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Probing the heat sources during thermal runaway process by thermal analysis of different battery chemistries

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HIGHLIGHTS

- Thermal runaway features of different batteries were tested using ARC.
- Thermal stabilities of different cell component materials were identified by DSC.
- The peaks of the DSC results matched well with the peaks in the ARC test results.
- The severity of thermal runaway is highly related with internal short-circuit.
- Proposed an analytical approach of battery thermal runaway mechanisms.

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ABSTRACT

Safety issue is very important for the lithium ion battery used in electric vehicle or other applications. This paper probes the heat sources in the thermal runaway processes of lithium ion batteries composed of different chemistries using accelerating rate calorimetry (ARC) and differential scanning calorimetry (DSC). The adiabatic thermal runaway features for the 4 types of commercial lithium ion batteries are tested using ARC, whereas the reaction characteristics of the component materials, including the cathode, the anode and the separator, inside the 4 types of batteries are measured using DSC. The peaks and valleys of the critical component reactions measured by DSC can match the fluctuations in the temperature rise rate measured by ARC, therefore the relevance between the DSC curves and the ARC curves is utilized to probe the heat source in the thermal runaway process and reveal the thermal runaway mechanisms. The results and analysis indicate that internal short circuit is not the only way to thermal runaway, but can lead to extra electrical heat, which is comparable with the heat released by chemical reactions. The analytical approach of the thermal runaway mechanisms in this paper can guide the safety design of commercial lithium ion batteries.

1. Introduction

Lithium ion batteries have been widely used in electric vehicles to solve the energy and environmental problems [1–3]. The safety problem of lithium ion battery must be solved before its commercial utilization [4–7]. Severe burning accidents of electric vehicles occurred one after another due to the thermal runaway of the lithium ion batteries [8]. Therefore, the thermal runaway mechanisms of the lithium ion batteries require in-depth study [9,10].

The thermal runaway features of the lithium ion batteries and the thermal stabilities of the components inside the lithium ion batteries have been reviewed several times [11–14]. A three-stage characteristics were put forward by Abraham et al. [15] to interpret the thermal runaway mechanisms of lithium ion batteries, including the anodic decomposition reactions at 90 °C, the exothermic reactions of cathode over 140 °C, the decomposition of the cathode and the oxidation of electrolyte over 180 °C. Feng et al. [16] divided the thermal runaway process into six stages, including the solid electrolyte interface (SEI) decomposition, the reactions of anode, the cathode decomposition, the electrolyte decomposition, the separator melting, and the massive internal short circuit.

For the components inside the lithium ion batteries, Fig. 1 summarizes the characteristics of the individual chemical reactions measured by the differential scanning calorimetry (DSC) from the references. All the reaction kinetics in Fig. 1 are for the cells with 100% state of charge (SOC) and from the DSC tests at a scan rate of 10 °C min^{-1}. The characteristics of the reactions and correlated references are listed in Table 1. The legend of Fig. 1 located at the bottom left illustrates the

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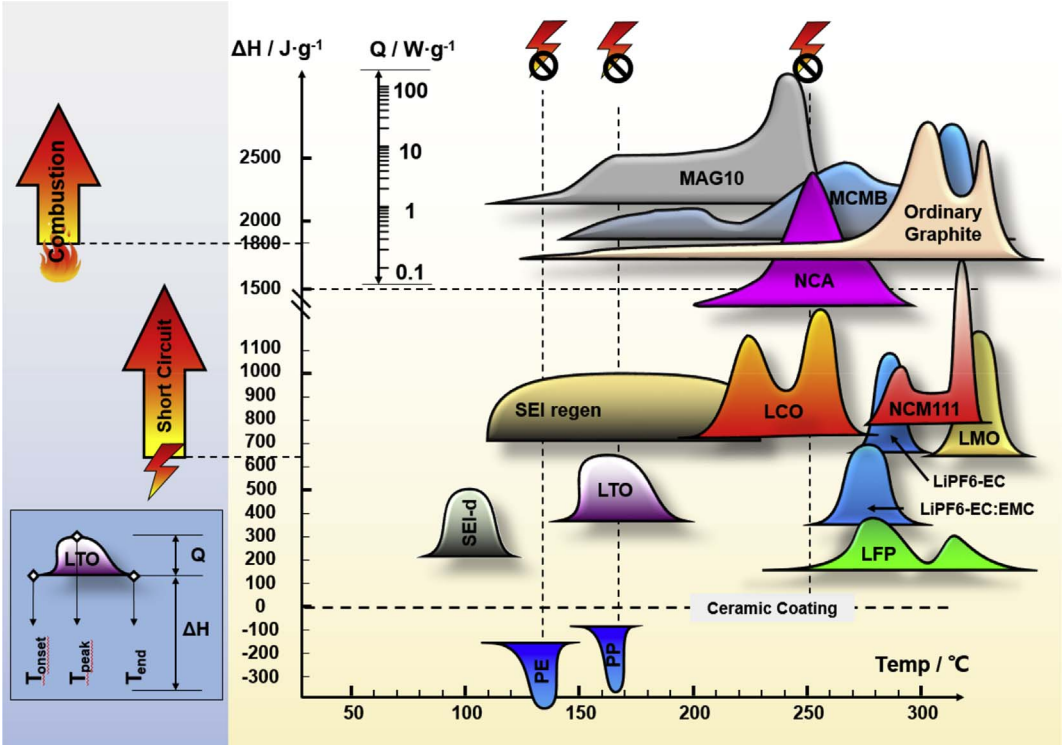

Fig. 1. The characteristic DSC results of the component materials inside the lithium ion battery.

Table 1
Comparison on the reactions characteristics of the component materials inside the lithium ion batteries from literature.

Component materials			Onset Temp. T_{onset}/°C	Peak Temp. T_{peak}/°C	Terminal Temp. T_{end}/°C	ΔH/J g^{-1}	References
Electrolyte	$LiPF_6$-EC		≈260	≈280	≈310	≈620	[19]
	$LiPF_6$-EC:EMC		≈250	≈275	≈300	≈330	[19]
Separator	Polyethylene (PE)		≈110	138.4	≈150	≈-150	[20]
	Polypropylene (PP)		≈150	169.4	≈175	≈-75	[20]
Cathode (with electrolyte)	$LiFePO_4$ (LFP)		250	≈280	360	147	[21]
	$LiMn_2O_4$ (LMO)		≈300	≈340	≈370	≈650	[22]
	$LiCoO_2$ (LCO)		≈200	≈248	≈270	≈706	[23]
	$Li(NiCoMn)_{1/3}O_2$ (NCM111)		≈270	≈315	≈325	790	[24]
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)		≈200	≈255	≈300	1460	[24]
Anode (with electrolyte)	$Li_4Ti_5O_{12}$ (LTO)		≈140	≈160	≈200	383	[25]
	Ordinary graphite		≈120	≈330	≈370	≈1700	[26]
	Artificial graphite	MCMB	≈130	≈310	≈330	≈1800	[27]
		MAG10	≈125	≈250	≈275	2222	[28]

characteristics of the reactions measured by DSC for the decomposition of LTO with electrolyte as an example. The characteristics of the reactions include the heat release power (Q), the enthalpy (ΔH) representing the total heat released, and the characteristic temperatures including the onset temperature (T_{onset}), the peak temperature (T_{peak}) and the terminal temperature (T_{end}). The x axis of Fig. 1 represents the characteristic temperatures, whereas the dual y axis is used to depict the heat generation features of the reactions. The colorful region marked with LTO indicates the reaction characteristics for the LTO decomposition with electrolyte. The border and shape of the region is determined by the T_{onset}, T_{peak}, T_{end} and Q. The height of the region reflects the Q at T_{peak}. The horizontal and vertical positions are determined by T_{onset} and ΔH, respectively. Complying with the legend, all the reactions characteristics can be depicted by the colorful regions with marked name as shown in Fig. 1, which provides comparable kinetics of different reactions for the cell components. The detailed chemical kinetics, which can support the drawing of Fig. 1, can be referred to in specific references as listed in Table 1.

Richard et al. [17] and MacNeil et al. [18] have identified that SEI decomposes at approximately 100 °C and regenerates at around 125 °C. Botte et al. [19] have compared thermal behaviors of the decompositions for types of electrolytes. Wong et al. [20] have reported the DSC results of the melting process for PE and PP. The thermal behaviors of the cathode materials [21–24] and the anode materials [25–28] in the presence of electrolyte have also been collected in Fig. 1.

Nevertheless, few researches tried to reveal the thermal runaway mechanisms of the full cell of lithium ion batteries by analyzing the reaction characteristics of the component materials. In addition, most of the researches and experiments focused on 18650 cells [29–34] or coin cells [17,35–37]. In general, the commercial batteries for electric vehicle use have larger capacity, for the sake of reducing the complexity of the pack formation. The higher stored energy and poorer cooling performance make the commercial large format batteries more prone to thermal runaway cases [38]. Therefore, in this paper, four types of commercial lithium ion batteries with large format were tested and their thermal runaway mechanisms were investigated and compared.