

The Significant Hazards of Thermal Runaway of Ultra-high-nickel Lithium-ion Batteries during Charging

Juyoung Oh¹, Ayushi Mehrotra¹, Yejun Lee¹, and Jack J. Yoh¹
¹Department of Aerospace Engineering, Seoul National University
Seoul, Korea 08826

1 Introduction

Recent decades have seen a rapidly accelerating pace in the development of the lithium-ion batteries (LIBs). Especially, technological development of the cathode materials toward ultra-high-nickel (≥ 90 wt. %) LIBs can make a significant impact on the enhancement in the mileage of the electric vehicles (EV). However, safety concerns as well as anxiety regarding thermal runaway (TR) exist because the Ni-rich cathode materials are prone to show thermal instability at high states of charge (SOC) than that of other cathode materials. Although various studies have attempted to reveal the mechanism of TR for the high-nickel LIBs, such lithium-nickel-cobalt-aluminum oxide (NCA, $\text{Li}[\text{Ni}_{(1-x-y)}\text{Co}_{(x)}\text{Al}_{(y)}]\text{O}_2$) cathode materials containing high amounts of Ni (91 wt. %) under various state of charge (SOC) levels have not been covered yet.

Previously conducted research mainly handled high-nickel LIBs whose Ni content is around 80 wt.%. For instance, for high-nickel/silicon-graphite LIBs whose cathode materials are based on NCM811, the main exothermic reactions and their reaction sequence during TR were identified by conducting thermal analysis [1]. They presented the main source of the increased heat release of the LIBs by comparing the observed thermal interactions between the main active materials and the electrolyte. In addition, TR properties of two types of commercial LIBs utilizing LFP and NCA (80 wt. %) cathode materials were investigated [2]. The LIBs showed a proportionally increasing severity of the TR with increasing SOC. A strong relationship between the battery components and SOC levels that can lead to thermal instability was identified in high-nickel LIBs.

The present study provides substantial results elucidating the critical factors causing TR of ultra-high-nickel LIBs by performing differential scanning calorimetry (DSC). Firstly, various SOC levels were utilized to discover the significant changes in the thermochemical properties of the main battery components and their mixtures upon charging states. Also, the electrolyte effects on the thermal behaviors of the respective components were identified.

2 Experimental details

2.1 Materials

The present study utilized ultra-high-nickel LIBs which contain more than 90 wt. % of Ni in the cathode active materials. Table 1 shows the specifications of the utilized LIBs. The four-different SOC levels (25%, 50%, 75%, and 100%) were used. The SOC levels were measured via the open circuit voltage (OCV) method which is the basis of a potential difference between two terminals of the battery. The nominal capacity is 131.0 Ah. The main active materials are NCA cathode and graphite with silicon suboxide (Gr-SiO_x) as anode. Figure 1 represents the four-main components comprising ultra-high-nickel LIBs namely, the cathode materials, the anode materials, the separator, and the electrolyte. In addition, the mechanism of the charging/discharging process is displayed. The separator allows the lithium-ions only to pass through it enabling proper charging and discharging cycles. Thus, the movement of the lithium ions from the cathode materials to the anode materials occurs during charging while the electrons from the ions move in the reverse direction through the external circuit. Particularly, 100% SOC signifies that all lithium-ions are intercalated to the anode graphite layers which can be said as complete lithiated graphite layers formed whereas 0% SOC implies that all lithium-ions are inserted into the NCA crystal structures.

Table 1: Utilized high-nickel lithium-ion batteries and their compositions.

Name	State of Charge (SoC)	Nominal capacity	Composition			
			Cathode	Anode	Separator	Electrolyte
NCA91	25% (3.57V)	131.0 Ah	NCA91	Silicon carbon nanocomposite (SCN)	MCS 13 μm (0.5 μm adhesive + 1 μm ceramic + 10 μm PE + 1 μm ceramic + 0.5 μm adhesive)	1.15M LiPF_6 -based
	50% (3.73V)					
	75% (3.97V)					
	100% (4.2V)					

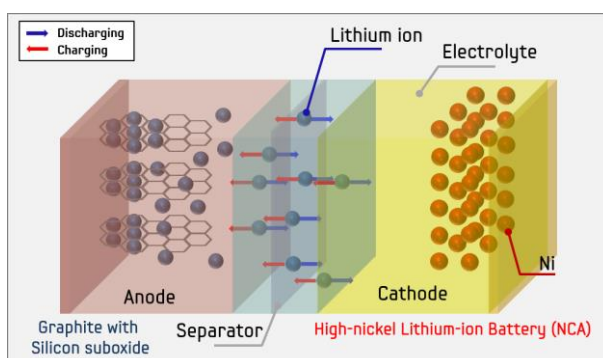


Figure 1: Representative diagram showing four main components consisting of ultra-high-nickel LIBs (Cathode, Anode, Separator, and Electrolyte) and charging/discharging process of the system.

2.2 Thermal analysis

To identify any fire or explosion hazards of ultra-high-nickel LIBs, the current study employed DSC 3+ from Mettler Toledo. The specimens were heated from 30°C~640°C at three-different heating rates (i.e. 5, 10, and 15 °C/min). During the measurements, a nitrogen atmosphere was provided via 40 ml/min of N_2 flow rate to avoid additional interaction with external impurities. To confirm the electrolyte effects on the exothermic characteristics of the main components of ultra-high-nickel LIBs, a certain amount of

the electrolyte ($\approx 2\text{-}3\text{mg}$) was added into the sample pan containing the active materials such as the cathode materials, the anode materials, and the cathode +anode +separator. Also, the sample weight of each component was measured as $2\text{-}3\text{mg}$ (the individual active materials), 1mg (the separator), $5\text{-}6\text{mg}$ (the active materials with electrolyte), $4\text{-}5\text{mg}$ (the separator with electrolyte), 7mg (the two active materials with separator), and 10mg (the full cell). The provided specimens were put into the HP Steel (reusable) $30\ \mu\text{L}$ pan to hermetically seal.

3 Results

3.1 SOC effects on the thermal behaviors of the main active materials

Figure 2(a) shows the changes observed in the thermal behaviors of the cathode materials (NCA91) depending on different SOC conditions. At SOC 75%, several exothermic peaks were observed and the temperature range of the main peak decreased from $200^{\circ}\text{C}\text{-}400^{\circ}\text{C}$ to $180^{\circ}\text{C}\text{-}280^{\circ}\text{C}$. Fully charged NCA91 represented two remarkable exothermic reactions at 145°C and 232°C , signifying partial decomposition/oxidation processes and the changes in the crystal structure of the cathode materials [3]. Also, delithiated NCA cathode materials can sustain complicated phase transitions by generating the lattice oxygen from 175°C to 600°C [2]. Thus, the observed thermal reactions of the cathode materials at SOC 75% and 100% levels may suggest that various phase transitions of the crystal structures and the additional exothermic reaction between the electrolytes and the released lattice oxygen can occur.

Meanwhile, Fig. 2(b) provides the DSC plots of the SCN anodes under four-different SOCs. Only a very tiny exothermic reaction peak was observed at SOC 25%. However, 50% and 75% SOCs showed overlapped endothermic and exothermic reactions around $70^{\circ}\text{C}\text{-}150^{\circ}\text{C}$. It is known that upon heating, lithium ions, which are highly reactive, can be separated from the partially lithiated anode [2]. Also, the observed endothermic reactions at around $70^{\circ}\text{C}\text{-}130^{\circ}\text{C}$ can be correlated to the decomposition of liquid lithium carbonate (Li_2CO_3) with graphite [2]. At 100% SOC, however, the endothermic reactions disappeared. Instead, a broad exothermic behavior releasing $440\ \text{J/g}$ of reaction heat was seen. It can be attributed to the increased amount of intercalated Li-ions of the anode layers that can interact with the graphite in the anode upon heating. Also, a solid electrolyte interphase (SEI) layer is formed on the surface of the graphite layers in the anode during charging/discharging cycles [2]. The decomposition of the SEI layer can intensify thermal instability by initiating the exothermic reaction at low temperatures.

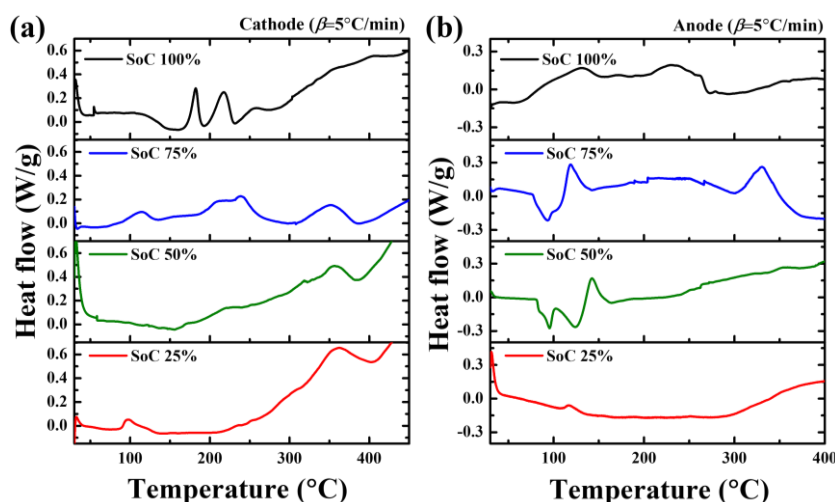


Figure 2: DSC thermograms of (a) the cathode materials and (b) the anode materials performed at $5\ ^{\circ}\text{C}/\text{min}$ under four-different SOCs.

3.2 Electrolytic effects on the four-main components of the ultra-high-nickel LIBs

Figure 3(a) indicates the thermal behaviors of the electrolyte heated at 5°C/min. The vaporization of the solvents and additives occurs at the lower temperature range (50°C~200°C) as well as exothermic reactions caused by LiPF₆, EC, and EMC could be identified after reaching 200°C [4].

Figures 3(b-d) display the electrolyte effects on the three main LIB components (cathode, anode, separator). Here, the cathode and the anode materials were fully charged (SOC 100%). Figure 3(b) shows the electrolyte effects clearly on the thermal behaviors of the cathode. For instance, only the cathode materials (dash line) presented two exothermic peaks signifying the partial decomposition and the changes in the crystal structure of the active materials [3]. Before the onset of the major exothermic reaction, little thermal reactions occurred as shown in an enlarged box. The thermal reaction between the cathode and the electrolyte showed a rapid increase in heat flow intensity, 36 W/g whose value is 138 times higher than that of the cathode one. Also, the released heat was measured by 829.4 J/g which is 8.4 times higher than heat release by cathode alone.

Figure 3(c) presents the electrolyte effects on the fully charged anode materials. When the electrolyte was added to the anode materials, a substantial exothermic reaction releasing about 366.50 J/g of heat occurred at 85°C, signifying that the electrolyte and the SEI layer can vigorously interact and produce side reactions accordingly. After the sudden heat release at 85°C, various small exothermic reaction peaks appeared and a sharp endothermic reaction observed at 335°C due to the electrolyte.

Figure 3(d) exhibits the separator case. The separator showed multiple exothermic and endothermic reactions. The electrolyte made the separator to follow a totally different reaction path. An endothermic reaction namely, the melting of the separator occurred at 61°C. This observation suggests that the separator with the electrolyte can be collapsed at a considerably reduced temperature and can result in the internal short-circuit (ISC) of the battery cells which is a major safety concern of the LIBs.

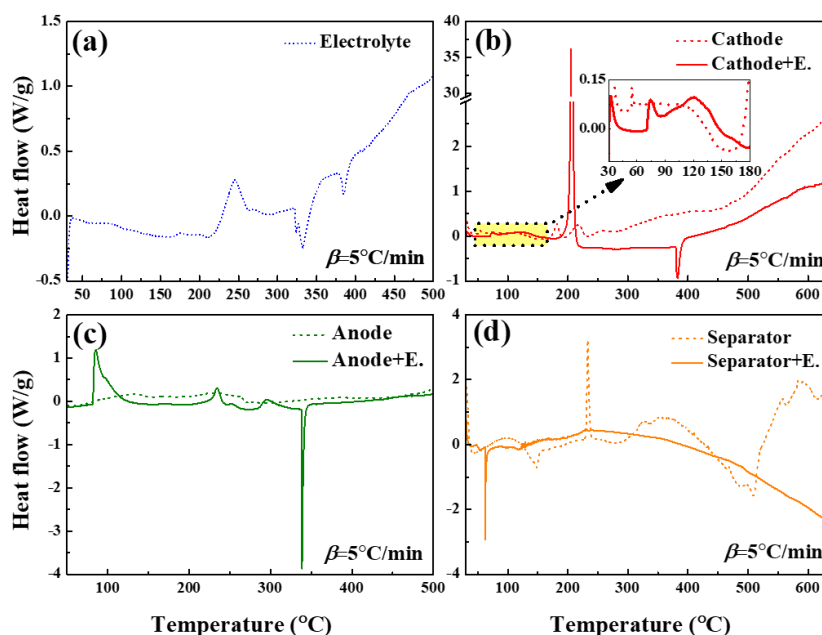


Figure 3: DSC thermograms of the main components (fully charged) of ultra-high-nickel LIBs conducted at 5°C/min and identified electrolyte effects on the thermal behaviors. (a) The electrolyte, (b) the cathode materials, (c) the anode materials, and (d) the separator.

3.3 Electrolyte effects on the active materials and the full cells under various SoC levels

In Fig. 4(a), the intensified exothermic reaction was clearly shown from the electrolyte-added cathodes at higher SOC conditions (\geq SOC 75%). The cathode materials displayed very tiny exothermic reactions even at fully charged condition. However, the reaction became further strong when the electrolyte coexisted indicating that the electrolyte can vigorously react with the lattice oxygen released by the

deconstruction/delithiation of the cathode structure. Figure 4(b) directly compares the DSC results between the anode materials and the electrolyte-added results. This case also shows explicit electrolyte effects at higher SOC levels. The anode materials alone (a solid line) represented barely any exothermic reaction while the electrolyte-added anode materials exhibited intensified SEI decomposition reaction.

In Fig. 5(a), although the strengthened exothermic reaction of the cathode materials was observed as increasing SOC levels, the intensified SEI layer breakdown reaction was not shown. Contrary to the results of Fig. 5(a), Fig. 5(b) represented the intense thermal behaviors of ultra-high-nickel LIBs by adding the electrolyte. Not only the enhanced exothermic reactions but also the decrease in the reaction temperature of both the SEI layer decomposition and the disintegration of the cathode materials appeared. Overall results highly support that the electrolyte can play a key role in worsening the thermal instability of the two active materials in ultra-high-nickel LIBs.

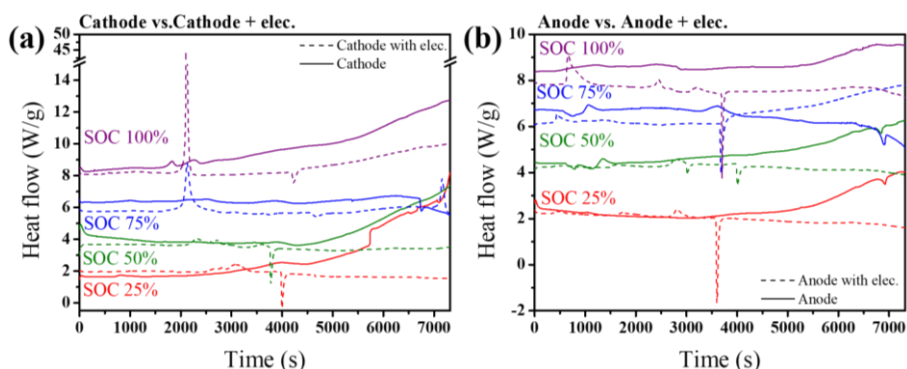


Figure 4: The effects of SOC and the electrolyte on the thermal behaviors of the active materials of ultra-high-nickel LIBs. (a) The cathode materials and (b) the anode materials.

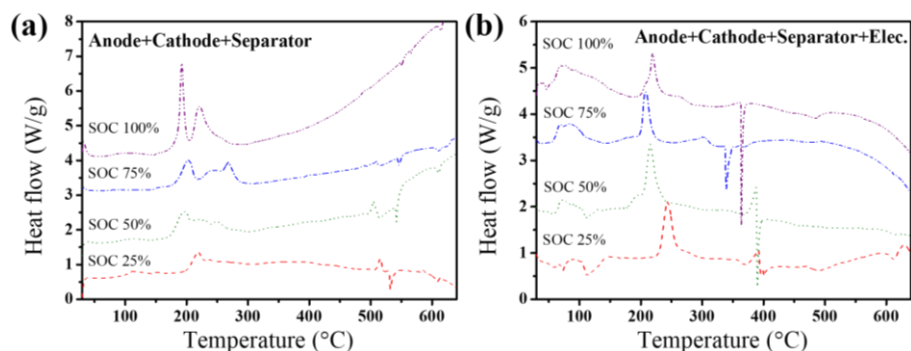


Figure 5: The effects of SOC and the electrolyte on the thermal behaviors of the full cells of ultra-high-nickel LIBs. (a) The full cells (Cathode+Anode+Separator) without electrolyte and (b) the full cells.

4 Conclusion

The present study has enunciated the significant hazards which can give rise to TR of ultra-high nickel LIBs by conducting thermal analysis using DSC measurements. Here, two important factors are considered which is highly ascribed to the cause of TR of the LIBs namely, SOC levels and the electrolyte addition.

As can be seen in Fig. 6, the two active materials of ultra-high-nickel LIBs followed their particular exothermic reactions when heated. The anode materials showed the anode delithiation process including SEI layer decomposition above 60°C while the cathode materials initiated the decomposition/oxidation process as well as changes in the crystal structure at around 160°C. The full cells that include the anode, the cathode materials, and the separator also displayed the above mentioned two exothermic reactions.

However, when the electrolyte was added, the two main thermal reactions were highly intensified. Especially, at high SOC levels (\geq SOC 75%), the exothermic reaction observed in the cathode materials developed into TR due to the self-heating effect which was ascribed to the repetition of the highly exergonic reaction between the lattice oxygen release and the electrolyte.

Comprehensively, the present study has elaborated that the critical factors that can be the main cause of TR for ultra-high-nickel LIBs can be the electrolyte and high SOC levels more than 75%. Thus, during charging, the probability of TR of the EVs with ultra-high-nickel LIBs can be increased even approaching 70°C of the cells due to the SEI layer decomposition can trigger. Accordingly, it should be thoroughly checked whether a rapid increase in the temperature during a quick charge of EVs can occur. In addition, the preventive measures to avoid the drastic increase in the temperature of the ultra-high nickel LIBs must be provided particularly in the summer season to progress further in enhanced LIBs technology.

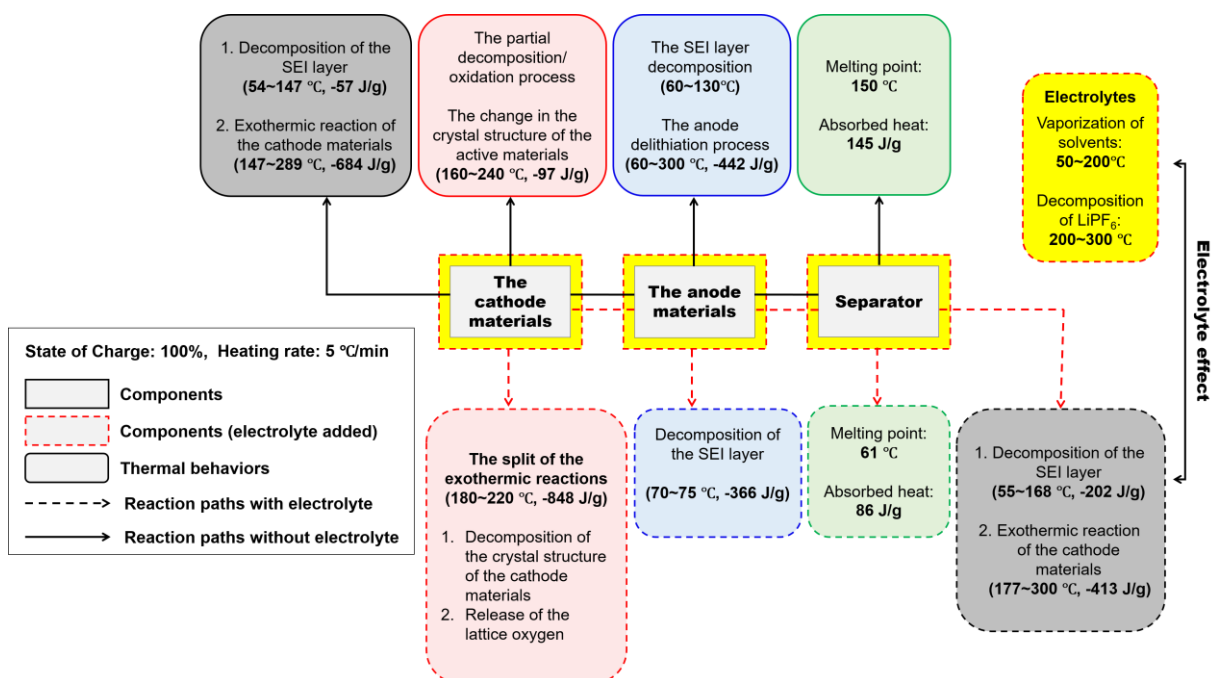


Figure 6: The reaction schematics including the exothermic reactions of each battery component of the ultra-high-nickel LIBs and their electrolyte effects on the thermochemical properties.

References

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