Trends in a study on thermal runaway mechanism of lithium-ion battery with LiNi$_{x}$Mn$_{y}$Co$_{1-x-y}$O$_2$ cathode materials

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Abstract
Safety failure, especially the “thermal runaway (TR),” result in safety anxiety and hinder the fast development of LIBs. Understanding the process and mechanism are the premise of mitigation TR. In this perspective, we briefly review the progress of the TR study of LIBs and then discuss the recent works on the mechanism study of LIB with different cathodes. We present our latest data of LiNi$_{x}$Mn$_{y}$Co$_{1-x-y}$O$_2$ cathode TR study and rethink the role of liquid electrolytes in TR. At last, we discuss the current-best known knowledge of investigating the TR mechanism and briefly summarize the strategies for TR alleviation.

KEYWORDS
electrolyte, LiNi$_{x}$Mn$_{y}$Co$_{1-x-y}$O$_2$ cathode, lithium-ion batteries, thermal runaway

1 | INTRODUCTION

Lithium-ion battery (LIB) is the dominating energy storage technology for power sources in consumer electronics and transportation, as LIBs present long cycle life and high energy and power densities.$^{1-3}$ However, safety failure, especially the “thermal runaway (TR),” result in safety anxiety and hinder the fast development of LIBs.$^{4,5}$ Understanding the process and mechanism are essential for mitigation TR. Here we briefly review the progress of the TR study of LIBs in the last 20 years and then discuss the recent works on the TR mechanism of LIB with different cathodes at materials/cell/module levels. We present our latest accelerated rate calorimeter (ARC) data of LiNi$_{x}$Mn$_{y}$Co$_{1-x-y}$O$_2$ (NMC)-based LIBs and rethink the role of liquid electrolytes in TR. At last, this perspective discusses the current-best known knowledge of the TR mechanism and briefly summarize the strategies for TR alleviation.

2 | THERMAL RUNAWAY OF LITHIUM-ION BATTERIES

Thermal runaway of LIBs is caused by exothermic reactions that emit huge amounts of heat at a very fast speed. Besides high temperature, sometimes it happens with...
burning or explosion. It may occur when LIBs are abused or aged. TR of a large format LIB can be a devastating disaster. Most of the time, TR is triggered by various kinds of abuse, including electrical abuse (including short circuit, overcharge, overdischarge, or fast charging), mechanical abuse (including extrusion, collision, or penetration), and thermal abuse. A latent defect may also slowly become a triggering factor during the cycle life or calendar aging. Normally, the TR of LIBs occurs with smoke, fire, or explosion during the process of intense heat release. Furthermore, TR propagates from one initiating cell to its neighboring cells and thus can lead to disastrous consequences at the module or system level. We briefly summarize the history of the TR study before the review of mechanism research (Figure 1).

Although LIB was commercialized in 1991,6 5 years later its thermal property and safety were paid noticeable attention. As the heat generation from LIB cell under high-rate discharge/charge or operated at elevated temperatures are remarkably higher than other battery systems (such as lead acid batteries), calorimetric equipment was used to help studying the thermal properties of LIB. In 1998 Selman and co-workers use an ARC in combination with a precision multimeter to investigate the heat dissipated from, and accumulated in, commercially LIB cells during cycling over various operating parameters.7 Then they built a one-dimensional thermal mathematical model, which is an essential research field in the study of LIB thermal properties, to simulate temperature profiles inside lithium-ion cells.8 They attributed the sharp drop of open-circuit voltage to be the melting of the separator, which is a well-recognized fact now. Subsequently, the use of ARC to determine the onset-of-thermal runaway (OTR) temperatures became a hot topic; LIB with various cathodes/anodes, electrolytes, and state-of-charge (SOC) are characterized.5,9–12 During the 2010s, as transportation became increasingly electrified, many LIBs beyond 20 Ah were developed and widely used, and their thermal properties were frequently characterized.13,14 Recently, the chemical crossover is proposed as the main cause for heat generated, especially for LIB with Ni-rich NMC cathodes and thermally stable separator.4,15 Meanwhile, data-driven computational models were established to simulate various abuse conditions, and in-situ synchrotron X-ray techniques and in-situ mass spectroscopy were used to help elucidate the TR mechanism.

Recently, solid-state lithium-ion batteries (SS-LIBs) are proposed to be the next generation LIB as the solid-state electrolytes (SSEs) have intrinsically better thermal stability than organic liquid electrolytes in conventional LIBs16–18 (Figure 1). The research of the thermal safety of SS-LIBs could be divided into three categories: the thermal stability of SSEs, the stability of the interfaces between SSEs and electrodes,19 and the thermal safety of SS-LIBs at the device level. The progress of the safety properties of SS-LIBs has been reviewed recently.16,18 In general, the SS-LIBs present a safety advantage under mechanical abuse. However, this is not enough to avoid TR. Nearly no SSEs could be chemically stable against both Li metal, which could be generated under over-charging, and high-voltage cathodes, and they would be either reduced by Li or be oxidized by the cathode. Both the reductive and oxidative reactions will possibly produce heat, bringing underlying danger for continuous heat accumulation and thermal runaway.

FIGURE 1 Schematic of history of study on thermal runaway mechanism of Li-ion battery
In this perspective, we first summarize the progress of the TR study of LIB with various cathodes and anodes, for depicting a general picture of the thermal property of different systems. Then the recent contributions of the TR study on NMC LIB are reviewed, with an emphasis on the cross-talk between cathodes and anodes. Our latest data of NMC cell TR study indicated that liquid electrolyte plays a positive role in mitigating TR for NMC LIB. At last, we propose promising strategies for TR investigation.

3 | THERMAL RUNAWAY OF LIB WITH VARIOUS CATHODES AND ANODES

The mechanism of TR can be interpreted by the chain reactions once the temperature rises sharply under aging or abuse conditions. During this process, tremendous heat rises the cell temperature, initiating the side reactions such as solid-electrolyte interphase (SEI) decomposition. These side reactions generate even more heat, forming the heat-temperature-reaction (HTR) loop until the cell ignites TR. During the HTR loop, the SEI decomposition, the melting of the separator, the reaction between the anode and the electrolyte, the cathode decomposition, and so forth, have been initiated sequentially. Once the ceramic coating of the separator collapses, a massive internal short circuit releases the electric energy of the cell instantaneously, leading to TR with possible burning of the electrolyte. As the reaction type, chemical kinetics and thermal conductivities of various cathodes and cathodes are different; the TR mechanisms of LIB with different electrodes are varied. As graphite and LTO are two dominating anodes of LIB and their TR mechanism have been systematically reviewed, here we only summarized the TR studies according to the cathode types.

At the early stage of TR, when the cell temperature increases to the onset of the cathode decomposition, exothermic reactions occur. LiCoO$_2$ (LCO), LiMn$_2$O$_4$ (LMO), LiFePO$_4$ (LFP), and NMC are the main cathode materials of commercial LIBs. Generally, the thermal stability of the cathode at full charge state follows the order as LFP > LMO > NMC111 > NCA > LCO. The characteristic temperatures during ARC TR ($T_1$, $T_2$, and $T_3$) are frequently utilized to evaluate the intrinsic thermal safety of LIB. Based on this criterion, it is noted that the LFP/LTO cell show the safest properties at both room and low temperatures. Other phosphate-based cathode materials, such as LiVPO$_4$F, presents superior thermal safety to LFP when used in LIB, which is attributed to their stability even at 300°C.

For NMC cathode, the reduction from Ni$^{4+}$ to Ni$^{2+}$ is the main reaction during middle stage TR because the Ni$^{4+}$ is more active than Co$^{4+}$ and Mn$^{4+}$. Thermal decomposition of the NMC cathode is as intensive as that of the LCO. There are typically three exothermic peaks at 220 –458°C, with the first two peaks being regarded as the NMC decomposition. It is noted that the content of Ni content determines the stability of NMC. The Al substitution could enhance the thermal stability but decrease the available capacity. As NMC LIB present high energy density, they are widely used in electric vehicles (EVs). Many TR properties of large NMC LIB cells are characterized recently. Wang et al. demonstrated that two endogenous routes of oxygen involved in intense exothermic reactions lead the NMC811 cell to an uncontrollable state. Around 41% of oxygen generated reacts with ethylene carbonate (EC) at the cathode/electrolyte interface, speeding up the self-heating rate and triggering TR subsequently. The residual oxygen will react with the lithiated graphite anode with huge heat generation, rising the temperature to >700°C during TR.

LCO is the first commercialized LIB cathode, but its thermal stability is relatively low, leading to the fact that LCO LIBs are easy to TR under overcharge or elevated temperature operation. In addition, LCO is typically more expensive than other cathodes, making it seldomly considered for large LIB cells for EVs. During the decomposition of the LCO cathode, Co$^{4+}$ is reduced to Co$^{2+}$ with oxygen released. While the decomposition of LMO involves the reduction of Mn$^{4+}$ accompanied by the release of oxygen. It is widely accepted that the cell using LMO cathode is more thermally stable than the LIB using LCO. Researchers blend LMO into the LCO or NMC cathode to improve their thermal stability, the amount of released oxygen at elevated temperatures is decreased and the safety improved.

Based on the criterion of self-heat rates and TR temperatures, NMC LIBs show inferior thermal stability than LFP LIBs. However, the much higher energy density of the former system enables it to occupy more than half of the EV battery market. Although tremendous efforts have been carried out for studying the TR mechanisms of NMC LIB, and the reaction between the cathode and the flammable electrolyte is claimed to be the trigger of the TR accident. Compared with the LFP cells, NMC cells present much more exothermic heat after the TR was triggered; however, the mechanism of the later stage of TR has not been systematically studied, and thus the reason for the devastating results of the NMC battery is still unclear.

4 | FUNCTION OF LIQUID ELECTROLYTE ON THERMAL RUNAWAY PROPERTIES

We argue that the early-stage mechanism of NMC cell TR deserves more intense research. Here we present an effective method for clarifying the contribution of liquid
electrolyte and separator to the early-stage TR of NMC cells. Here we use a Li(NiCoMn)\textsubscript{1/3}O\textsubscript{2} (NCM111) pouch cell with 1.0 M LiPF\textsubscript{6} (EC:DEC = 1:1) electrolyte and 20.0 Ah capacity as the control cell. All the control cells were cycled at 0.1 C 10 times, charged to 100% SOC, peeled off aluminum laminated films (ALFs) in an Ar-filled glove box, and vacuum dried in the transfer bin of the glove box for 120 h to remove the solvent (Figure 2A, the cell is marked as “With separator and without electrolyte”). These cells were either peeled off the separator and resealed directly with ALFs (named “Without separator and electrolyte,” see Figure 2A), or refill the electrolyte (1.0 M LiPF\textsubscript{6} with EC:DEC = 1:1) and sealed (named “With both separator and electrolyte”). All these operations were carried out in the glove box. We specifically design these cells to clarify the influence of liquid electrolyte and separator properties on the TR performance at an early stage. As shown in Figure 2B, all cells present typical TR properties of NMC cells, exhibiting higher than 700°C final temperatures. Therefore, although liquid electrolyte is flammable, it is not mandatory for an intense TR. These data also demonstrated that the reaction between cathode and anode is the main heat source during TR.

From the enlarged figure of TR profiles before 150°C (inset in Figure 2B), the cell without separator and electrolyte has the highest temperature increasing rate, demonstrating the instability and most intense exothermic reactions. The cell refill electrolyte obtains the lowest temperature rising rate, exhibiting the slowest reaction between oxygen and charged anode. This is the result of the fact that highly reactive oxygen species could be reduced to relatively lower reactive oxygen gas by electrolyte, that is, the presence of liquid electrolyte could form an oxygen retarding film. Furthermore, this oxygen-retarding function is weak for the cell with separator but without electrolyte, which shows a higher temperature rising rate. It is interesting that the temperature of the cell with electrolyte rises faster at >150°C, indicating that electrolytes participate in the complex reaction. The detailed mechanism for this phenomenon needs further investigation.

5 | CONCLUDING REMARKS

Based on the progress of the TR study of NMC LIBs and our data presented here, we show that the role of liquid electrolytes in the TR process should be rethought, as it could act as an oxygen retarder for hindering the oxygen-triggered intense exothermic reactions during the later stage of TR. However, a systematic study with cutting-edge characterization technology is required for elucidating the TR mechanism. Here we make a perspective for future research and present the promising methods in Figure 3.

The TR research could be divided into two categories: thermochemistry and thermophysics, focusing on the reaction and heat conduction, respectively. Thermochemistry of TR involves high-precision characterization of intermediate products and materials change at multiscale, while thermophysics high-precision measurement and simulation of heat conduction and other parameters at multi-scale during TR. As the catastrophic failure of LIBs happens over very short time periods but across multiple length scales during TR, a
A combination of high-speed operando tomography, thermal imaging, and electrochemical measurements is mandatory for studying the mechanisms. Multiscale X-ray computed tomography, 4D nano-tomography, and high-speed imaging techniques are frequently used as a comprehensive approach for understanding battery failure. In-situ synchrotron X-ray techniques combined with in-situ mass spectroscopy can characterize the SEI decomposition, gas release, and lithium leaching of the lithiated graphite anode during heating, demonstrating their power for interface evolution study. As the amount of data of both electrochemical and thermal characterization during TR are huge, high-accuracy data-driven computational models supported by machine learning are required for simulation.  

For the ARC TR test, researchers should develop high-precision calorimetry technologies and rational design of ARC tests. Furthermore, the TR suspension technologies, such as terminating TR by liquid nitrogen, can help understand different TR stages. Post-mortem analysis deserves more research efforts as multi-scale tomography approaches could be used for revealing significant morphological and phase changes, such as the evolution of SEI and CEI could be depicted by cryo-TEM or NMR techniques during post-mortem analysis. In addition, reassembled cells could differentiate the degradation contribution from different components, such as cathode, anode, separator, electrolyte, and so forth.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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