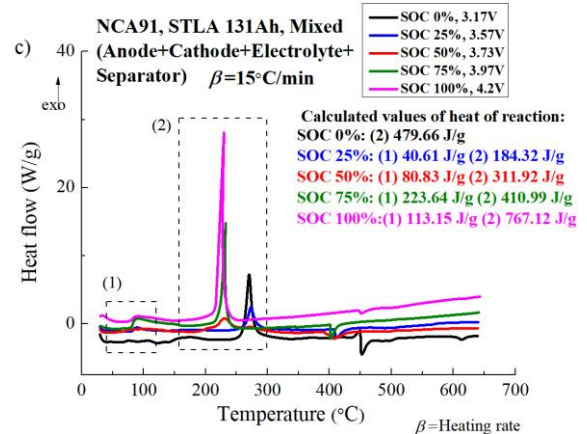

Figure 2: DSC results for NCA 91. a) The Cathode+electrolyte side reaction at 5˚C/min, b) full cell reaction for 10˚C/min, and c) full cell reaction for 15˚C/min.

3.3 Comparisons between results of NCA 88 and NCA 91 at 100% SOC

Figure 3(a) and (b) compares the DSC results of NCA 88 and NCA 91 at 100% SOC for 10˚/min and 15˚C/min heating rate, respectively. On comparing the results at 100% SOC, it was observed that the onset temperature of the TR phenomenon was lower for NCA 91. However, for heating rate 5˚C/min, the difference in TR effect of NCA 88 and 91 are insignificant. Comparing Fig. 3(a), (b), it can be clearly observed that the onset temperature of the TR phenomenon is lower for NCA 91 as compared to NCA 88. This indicates that on increasing the quantity of Nickel, the cell becomes thermally unstable. The

heat of reaction (ΔH) observed for the TR phenomenon in NCA 91 is almost two times in comparison to NCA 88. This shows that both the evolved oxygen gas and the cathode decomposition phenomenon are dependent on the percentage of Nickel in the cathode. As the oxygen evolved increases with the delithiation state, more aggressive and exothermic TR phenomenon is observed for SOCs greater than 50%, especially for a fully charged cell (SOC 100%) as observed from Fig. 3.
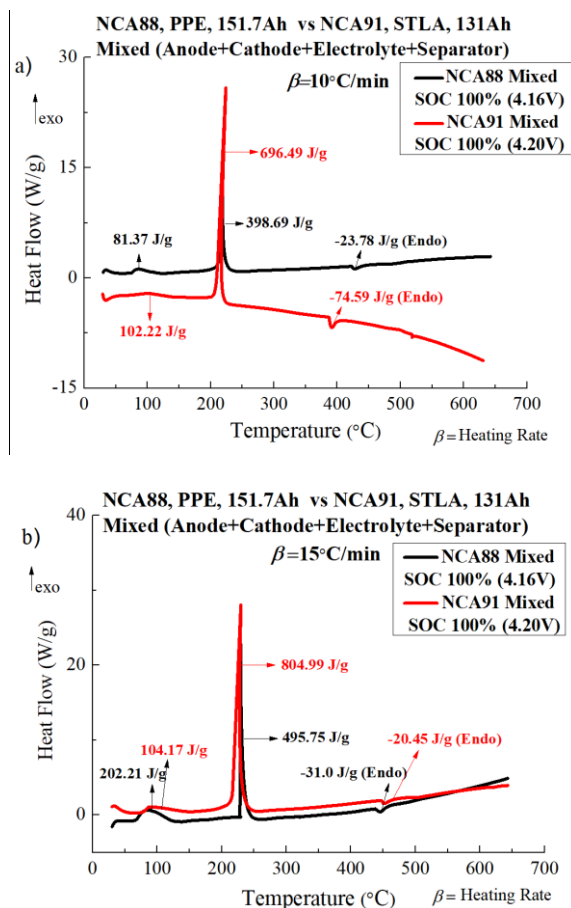

Figure 3: DSC results for SOC 100% NCA 88 vs NCA 91 at a) 10˚C/min b) 15˚C/min

4 Conclusions

In the present study, thermal runaway analysis was performed on two high-Nickel, LIB samples, NCA 88 and NCA 91 cathodes using the Differential Scanning Calorimetry (DSC) technique. The key outcomes of this study are as follows:

1. The probability of the TR phenomenon increases with increase in the state of charge (SOC). For SOCs greater than 50% the probability of TR increases significantly. This is especially observed for SOC 75% and 100%.

2. On increasing the Nickel percentage, the onset temperature of the TR phenomenon decreases. For NCA 91, the TR onset temperature is lower than that for NCA 88. The trigger reaction for the thermal runaway is identified to be the decomposition of the SEI (Solid Electrolyte Interphase) layer at around 60˚C.

3. The oxygen gas evolved on the decomposition of the cathode material at around 200˚C helps in intensifying the TR phenomenon. The evolved O_2 reacts exothermically with the electrolyte to further accelerate the thermal runaway of the cell.

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