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Thermal runaway mechanism of lithium ion battery for electric vehicles: A review

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ABSTRACT

The safety concern is the main obstacle that hinders the large-scale applications of lithium ion batteries in electric vehicles. With continuous improvement of lithium ion batteries in energy density, enhancing their safety is becoming increasingly urgent for the electric vehicle development. Thermal runaway is the key scientific problem in battery safety research. Therefore, this paper provides a comprehensive review on the thermal runaway mechanism of the commercial lithium ion battery for electric vehicles. Learning from typical accidents, the abuse conditions that may lead to thermal runaway have been summarized. The abuse conditions include mechanical abuse, electrical abuse, and thermal abuse. Internal short circuit is the most common feature for all the abuse conditions. The thermal runaway follows a mechanism of chain reactions, during which the decomposition reaction of the battery component materials occurs one after another. A novel energy release diagram, which can quantify the reaction kinetics for all the battery component materials, is proposed to interpret the mechanisms of the chain reactions during thermal runaway. The relationship between the internal short circuit and the thermal runaway is further clarified using the energy release diagram with two cases. Finally, a three-level protection concept is proposed to help reduce the thermal runaway hazard. The three-level protection can be fulfilled by providing passive defense and early warning before the occurrence of thermal runaway, by enhancing the intrinsic thermal stability of the materials, and by reducing the secondary hazard like thermal runaway propagation.

1. Introduction

The effort to save the modern society from energy crisis and environmental pollution has been made for years with challenges and hopes mutually emerging. Nowadays, the advanced technology can convert nuclear, wind or solar energy into electric energy with cleaner process and higher efficiency [1]. The coming era of electric energy is changing the energy storage system of vehicle from fossil fuels to electrochemical energy storage systems [2], thereby changing the propulsion system from engine to motor. The change of energy storage and propulsion system is driving a revolution in the automotive industry to develop new energy vehicle with more electrified powertrain system [3].

Electric vehicle (EV), including hybrid electric vehicle (HEV) and pure battery electric vehicle (BEV), is the typical products for new energy vehicle with more electrified powertrain system. The dramatic increase in the EV production in China since 2015, as shown in Fig. 1, is just an epitome of the rapid growth in the world EV market. Battery is the core component of the electrochemical energy storage system for EVs [4]. The lithium ion battery, with high energy density and extended cycle life, is the most popular battery selection for EV [5]. The demand of the lithium ion battery is proportional to the production of the EV, as shown in Fig. 1. Both the demand and the production of the lithium ion battery have exceeded 25GWh in 2016.

The range anxiety is one of the barriers for the widespread application of BEV, because it undermines the customers' confidence in using the BEV for longer trips as they did using traditional fossil-fueled cars [6]. The total range for current commercial BEV is approximately 150–200 km, e.g., 172 km for Nissan Leaf and 183 km for BMW i3. The limitation in the total range comes from the limited spaces for placing the battery pack onboard the EV. For instances, the total volume of the battery pack is approximately 220 L for a elecric car, and 400 L for a SUV. In order to extend the total range of a electric car or SUV, the volumetric energy density, with a unit of $Wh{\cdot}L^{-1}$, should be increased. Similarly, the gravimetric energy density also requires improvement for the range extension of the electric buses.

China has been developing the lithium ion battery with higher energy density in the national strategies, e.g., the "Made in China 2025"

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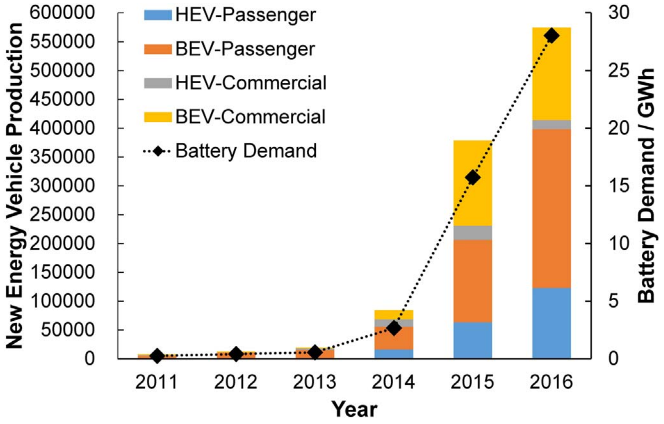

Fig. 1. The EV production and the demand of lithium ion battery for EV in China.

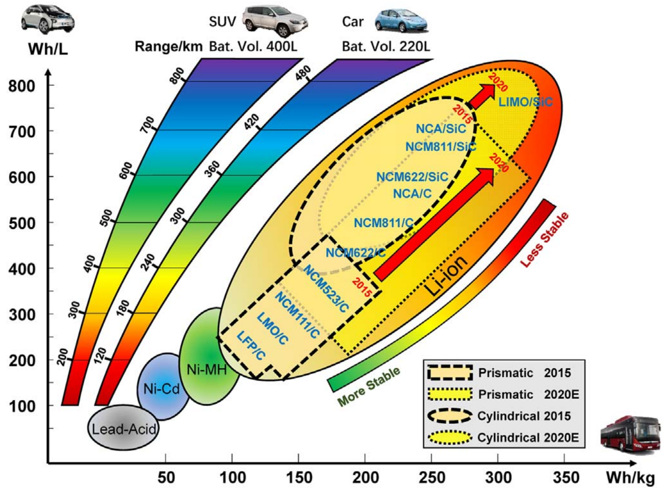

Fig. 2. The roadmap of the lithium ion battery for pure electric vehicle: the demand of longer range and the potential of less thermal stable materials.

project [7]. Fig. 2 shows the roadmap of the lithium ion battery for EV in China. The goal is to reach no less than 300 Wh kg^{-1} in cell level and 200 Wh kg^{-1} in pack level before 2020, indicating that the total range of an electric car can be extended to 400 km or longer. To reach that goal, the cathode material may have to change from $LiFePO_4$ (LFP*) and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ (NCM111) to Ni rich NCM cathode like $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622), $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811), or Li-rich manganese-based oxide etc., whereas the anode material may have to change from carbon (C, including graphite) to a mixture of Si and C.

**The abbreviations in* Fig. 2 *are listed in* Table 1 *for references.*

However, the materials with higher energy density may have lower thermal stability [8], leading to safety problems, e.g., thermal runaway (TR). The utilization of NCM111 as cathode has already aroused safety concerns, not to mention the Ni rich NCM cathode in the roadmap. The Chinese government ceased the use of NCM-based lithium ion battery in EV buses for several months in 2016, due to the occurrence of several TR accidents since 2015. The fear of using NCM or other cathode material with higher energy density comes from the lack of knowledge on the TR mechanisms. Although the NCM-based lithium ion battery was allowed to be utilized in EV buses after the more stringent compulsory test standards have been upgraded, it is found that many engineers and researchers are still not well equipped with sufficient knowledge on the TR mechanisms. Therefore, we feel it urgent to provide a review on the TR mechanisms of the lithium ion battery for EV. This review can provide guidance for engineers and researchers to conduct safety design of battery pack with higher energy density, and alleviate the fear of the battery safety problem.

2. Accidents with the lithium ion battery failure

Table 2 listed several selected accidents of lithium ion battery failure in last ten years [9–12]. Most of lithium ion battery involved are for EV, whereas two of them are for aircraft (Boeing 787 Dreamliner). Battery fire accidents occurred more frequently since 2015, in accordance with the burst in the EV market in 2015.

The TR and TR-induced smoke, fire, and even explosion, are the most common features during the accidents of lithium ion battery. Smoke, fire and explosion are serious safety problems that arouse concerns from the public. The fear of accident hinders the fully acceptance of the EVs from the market, therefore many countries require the lithium ion battery to pass compulsory test standards, e.g., UN 38.3, UN R100, SAE-J2464, IEC-62133, GB/T 31485 etc., before its application in EV. The probability of the accident caused by lithium ion battery can be substantially diminished after passing those test standards.

However, why accidents involving with TR still occurs sporadically, even if the battery can pass those compulsory test standards? The answers may come from two views: 1) the probability of the self-induced failure; 2) the abuse condition in practical use.

In the view of probability, the self-induced failure of the lithium ion battery exists but at a very low level. Self-induced internal short circuit, also called the spontaneous internal short circuit, was believed to be the probable cause of the battery failure for Boeing 787 (Accident No. 4 & 5 in Table 2). For the EV, the self-induced failure rate in vehicle level can be calculated by $P = 1 - (1 - p)^{m-n}$, where P is the failure rate considering m EVs, each of which contains n cells within its battery pack. Take Tesla Model S as an example, where $n = 7104$. Assume that the self-induced failure rate p of the 18,650 cells is 0.1 ppm, which denotes the defect rates during manufacturing, then when the quantity of the EV equals $m = 10,000$, the failure rate $P = 0.9992$, indicating that the failure rate is approximately 1 over 10,000. Comparing with the traditional vehicle (7.6 fire accidents per 10,000 vehicles in US [13]), the probability of the EV accident seems to be much lower.

The abuse condition can be unpredictable in practical use, leading to field failure of battery TR. For instances, the high-speed crush in accident No. 3, the metal intrusion in accident No. 6, the unintended overcharge in accident No. 7, and the unknown charging failure in accident No. 9 etc., represent the unpredicted abused conditions, which might be more severe than that regulated in the test standards. The deterioration during life cycle may also cause unpredicted abuse conditions. For instances, the battery pack was out of warranty after a 7-year service in the accident No. 8, and the EV bus fire was caused by

Table 1
The abbreviations used in Fig. 2.

Abbrev.	Electrode	Formula	Abbrev.	Electrode	Formula
LFP	Cathode	$LiFePO_4$	**NCM811**	Cathode	$Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$
LMO	Cathode	$LiMn_2O_4$	**NCA**	Cathode	$Li[Ni_xCo_yAl_z]O_2$, $x \geq 0.8$
NCM	Cathode	$Li[Ni_xCo_yMn_z]O_2$	**LIMO**	Cathode	$xLi_2MnO_3 \cdot (1-x)LiMO_2$
NCM111	Cathode	$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$	**C**	Anode	Graphite, Carbon, or MCMB
NCM523	Cathode	$Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$	**Si**	Anode	Si, or SiO_x
NCM622	Cathode	$Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$	**SiC**	Anode	Composite anode with Si and C