



A comparative study of thermal runaway of commercial lithium ion cells

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ARTICLE INFO

Article history:

Received 12 March 2018
Received in revised form
21 June 2018
Accepted 24 June 2018
Available online 26 June 2018

Keywords:

Lithium-ion batteries
Safety
Thermal runaway
State of charge
Enthalpy

ABSTRACT

Thermal runaway of three lithium ion cells (“A” - NCA/Graphite, “B” - LFP/Graphite, “C” - NCA/LTO) at 0%, 50%, and 100% state of charge (SOC) is studied by Accelerating Rate Calorimetry (ARC). Thermal behaviour of harvested positive and negative electrodes at three SOC (0%, 50%, and 100%) is analyzed using Differential Scanning Calorimetry (DSC). Thermal stability of recovered separators is also investigated by DSC. Harvested electrodes and separators are studied alone and in contact with a liquid electrolyte. The thermal behaviour of each component and its contribution is quantified and thoroughly discussed. A crucial negative impact of the state of charge and presence of highly flammable liquid electrolyte on the thermal instability of the investigated cells and “electrode - electrolyte” systems is clearly revealed. Among studied cells, LiFePO₄/Graphite one is the safest due to intrinsic thermal stability of lithium iron phosphate LiFePO₄ based cathode and despite the fact of using a microporous polyolefin separator with limited thermal stability.

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1. Introduction

Nowadays, lithium-ion batteries (LIB) are the dominating chemical power source for various applications such as: portable electronics, power tools, electrical vehicles, and stationary energy storage [1,2]. The thermal instability of lithium ion batteries is mainly caused by exothermic reactions of the liquid electrolyte with positive and negative electrodes which can occur inside a LIB and result in thermal runaway with related safety concerns (electrolyte leak, venting, flame, fire, or even explosion) [3,4]. Since appearing on the market in 1991, the safety and abuse tolerance of commercial LIBs have been significantly improved. Nevertheless, safety still remains one of the key challenges of modern lithium ion batteries [3,5–7]. As result of such controversial situation, continuous toughening of LIB transportation conditions considerably impedes faster LIB's penetration in emerging markets which require safe and reliable batteries working in a wide temperature range.

Typically, LIB's core is composed by four main components: positive electrode, negative electrode, liquid electrolyte, and

microporous separator. Below, we briefly discuss the most essential details of the thermal behaviour of each battery component.

Liquid electrolytes of modern lithium ion batteries are usually composed by a mixture of organic solvents (typically linear and cyclic carbonates etc.), lithium salt, and functional additives [8]. Linear carbonates are highly flammable substances with flash point below 31 °C [8]. Therefore, the liquid electrolyte can be considered as one of the main causes and triggers of LIB thermal runaway under abuse conditions and even during intensive battery operation without proper thermal management [3,6]. Many attempts have been performed to develop safer liquid electrolytes using ionic liquids, fluorinated solvents, and flame retardant additives [9]. However, due to various issues with trade-off between electrochemical performance, cost, and efficiency, new proposed electrolytes are still not implemented in the mass production where classical carbonate based liquid electrolytes are widely used nowadays.

The negative electrodes of commercial LIBs are commonly based on graphite and lithium titanium oxide Li₄Ti₅O₁₂ (LTO). Graphite based anode is thermally unstable in the 90–120 °C range due to the decomposition of metastable components of the solid electrolyte layer (SEI) [10–12]. In addition, lithium intercalated in the graphite can react with the electrolyte components and binder at temperature higher than 120 °C [10]. Alternative to graphite, lithium

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titanium oxide based anode is safer than lithiated graphite anode due to intrinsic thermal stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ceramic [13]. Nonetheless, the thermal tolerance of the LTO anode is limited by the reactivity of the intercalated lithium ions with the electrolyte solvents at temperature higher than 100°C [14].

Overwhelming majority of lithium ion batteries are equipped with positive electrodes based on layered metal oxides $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM), and lithium iron phosphate LiFePO_4 (LFP) with olivine structure. Upon heating and, especially, in charged state, NCA and NCM based cathodes are thermally unstable and decompose with oxygen release from the crystalline lattice [15]. Then, this oxygen acts as an internal oxidizer and provokes fast increase of internal temperature due to occurring undesirable exothermal reactions inside a sealed LIB [2,15]. In turn, cells with LFP cathodes demonstrate much better thermal stability in comparison with lithiated oxides due to strong P–O covalent bonds in $(\text{PO}_4)^{3-}$ polyanion [4,15]. Nevertheless, safety tolerance of LIBs with lithium iron phosphate cathode is still an issue due to limited thermal stability of graphite anode and carbonate based liquid electrolyte.

Thermal and dimensional stability of a LIB separator also have direct and essential impact on safety tolerance because its shrinkage and further melting upon heating, accompanied by short circuiting, accelerates the thermal runaway. Several approaches as using thermal stable polymer matrix or fibers together with ceramic coating are used to improve the thermal stability of separators [16]. It should be stressed, however, that the thermal stability range of commercial microporous separators is limited by thermal properties of polyolefin polymers.

Thus, we can conclude that abovementioned lithium ion battery components demonstrate different but quite limited thermal stability which negatively affects LIB's safety. Therefore, it is very important to investigate the thermal behaviour of the whole battery as well as of each specific cell component and their combinations to understand safety limitations for further improvement of the thermal and abuse tolerance. To assist in the development of advanced batteries for different applications, various abuse tests have been designed for cells, modules and battery packs [17]. However, all these tests are not able to provide comprehensive information about thermal behaviour of cell components and their combinations under controlled conditions.

To do this, we selected two experimental techniques: Accelerating Rate Calorimetry (ARC) and Differential Scanning Calorimetry (DSC). Accelerating Rate Calorimetry is a well-known method for the study of thermal hazards and the behaviour of batteries and their components [4,18–20]. The adiabatic control together with the ability to maintain the calorimeter at a temperature similar to the investigated sample allows studying self-heating processes and simulating real life situations [18]. In turn, Differential Scanning Calorimetry is very common and informative method of analysis of the thermal behaviour of battery materials and their mixtures [10,19,21,22]. Therefore, we used DSC technique to supplement the experimental data obtained from ARC study.

In this research, three commercial lithium ion cells with electrodes based on three very common chemistries have been

comprehensively and systematically investigated by ARC and DSC methods for better understanding of the thermal runaway. Additional purpose of the study was to shed more light on triggers of the thermal runaway in each investigated LIB. It was found that the chemistry of negative and positive electrodes, separator type, and the state of charge have significant impact on the thermal stability of the investigated batteries. The crucial negative impact of highly flammable liquid electrolyte and high state of charge on the LIB thermal stability was clearly demonstrated and thoroughly explained.

2. Experimental

General description of three investigated lithium ion cells is presented in Table 1.

2.1. Accelerating Rate Calorimetry (ARC)

The ARC tests of the studied cells were conducted in an EV-Accelerating Rate Calorimeter (Thermal Hazard Technology, UK) under adiabatic conditions with precise control of temperature. In this study, a heat-wait-see procedure methodology was used. The calorimeter was calibrated in the $30\text{--}270^\circ\text{C}$ interval using a piece of aluminum for weight simulation of each studied cell to make the system to be adiabatically and isothermally stable (instrument drift less than $0.01^\circ\text{C}\cdot\text{min}^{-1}$). In order to adjust the state of charge (SOC), a cell was discharged at nominal current to end-of-discharge voltage specified by the manufacturer and then was fully charged. Afterwards, the cell was left at rest during 1 h. Lastly, the cell was discharged to target SOC at nominal current and $25\pm 1^\circ\text{C}$ using a BaSyTec Cell Test System (Germany). Main details of the performed ARC tests are described in Table 2. Each tested cell was held by metal clamps to avoid its disconnection during the ARC test.

2.2. Differential scanning calorimetry (DSC)

The investigated lithium ion cells for DSC studies were activated by five full charge-discharge cycles in accordance with each LIB datasheet. Then each cell was completely discharged at $25\pm 1^\circ\text{C}$ using a BaSyTec Cell Test System (Germany). Afterwards, fully discharged cylindrical cells ("A" & "B") were carefully disassembled inside a dry room with dew point about -50°C [11]. Then, immediately after cell disassembling, the harvested electrodes and separator were thoroughly rinsed in anhydrous dimethyl carbonate solvent (DMC, <20 ppm of H_2O , Aldrich). Afterwards, all rinsed components were separately dried at 60°C during 30 min under

Table 2
ARC experiment settings.

Start temperature, $^\circ\text{C}$	50
End temperature, $^\circ\text{C}$	420
Slope sensitivity, $^\circ\text{C}\cdot\text{min}^{-1}$	0.02
Heat step temperature, $^\circ\text{C}$	5
Wait time, min	40

Table 1
Main features of the investigated cells.

Cell			Anode			Cathode		Separator	
Type	Design	Q, Ah	Main compound	LL, $\text{mg}\cdot\text{cm}^{-2}$	Main compound	LL, $\text{mg}\cdot\text{cm}^{-2}$	Type	δ , μm	
"A"	C	3,3	Graphite	16,6	NCA	27,6	Ceramic coated microporous polyolefin	17	
"B"	C	1,1	Graphite	5,7	LFP	13,0	Microporous polyolefin	21	
"C"	SP	16	LTO	11,9	NCA	11,6	Ceramic-polymer composite	37	

Note: C - cylindrical, SP - soft package, LL - loading level without current collector, NCA - $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, LFP - LiFePO_4 , LTO - $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

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