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PREFACE

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 focuses on showing the latest research findings and innovations in the field of ecology, environmental protection and sustainable development. The conference will be held in Sokobanja (Serbia) in hotel Sunce in the period of 18–21 June 2024.

The aim of the conference is to connect the experts in various fields in order to transform attitudes and behaviors in everyday practices, as well as in the industry and economy sector which is essential for achieving the desired changes that our society must undergo.

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology; the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica; the University of Zagreb, Faculty of Metallurgy – Sisak; the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Society of Young Researchers – Bor.

These Proceedings encompass 119 papers from the authors coming from the universities, research institutes and industries in 15 countries: Brazil, Norway, USA, Spain, Austria, Libya, Italy, Israel, Slovenia, Croatia, Romania, Bulgaria, Montenegro, Bosnia and Herzegovina, North Macedonia, and Serbia. It is a great honor and pleasure to cordially wish a warm welcome to all the participants of the conference.

As a part of this year's conference, the 6th Student Section – EcoTERS'24 will be held. We appreciate the contribution of the students and their mentors who have also participated in the conference and hope that students will continue to explore and to be curious, since education is a never-ending process, and knowledge is continuously growing.

The organization of the EcoTER'24 conference has been financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The support of the Donors and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'24 conference. The organizing committee would like to extend their appreciation and gratitude to the Platinum donors of the conference – Serbia ZiJin Copper doo Bor and HBIS SERBIA, to the Gold donor of the conference – Elixir Group, as well as to the Silver donor of the conference – Serbian Chamber of Engineers.

We would like to express our sincere appreciation to all the authors who have contributed to the Proceedings. We would also like to express our gratitude to the members of the scientific, organizing and honorary committees, reviewers, speakers, chairpersons and all the conference participants for their support of the EcoTER'24. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'24.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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CAUSES AND POSSIBLE CONSEQUENCES OF THERMAL RUNAWAY IN LITHIUM-ION BATTERIES

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Abstract

Advances in lithium-ion battery (LIB) technology have facilitated its widespread use, including in electric vehicles and electronic devices. However, with the increasing use of LIBs, the risk of thermal runaway is also increasing. This article explains the causes and mechanisms of thermal runaway in LIBs and the possible consequences of this process. One way to mitigate the risk of thermal runaway is to improve battery design to minimise internal defects and increase thermal stability. In addition, the development of advanced thermal management systems capable of detecting and controlling thermal anomalies can be crucial. Understanding the causes and consequences of thermal runaway in LIBs is essential for their further development and safe application in various fields.

Keywords: LIBs, thermal runaway, mechanism.

INTRODUCTION

Lithium-ion batteries (LIBs) have become a key power source for a wide range of electronic devices and electric vehicles due to their high energy density, long lifespan, and low greenhouse gas emissions [1–3]. Over time, lithium-ion batteries have gradually replaced lead-acid batteries, nickel-metal hydride batteries, and nickel-cadmium batteries [4,5]. However, as the use of LIBs expands, awareness of their potential safety risks also grows.

Lithium-ion batteries usually consist of two intercalation materials that form the cathode and the anode in the electrochemical cell. To avoid short circuits, the cathode and anode are separated by a porous membrane, the separator. The separator is impregnated with an electrolyte that facilitates the diffusion of lithium ions between the electrodes [6].

During the battery charging process, oxidation and reduction occur at the cathode and anode, respectively. Li^+ ions are released from the cathode structure, move through the electrolyte, receive energy from the source, and are inserted into the anode structure, according to the following reactions [7,8]:

$$\text{Cathode reaction: } Li_xCoO_2 \rightarrow CoO_2 + xLi + xe^- \ (Co^{4+} \text{ to } Co^{3+}) \quad (1)$$

$$\text{Anode reaction: Graphite} + xLi^+ + e^- \rightarrow Li_xC_6 \quad (2)$$

During the battery discharge process, Li^+ ions are released from the anode structure, move through the electrolyte, generate energy, and are inserted into the cathode structure, as shown in reactions 3 and 4 [7,8]:

Cathode reaction: $CoO_2 + xLi + xe^- \rightarrow Li_xCoO_2\ (Co^{4+}\ to\ Co^{3+})$ (3)

Anode reaction: $Li_xC_6 \rightarrow Graphite + xLi^+ + e^-$ (4)

The overall reaction that take place in the battery during the charging and discharging process can be represented by the following reaction [7,8]:

Summary reaction: $yC + Li(Z)O_2 \leftrightarrow Li_xC_y + Li_{(1-x)} + (Z)O_2$ (5)

where: x ~ 0.5; y = 6; Z can be cobalt, manganese or nickel.

Thermal runaway is a serious safety issue in LIBs where an irreversible process occurs within the battery that is accompanied by an increase in temperature that can lead to a fire or explosion. Understanding the causes and consequences of thermal runaway is critical to improving the safety of LIBs and minimising potential risks to users and the environment.

This paper aims to provide an overview of the main factors that contribute to thermal runaway in LIBs and the possible consequences of this process. By analysing relevant literature and research, the focus will be on the mechanisms by which thermal runaway occurs, factors that influence the likelihood of this process, and strategies to prevent and overcome this challenge.

THERMAL RUNAWAY IN LITHIUM-ION BATTERIES

Thermal runaway is a process of uncontrolled temperature increase. In the context of batteries, thermal runaway can occur when the battery generates more heat than it can dissipate. The excess heat can accelerate chemical reactions within the battery, causing the temperature to increase, which can lead to a fire or even an explosion [9–11].

In practise, improper handling of LIBs often leads to the triggering of thermal chain reactions within the cell, resulting in the decomposition of battery components, the emission of toxic gases and even an explosion. Figure 1 shows the most common causes and possible consequences of thermal reactions within the battery.

Figure 1 shows numerous causes that can lead to thermal runaway in LIBs. The first cause can be physical damage to the battery, overload, overcharge/discharge or other factors that cause a localised temperature increase. As the battery heats up, the rate of chemical reactions within the battery can increase. The intense chemical reactions within the battery release gases that can increase the internal pressure and cause the battery to expand or even explode. If the battery explodes or ignites, it can react with the oxygen in the air, resulting in a more intense fire [12].

The improper use of LIBs not only leads to economic losses, but can also have a negative impact on human health and lives. Careful handling of LIBs is required at all times, as incorrect handling can lead to numerous side reactions and the formation of various chemical compounds. Thermal decomposition of chemical compounds releases toxic gases that can lead to health problems such as chronic damage, paralysis and even death.

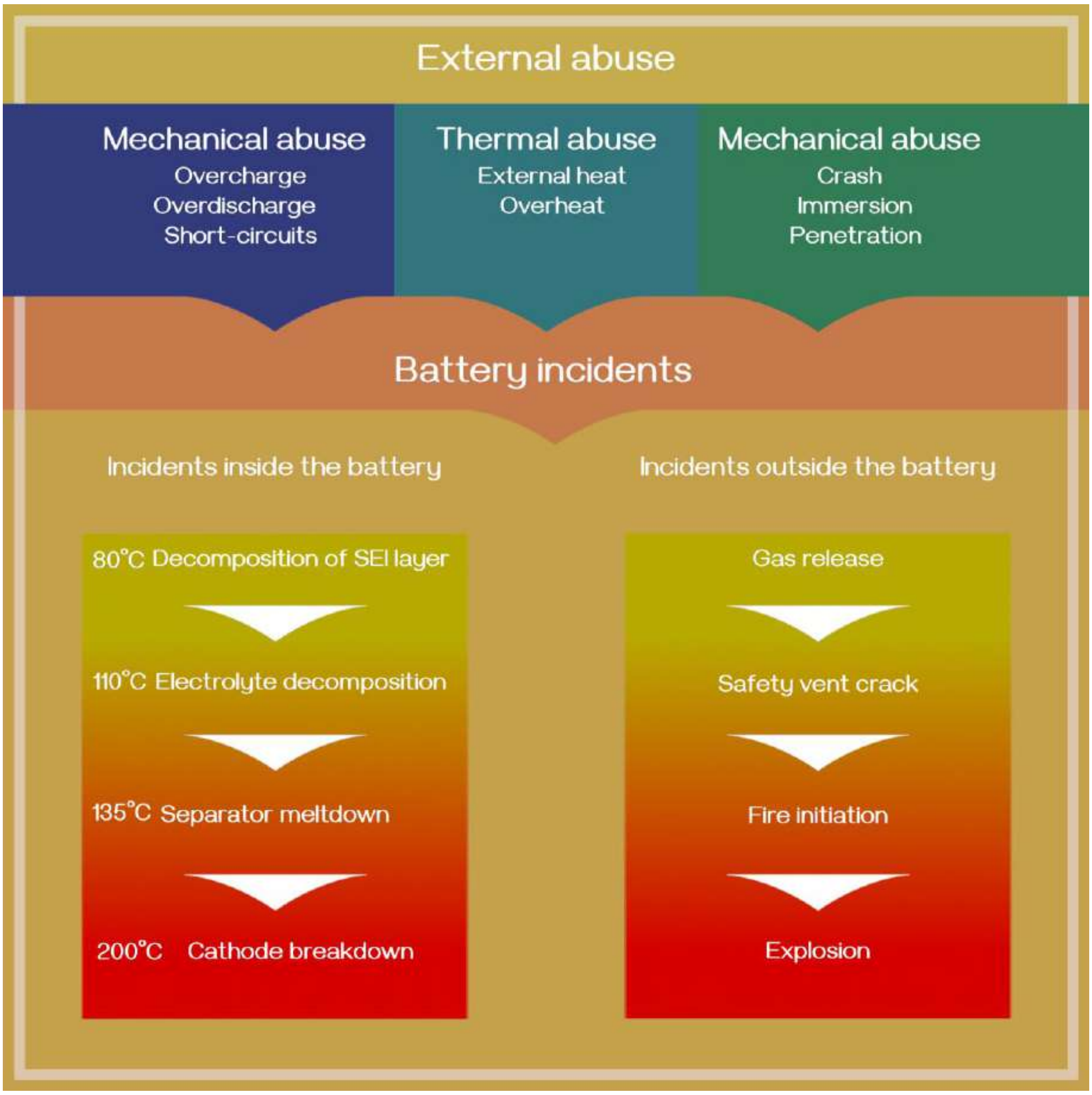

Figure 1 *Causes and possible consequences of thermal runaway in LIBs*

Different types of lithium-ion batteries release different concentrations of gases when the electrolyte ignites and the cell decomposes. Table 1 shows the concentrations of gases emitted during the thermal decomposition of LIBs consisting of different types of cathode materials [12].

Table 1 *Gas composition resulting from thermal runaway in commercial LIBs [12]*

Gas	Unit	Cathode material		
		[a]LCO/NMC	[b]NMC	[c]LFP
H_2	mol %	30.0	30.8	30.9
CO_2	mol %	24.9	41.2	53.0
CO	mol %	27.6	13.0	4.8
CH_4	mol %	8.6	6.8	4.1
C_2H_4	mol %	7.7	8.2	6.8
C_2H_6	mol %	1.2	/	0.3

[a]lithium cobalt oxide/lithium nickel cobalt manganese oxide; [b]lithium nickel cobalt manganese oxide; [c]lithium iron phosphate.

MECHANISM OF THE THERMAL RUNAWAY OF THE LITHIUM-ION BATTERIES

The thermal runaway of LIBs consists of several phases. In each phase, exothermic reactions take place, not necessarily one after the other, but often simultaneously. Understanding the mechanisms of thermal runaway not only helps to identify key problems in the operation of LIBs, but also enables the development of preventive measures and technologies that can minimise the risk of such an incident.

In the first phase, when the temperature inside the battery rises to 70–90°C, the film at the solid electrolyte interface (SEI) decomposes and the following reactions can take place [12–15]:

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + 0.5O_2 \quad (6)$$

$$2Li + (CH_2OCO_2Li) \rightarrow 2Li_2CO_3 + C_2H_4 \quad (7)$$

In the second phase, a reaction occurs between the electrolyte and the anode. From the anode, the intercalated lithium reacts with organic electrolytes, and the process is accompanied by the formation of flammable gases and a further temperature increase [14,15]:

$$2Li + C_3H_4O_3(EC) \rightarrow Li_2CO_3 + C_2H_4 \quad (8)$$

$$2Li + C_4H_6O_3(PC) \rightarrow Li_2CO_3 + C_3H_6 \quad (9)$$

$$2Li + C_3H_6O_3(DMC) \rightarrow Li_2CO_3 + C_2H_6 \quad (10)$$

In the third phase, at temperatures above 130°C, the separator melts because it is made of polyethylene (PE)/polypropylene (PP). As a result, a series of internal short circuits occur between the electrodes (and the voltage at the battery terminals drops to zero volts), and the energy accumulated in the battery through charging is released. This leads to a further increase in temperature in the battery [15].

In the fourth phase, with a further increase in temperature, the active cathode materials begin to decompose, and oxygen is released. With a cathode made of $LiMeO_2$ where M stands for the composition of Ni, Co, and Mn, for example, the following reactions occur [16]:

$$3x\,LiMO_2 + 2(1 - x)MO_2 \rightarrow 3x\,LiM_2O_4 + (1 - 2x)M_3O_4 + (1 - 2x)O_2 \quad (11)$$

$$6x\,LiM_2O_4 + 2(1 - 2x)M_3O_4 \rightarrow 6x\,LiMO_2 + 6(1 - x)MO + (1 + x)O_2 \quad (12)$$

$$2MO_2 \rightarrow 2MO + O_2 \quad (13)$$

The oxygen released during the reactions (11–13) can react with electrolytes in LIBs. For example, the combustion of ethylene carbonate (EC) can be represented by the following reaction [15]:

$$2.5O_2 + C_3H_4O_3(EC) \rightarrow 3CO_2 + 2H_2O \quad (14)$$

In the fifth phase, the electrolyte not only reacts with the electrodes, but is also degraded at temperatures of 200–300°C. In the case of diethyl carbonate (DEC), for example, the following reactions occur [15,17]:

$$LiPF_6 \rightarrow LiF + PF_5 \quad (15)$$

$$C_2H_5OCOOC_2H_5 + PF_5 \rightarrow C_2H_5OCOOPF_4 + HF + C_2H_4 \quad (16)$$

$$C_2H_5OCOOPF_4 \rightarrow PF_3O + CO_2 + C_2H_4 + HF \quad (17)$$

$$C_2H_5OCOOPF_4 \rightarrow PF_3O + CO_2 + C_2H_5F \quad (18)$$

$$C_2H_5OCOOPF_4 + HF \rightarrow PF_4OH + CO_2 + C_2H_5F \quad (19)$$

In addition to the reactions already mentioned, reactions between the binder and the battery components can also occur during thermal runaway in LIBs. Polyvinylidene fluoride (PVDF) and carboxymethyl cellulose (CMC) are most commonly used as binders in lithium-ion batteries [14]:

$$-CH_2-CF_2 + Li \rightarrow LiF + -CH{=}CF- + 0.5H_2 \quad (20)$$

$$CMC-OH + Li \rightarrow CMC-OLi + 0.5H_2 \quad (21)$$

Other mechanisms by which thermal runaway occurs can also be found in the scientific literature; however, only the most frequently investigated chemical reactions are presented in this paper.

CONCLUSION

Thermal runaway is a serious challenge in the operation of LIBs, and its causes and potential consequences are topics of great interest to researchers and industry. In this review paper, several key causes of thermal runaway were identified, including overcharge/discharge, short circuits, mechanical damage, and high temperatures. In addition, the potential consequences of thermal runaway were analysed, including physical damage to LIBs and the emission of flammable gases that can cause fires and explosions.

To effectively manage the risks of thermal runaway, advanced detection and control technologies must be developed and battery designs improved to increase resilience to these challenges. In addition, continuous research and development of new materials and technologies are crucial to reduce the risk of thermal runaway and increase the safety of LIBs.

Studying and understanding the mechanisms of thermal runaway in LIBs plays a crucial role in ensuring the safe and reliable use of this technology in various applications, from mobile devices to electric vehicles and renewable energy sources.

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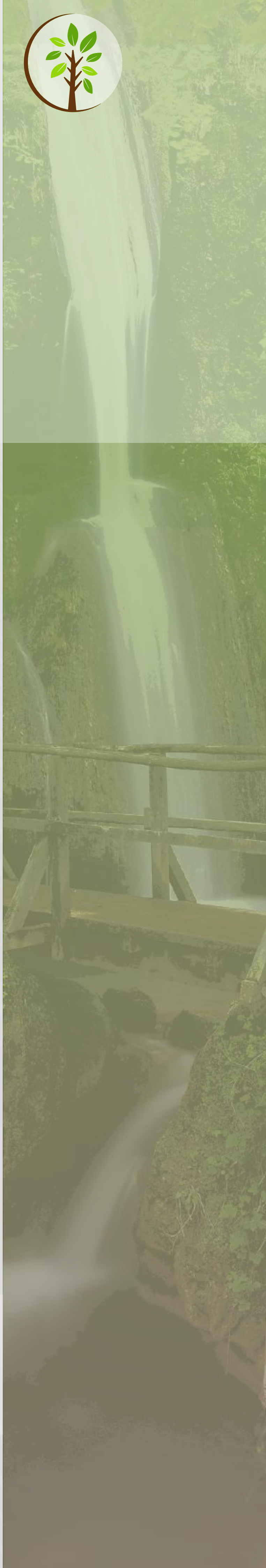

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