

PAWEŁ LISZAJ (ORCID: 0009-0009-5117-6640)¹

IZABELA MAJCHRZAK-KUCĘBA (ORCID :0000-0002-7746-7659)¹

ADRIAN BARASIŃSKI (ORCID: 0009-0001-1735-2534)²

THERMAL PROCESSES IN DAMAGED LITHIUM-ION CELLS. SELECTED ASPECTS OF ENVIRONMENTAL IMPACT

The ongoing energy transition has led to a systematic increase in the use of lithium-ion batteries, resulting in a growing stream of waste generated at the end of their life cycle. As a result of the residual energy and complex material composition, spent lithium-ion cells pose significant environmental and technological challenges. This study investigates the thermal processes occurring in mechanically damaged cylindrical 18650 NMC lithium-ion cells based on temperature measurements and mass changes before and after the experiment. The experimental procedure included measurements of the resting voltage, determination of the initial mass, and controlled mechanical damage using a puncture method. Changes in surface temperature were monitored using thermal imaging techniques. The results demonstrated rapid initiation of thermal processes accompanied by intensive emission of decomposition products and significant mass loss. Maximum surface temperatures reached 790 °C, while the relative loss of mass ranged from 25.7 to 43.8% of the initial cell mass, indicating the intensive release of volatile decomposition products. The results obtained underline the importance of safe collection, storage, and management of spent lithium-ion batteries in the context of environmental protection and waste management.

1. INTRODUCTION

The accelerating pace of technological development and the evolving needs of modern societies drive the growing demand for solutions that enable effective energy management. The modern economy is based on systems that require high reliability, mobility, and continuity of power supply, making energy storage issues of strategic importance [1]. It is particularly important to ensure the safety of technologies used in energy storage and

¹Częstochowa University of Technology, Faculty of Infrastructure and Environment, Dąbrowskiego 69, 42-201 Częstochowa, Poland, corresponding author P. Liszaj, email address: pawel.liszaj@pcz.pl

²Częstochowa University of Technology, Faculty of Electrical Engineering, Dąbrowskiego 69, 42-201 Częstochowa, Poland.

utilization processes, both during operation and after their end of use. As technology advances, the importance of analyzing the risks associated with power equipment failures and their potential environmental impact is increasing. Problems related to material degradation, the emission of decomposition products, and the generation of waste that require specialized management are important areas of scientific and engineering research [2–5]. In this context, the identification of mechanisms that lead to emergency states and the assessment of their technical and environmental effects are of particular importance.

The last decade has seen a dynamic development of energy storage technologies, in particular systems using lithium-ion batteries. Cells of this type are characterized by high energy density, high energy efficiency, and favorable cyclic durability, determining their wide application in mobile devices and energy storage systems. At the same time, the increasing scale of use of these systems increases the probability of failures related to their operation, transport, storage, and management at the end of their life cycle [1, 3]. This issue is of particular importance in the context of environmental protection, because damaged and used cells constitute a waste stream that contains metals and chemical compounds that can have harmful impacts on the environment [5, 6].

Lithium-ion cells are electrochemical systems in which energy is stored and released by reversible migration of lithium ions between electrodes through an electrolyte and a separator that ensures ion flow while preventing direct contact between the anode and the cathode [7, 8]. During the charging process, lithium ions move from the cathode to the anode, where they intercalate into the structure of the graphite anode electrode, while during discharge the reverse process occurs. This mechanism is shown in Fig. 1.

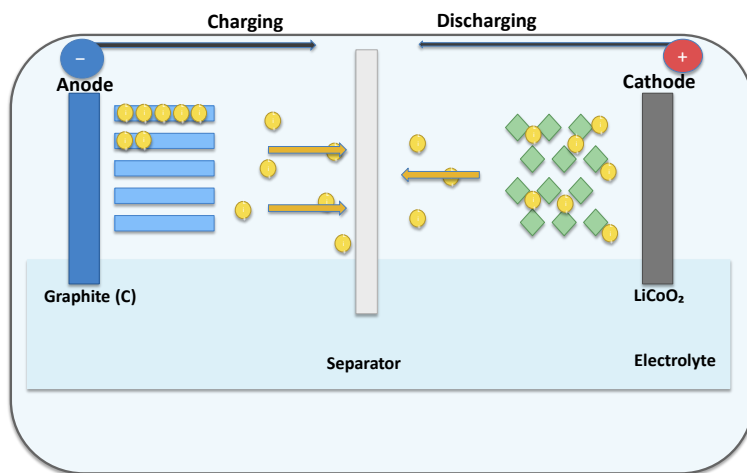


Fig. 1. Diagram of the principle of operation of a lithium-ion battery (based on [6])

Despite the numerous advantages of lithium-ion technology, its sensitivity to overheating, overcharging, and mechanical damage, which can lead to destabilization of the

electrochemical system. Disruption of the internal balance can initiate uncontrolled exothermic reactions, leading to thermal ejection, one of the most serious operational and environmental hazards associated with the use of lithium-ion batteries. Despite numerous studies on thermal runaway, there are still few quantitative analyses of mass changes in damaged waste cells, especially under actual storage conditions.

The operational safety of a lithium-ion cell is closely related to the structure of its individual components and the properties of the active materials used, which determine both the operating parameters and the susceptibility – parameter of the system to thermal destabilization. The anode is most often made of graphite, which remains the dominant anode material in lithium-ion cells because of its high electrochemical stability and the ability to reversibly intercalate lithium ions. The cathode is typically made of lithium-containing materials such as transition metal oxides (e.g., nickel, manganese, and cobalt) or phosphates (e.g., LiFePO_4), which have greater thermal stability at the expense of lower energy density [3,7]. The electrolyte also plays an important role, which is usually a solution of lithium salts in a mixture of organic carbonate solvents, which is responsible for the transport of lithium ions between electrodes and affects the safety of cell operation [8]. During cell operation, gradual degradation processes occur, including structural changes in electrode materials, increased internal resistance, and the interphase layer of the decomposition of the solid electrolyte (SEI), leading to deterioration of performance parameters and increased susceptibility to failures [9].



Fig. 2. Thermal runaway in an NMC 18650 cell during the nail puncture test

Therefore, a violation of the thermal or mechanical equilibrium of a cell can lead to the initiation of the thermal runaway phenomenon, understood as a self-sustaining process of rapid increase in temperature caused by a cascade of exothermic chemical reactions occurring within the cell [3, 9] caused by overheating, overcharging, internal short circuit, or mechanical damage leading to destabilization of the internal structure [4, 7]. As the process develops, the electrolyte and electrode materials decompose intensively, accompanied by rapid gas release, intense sparking, pressure build-up inside the housing, and rapid temperature increase. This leads to ignition, explosion, or ejection of burning fragments of active material, as shown in Fig. 2 [2, 3].

These phenomena pose a serious threat to both the users of the devices and the technical infrastructure in which the battery systems are operated. It should be emphasized that the course of emergency phenomena is largely dependent on the design of the cell. In practice, cylindrical, prismatic, and envelope cells are used, differing in geometry, mechanical properties, and heat dissipation conditions. Cylindrical cells are the most widely used solutions because of their high repeatability in production, good mechanical strength, and favorable heat dissipation conditions due to their geometry. Prismatic cells, on the other hand, allow for an increase in packing density in battery modules, which is particularly important in large-scale applications [1, 3]. Envelope cells, on the other hand, despite their lower structural rigidity, are widely used in mobile devices due to the possibility of adjusting their shape to design requirements [7].

During the thermal processes that take place in damaged cells, numerous gaseous products are formed. Components of the gas phase include hydrogen, carbon monoxide, carbon dioxide, methane, and other light hydrocarbons, formed mainly as a result of the decomposition of electrolyte and electrode materials [2, 7]. Under high-temperature conditions, hydrogen fluoride can also be emitted, associated with the decomposition of electrolyte salts and the secondary reactions of their decomposition products [2]. These products can pose significant risks to the environment and human health, especially in the event of fires in large-scale energy storage systems or waste collection points. The growing use of lithium-ion batteries makes the problem of safe operation and battery waste management increasingly important in the context of the circular economy. In many countries, intensive research is conducted on the mechanisms of initiation and propagation of the thermal runaway phenomenon, as well as methods to reduce its effects, including methods to extinguish fires and minimize environmental impact [9–12]. Lithium-ion cell damage events can generate significant economic costs because of the high dynamics of the accompanying exothermic processes. Therefore, quantitative analysis of the course of thermal processes under cell damage, based on temperature and mass before and after the experiment, remains an important direction of research. The purpose of this study was to investigate the thermal behavior of mechanically damaged end-of-life cylindrical NMC 18650 lithium-ion cells by analyzing the evolution of surface temperature and mass loss after puncture. The study also evaluates the environmental implications of these processes in the context of the safe management of spent lithium-ion batteries.

2. MATERIALS AND METHODS OF TESTING

The tests were carried out using waste cylindrical lithium-ion cells type 18650, identified on the manufacturer's designations as cells with NMC chemistry. The scope of the work included the initial characteristics of the samples, controlled mechanical damage to the cells, recording of the changes in surface temperature, and analysis of mass changes before and after the experiment. The adopted procedure was a simplified model of mechanical damage that could lead to internal short circuits and the initiation of intense thermal processes. The evaluation of the course of the experiment was made on two basic parameters: temperature changes recorded by the thermal imaging camera and loss of sample weight after the end of the process.

Characteristics of the cells tested. The research material consisted of waste cylindrical lithium-ion cells type 18650 with NMC chemistry. The samples were previously exploited and then stored for about two years in outdoor conditions, without a controlled temperature and humidity environment. During storage, cells were exposed to changing weather conditions, including temperatures as low as -20°C .

Before the experiments began, each sample was labeled with an individual identifier and subjected to a visual evaluation that included the condition of the housing surface, the presence of deformations, traces of corrosion, and other visible damage. Cells with preserved external integrity were qualified for the test. As part of the initial characterization, the resting voltage and initial weight were measured. The voltage was measured using a digital multimeter (UNI-T UT 55), obtaining values in the range of 3.98–3.99 V. These values indicated the presence of residual energy in the cells, but they did not constitute the basis for an unambiguous determination of the state of charge without knowing the open-circuit voltage (OCV) to state-of-charge (SOC) characteristics of a particular type of cell. The weight measurement was made using a laboratory electronic balance (RADWAG WTC 600) with an accuracy of 0.01 g.

Mechanical damage and course of examination. The main stage of the research consisted of controlled mechanical damage to the cells by puncturing them. The method used was a simplified model of damage that could lead to internal short circuits and rapid temperature increases. The tests were carried out according to the same procedure for all samples. After the puncture was performed, the course of the phenomena was observed in real time, from the moment of the damage to the end of the active phase of the process.

Changes in surface temperature were recorded using a thermal imaging camera (FLIR E60). Measurements were carried out at fixed time points: 1, 5, 10 and 15 s from the moment of damage. Note that the thermal imaging measurement was made to determine the surface temperature or visible hot zones and not directly the internal temperature of the cell. The results could depend on the emissivity of the surface, the presence of flame, smoke, and changes in the geometry of the sample during the process.

Measurement of the mass of cells after the test. After the experiment was complete, each sample was left to cool to ambient temperature, and then a final mass measurement was performed. The measurement was carried out using a laboratory electronic balance with an accuracy of 0.01 g. Each sample was individually weighed, keeping the cell positioned uniformly placed on the measuring pan. Based on the difference between the initial and final weights, the loss of mass was determined. This parameter was treated as an indirect indicator of the intensity of thermal processes that occur after cell damage. However, it did not constitute a direct measurement of the composition or amount of gases emitted.

3. RESULTS

During the investigation, the course of surface temperature and mass changes was recorded for 15 tested lithium-ion cells of type 18650. Analysis of the results included the characterization of thermal processes that occur after mechanical damage to the cells and comparison of the weight values of the samples before and after the experiment. The surface temperature showed a clearly dynamic nature of the changes that occur after the initiation of mechanical damage. Already in the first second after puncture of the cells, a significant increase in temperature was recorded, ranging from 70 to 124 °C. The highest value was recorded for sample 9 (124 °C) and the lowest for samples 2 and 6 (70 °C). At this stage, the thermal response of individual samples was varied, which may indicate differences in their technical condition, degree of degradation, or conditions of previous storage.

In the following seconds, a rapid intensification of thermal processes was observed. After 5 s from the moment of initiation of damage, the surface temperature increased to values in the range of 429–603 °C. The highest temperature was recorded for sample 14 (603 °C) and the lowest temperature for sample 4 (429 °C). In most cases, the temperature values exceeded 480 °C, indicating a developed phase of exothermic reactions taking place in the damaged cells. After 10 s of puncture, the temperature reached maximum values for most samples and ranged from 560 to 790 °C. The highest value was recorded for sample 5 (790 °C) and the lowest for sample 3 (560 °C). This stage may correspond to the phase of the highest intensity of thermal processes, associated with the rapid decomposition of the cell's internal materials and the emission of reaction products. After 15 s from the initiation of damage, the surface temperature ranged from 490 to 722 °C. The highest value was recorded for sample 9 (722 °C) and the lowest for sample 14 (490 °C). In some cases, stabilization of the temperature or a decrease in temperature was observed from the values recorded after 10 s, which may indicate a gradual extinction of the most intense reactions or a reduction in the availability of reactants participating in the process.

The obtained results allow us to distinguish the characteristic course of thermal phenomena, including the initial phase of rapid temperature increase, then the stage of intensification of the reaction and reaching maximum values, and then the phase of stabilization or gradual decrease in temperature. However, it should be emphasized that the measurements were carried out using the thermal imaging method and concerned the surface temperature or visible hot zones, which means that these values may differ from the actual temperatures inside the cell. A graph of the temperature change of the tested cells as a function of time is shown in Fig. 3.

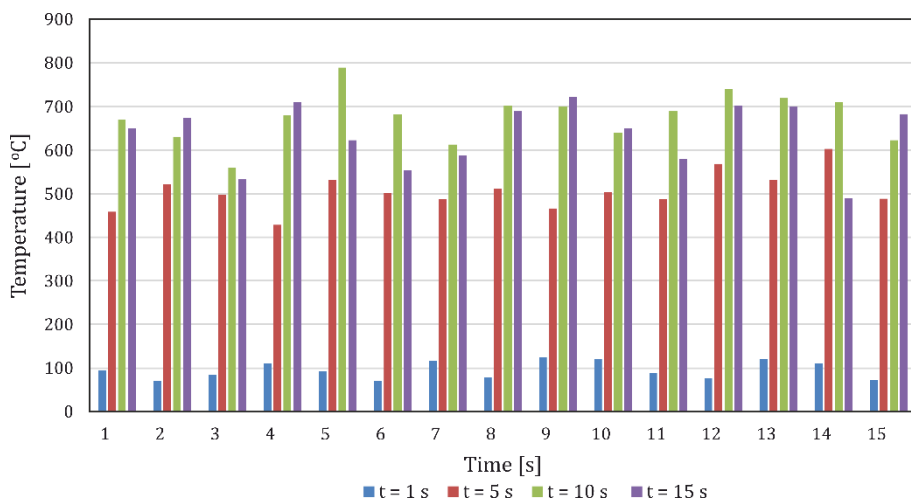


Fig. 3. Surface temperature profiles of the tested cells as a function of time

At the same time, an analysis of changes in the mass of the tested cells was carried out. The initial weight of the samples ranged from 44.44 g to 44.87 g. After the end of the experiments, the final weight was significantly reduced and was in the range of 25.11 g to 33.28 g. The lowest value was recorded for sample 12 (25.11 g), while the highest value was recorded for sample 3 (33.28 g).

The total weight loss ranged from approximately 11.5 to 19.6 g, while in relative terms it corresponded to a weight loss in the range of 25.7–43.8% of the initial value. The largest weight loss was recorded for sample 12 (approximately 19.6 g) and the smallest for sample 3 (approximately 11.5 g). The results obtained indicate that the processes occurring after mechanical damage led to a significant loss of material mass, which is consistent with the emission of volatile decomposition products, electrolyte degassing, and loss of part of the material during the intensive course of the reaction. A graph of the mass of the tested cells before and after a short circuit is shown in Fig. 4.

A comparison of the temperature and mass results indicates that the increase in surface temperature was accompanied by a marked decrease in the weight of the samples after the end of the experiment. In some cases, a tendency can be observed in which higher

maximum temperature values correspond to greater mass losses, which may suggest a higher intensity of the decomposition processes. However, this relationship is not unambiguous for all samples, so it can only be treated as a qualitative observation.

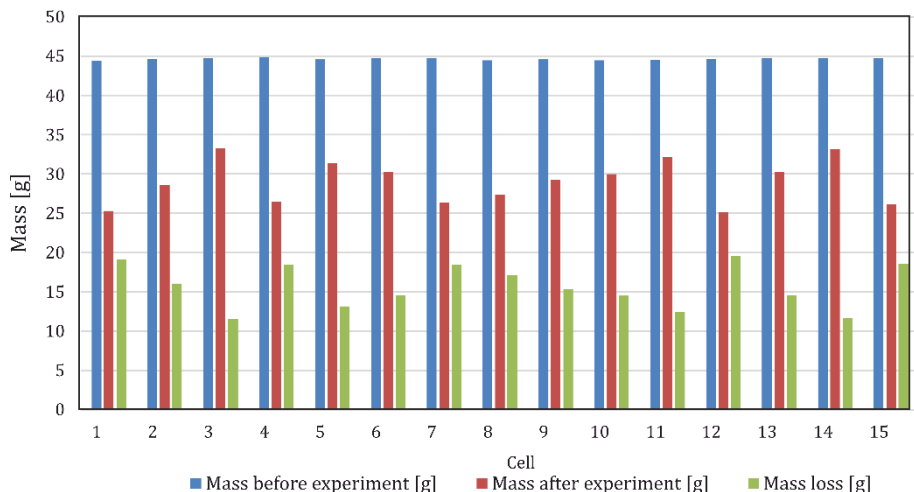


Fig. 4. Mass of the cells tested before and after the short-circuit experiment

In the analyzed test series, a significant difference was found in both the maximum temperature values and the size of the mass loss between individual samples, despite the use of a uniform experimental procedure and similar initial parameters. These results indicate the heterogeneous nature of the processes that occur in the damaged lithium-ion cells and the significant influence of factors such as technical condition, degree of degradation, or operating history of the tested samples. From an environmental point of view, the results indicate that these processes can lead to the emission of gaseous substances that are potentially harmful to air quality, especially under conditions of uncontrolled storage or treatment of battery waste.

4. SUMMARY

The research showed that mechanical damage to cylindrical lithium-ion cells type 18650 leads to the rapid initiation of intense thermal processes, accompanied by a rapid increase in surface temperature and a significant loss in sample weight. The obtained results confirm that the violation of the mechanical integrity of the cell may be a factor triggering the dynamic destabilization of the electrochemical system, leading to the development of exothermic reactions and the emission of decomposition products. From the point of view of environmental protection, the results obtained indicate the risk of the emission of hazardous substances, including toxic and flammable gases, which may be

formed as a result of cell damage. When uncontrolled, these processes can contribute to deterioration of air quality and pose a risk to human health and the environment.

The analysis of temperature courses indicates that the development of thermal phenomena is dynamic and multistage. In the initial phase, a rapid increase in temperature is observed due to the local heating of the fault zone and the initiation of internal reactions. Then there is the stage of intensification of exothermic processes, in which the temperature reaches maximum values. In the later phase, depending on the sample, stabilization or decrease in temperature is observed, which may be associated with a reduction in the availability of reactants, a change in reaction conditions, or a partial extinction of the process. This course is consistent with the general description of the development of thermal phenomena in damaged lithium-ion cells presented in the literature [1, 5, 9].

An important aspect of the results obtained is the high dynamics of temperature changes in a short time from the moment of cell damage. This means that from the point of view of technical safety, not only the value of the maximum temperature is crucial, but above all the speed of its rise. This parameter determines the actual time available for the reaction of protection systems and intervention actions in the event of mechanical damage.

The analysis of mass changes showed a clear loss of mass in all tested samples, falling within a wide range of relative values. This phenomenon should be associated with the emission of gaseous and volatile electrolyte decomposition products and electrode materials, as well as with the loss of part of the material during intensive thermal processes. Mass loss can be considered a useful, indirect indicator of the intensity of the phenomena occurring, but it is not a direct measure of the amount or composition of the substances emitted. Therefore, its interpretation should be carried out considering the limitations of the measurement method.

The comparison of temperature and mass results indicates the co-occurrence of high temperatures and significant mass losses in the analyzed samples. In some cases, a trend can be observed in which higher values of the maximum temperature are accompanied by higher mass losses, which may suggest a higher intensity of the processes of decomposition and emission of reaction products. An important result of the research is also the finding of significant variation during thermal processes between individual samples. The pattern of the course of the phenomenon, on the other hand, was the effect repeated in each of the tested samples. After the occurrence of an internal short circuit, the cells sparked intensely, after which an open flame appeared. After the flame went out, the cells smoked intensely, as shown in Fig. 5.

These differences were observed in both the values of maximum temperatures and the amount of mass loss, despite the use of a uniform experimental procedure and similar initial parameters. This may indicate a significant influence of factors such as the technical condition of the cell, the degree of degradation of the active materials, the history of operation, and the conditions of previous storage. This result highlights the difficulty of unambiguously predicting the course of emergency events in the case of real, spent lithium-ion cells. In the context of waste management, these results indicate the need to take into

account the risk of thermal process initiation in systems for the collection, transport, and storage of waste lithium-ion batteries. Of particular importance is the identification and proper protection of damaged or degraded cells.



Fig. 5. Photographic documentation of the research carried out

In terms of application, the results obtained indicate that damaged or degraded lithium-ion cells can be a significant source of thermal hazards in technical systems and in the waste stream. This is particularly important in the context of storage, transport, and processing of waste batteries, where even partially discharged cells can retain the ability to react violently after their structure is compromised. The results of the research confirm the need to consider the short time of initiation of thermal phenomena in the design of safety systems and procedures for dealing with damaged cells. In practice, this means that appropriate procedures must be used for segregation, packaging, and protection of cells at the collection and transport stages. It is also important to implement temperature monitoring systems and reduce the risk of mechanical damage to cells in places where lithium-ion waste cells are collected.

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