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Badanie zagrożenia wystąpienia pożaru ogniw akumulatorów stosowanych w samochodach elektrycznych

Research on the Fire Hazards of Cells in Electric Car Batteries

Исследования пожарной опасности элементов питания аккумуляторных батарей электромобилей

ABSTRACT

Aim: To carry out an analysis of the latest research in the field of fire hazard lithium-ion cells, which are used in accumulator batteries of electric cars. Proceeding from the obtained results of the research, to determine the direction of the subsequent research in the field of fire safety of lithium-ion accumulator batteries of electric cars.

Methods: This work is based on the fundamental research of scientists from the US, China and other countries of the world, the results of which were presented in a variety of world scientific journals, conferences and national reports.

Results: An analysis of literature sources has shown that research in the field of fire safety of lithium-ion batteries is carried out all around the world, as this technical device is constantly being modified and improved, as dictated by today's realities.

The obtained research results show that the elementary lithium-ion cell contributes during combustion to the production of 6 to 10 kW of energy and a rather large number of dangerous combustion products, especially HF, POF_3. Also, the results of the studies show unambiguously that the amount of energy released by lithium-ion cells supply as well as the amount of hazardous combustion products will depend on the degree of their charge. Furthermore, the shown research results unequivocally confirm that the amount of energy released by the lithium-ion battery depends on the degree of its charge. Based on the results of full-scale experiments, the average amount of water necessary to extinguish the battery of an electric car varies from 2500 to 6000 litres, which can exceed the amount of water carried by a single fire truck.

The amount of thermal radiation at a distance of 1.5 meters from the model of a burning car with decor elements, is between 8.1 and 11.9 kW/m^2. Laboratory analysis of samples of water, used to extinguish a car, showed the presence of hydrogen chloride (HCl) and hydrogen fluoride (HF) in concentrations 2–3 times higher and more than 100 times higher, than normal registered levels, respectively. No other corrosive or toxic compounds were found in the water samples.

Conclusions: Subsequent work to investigate the fire safety of electric car accumulators and their supply elements can be devoted to conducting full-scale experiments on the extinguishing of real consumer electric cars. Followed by an assessment of the problems of access to batteries and the difficulty of their extinguishing, the risk of electric shock from the battery of an electric car and the possibility of using various extinguishing media should be explored. It is also very urgent to develop a mathematical model for the heating of a lithium-ion battery that takes into account the geometric shape of the element and its chemical composition.

Keywords: lithium-ion battery, electric car battery, electric car fire hazard, extinguishing of electric car
Type of article: review article

Received: 17.05.2018; Reviewed: 16.10.2018; Accepted: 20.12.2018;
Percentage contribution: O. Lazarenko – 40%; V. Loik – 20%, B. Shtain – 20%; D. Riegert – 20%;
Authors' ORCID IDs: O. Lazarenko – 0000-0003-0500-0598; V. Loik – 0000-0002-3772-1640, B. Shtain – 0000-0002-2580-406X;
D. Riegert – 0000-0001-8003-8452;
Please cite as: BiTP Vol. 52 Issue 4, 2018, pp. 108–117, https://dx.doi.org/10.12845/bitp.52.4.2018.7;

АННОТАЦИЯ

Цель: Провести анализ последних исследований в области пожарной опасности литий-ионных элементов питания, которые используются в аккумуляторных батареях электрокаров. Исходя из полученных результатов исследований определить направления последующих исследований в области пожарной безопасности литий-ионных элементов питания и аккумуляторных батарей электрокаров.

Методы: Данная работа основывались на фундаментальных исследованиях ученых США, Китая и других стран мира, результаты которых были представлены в разнообразных мировых научных журналах, конференциях и национальных докладах.
Результаты: Проведенный анализ литературных источников показал, что исследования в области пожарной безопасности литий-ионных элементов питания проводятся по всему миру, поскольку данное техническое приспособление постоянно модифицируется и усовершенствуется, что по большей мере продиктовано сегодняшними реалиями.
Полученные результаты исследований показывают, что элементарный литий-ионный элемент питания во время горения способен продуцировать от 6 до 10 кВт энергии и довольно большое количество опасных продуктов горения, особенно HF, POF_3. Также показанные результаты исследований однозначно подтверждают, что количество выделяемой энергии литий-ионным элементом питания напрямую зависит от степени его заряда.
Исходя из результатов полномасштабных экспериментов среднее количество воды необходимое для тушения аккумуляторной батареи электрокара колеблется от 2500 до 6000 л, что может превышать объем вывозимой воды одним пожарным автомобилем.
Величина теплового излучения на расстоянии 1,5 метров от макета горящего автомобиля с элементами декора составляет от 8,1 до 11,9 кВт/м^2. Лабораторный анализ образцов воды, которой осуществлялось тушение автомобиля, показал наличие хлорида (HCl) и фторида (HF), в концентрации в 2–3 раза выше нормальных регистрируемых уровней и более чем в 100 раз выше, соответственно. Никаких других коррозионных или токсичных соединений в образцах воды не обнаружено.
Выводы: Последующие работы по исследованию пожарной безопасности аккумуляторных батарей электрокаров и элементов их питания могут быть посвящены проведению полномасштабных экспериментов пожаротушения реальных потребительских электрокаров с последующей оценкой проблем доступа к аккумуляторным батареям и сложности их тушения водой, опасности поражения личного состава электрическим током от аккумуляторной батареи электрокара, эффективности тушения аккумуляторных батарей с использованием различных огнетушащих средств. Также весьма актуальной остается задача разработки математической модели процесса нагрева литий-ионного элемента питания которая учитывала бы геометрическую форму элемента питания и его химический состав.
Ключевые слова: литий-ионный элемент питания, аккумуляторная батарея электрокара, пожарная опасность электромобиля, тушение электромобиля
Вид статьи: обзорная статья

Принята: 17.05.2018; Рецензирована: 16.10.2018; Одобрена: 20.12.2018;
Процентное соотношение вклада в создание статьи: O. Lazarenko – 40%; V. Loik – 20%, B. Shtain – 20%; D. Riegert – 20%;
Идентификаторы ORCID авторов: O. Lazarenko – 0000-0003-0500-0598, V. Loik – 0000-0002-3772-1640, B. Shtain – 0000-0002-2580-406X, D. Riegert – 0000-0001-8003-8452;
Просим ссылаться на статью следующим образом: BiTP Vol. 52 Issue 4, 2018, pp. 108–117, https://dx.doi.org/10.12845/bitp.52.4.2018.7;

ABSTRAKT

Cel: Wykonano analizę najnowszych badań w zakresie zagrożenia pożarowego, jakie mogą powodować akumulatory litowo-jonowe stosowane do zasilania samochodów elektrycznych. Na podstawie uzyskanych wyników badań ustalono kierunek dalszych badań w zakresie bezpieczeństwa pożarowego akumulatorów litowo-jonowych i samochodowych.
Metody: Praca została oparta na analizie badań naukowców m.in. z USA i Chin, których wyniki zostały przedstawione w różnych czasopismach naukowych o zasięgu międzynarodowym, a także w materiałach konferencyjnych o zasięgu krajowym.
Wyniki: Analiza literatury wskazuje, że badania w zakresie bezpieczeństwa pożarowego akumulatorów litowo-jonowych prowadzone są na całym świecie, co jest podyktowane ciągłym rozwojem tego typu urządzeń. Uzyskane wyniki badań wskazują, że pojedyncza bateria litowo-jonowa może wytworzyć od 6 do 10 kW energii i dużą ilość niebezpiecznych produktów spalania, zwłaszcza HF, POF_3. Ponadto przedstawione wyniki badań jednoznacznie potwierdzają, że ilość energii uwalnianej przez baterię litowo-jonową zależy bezpośrednio od stopnia jej naładowania. Opierając się na wynikach badań w pełnej skali, średnia ilość wody potrzebnej do ugaszenia palącej się baterii samochodu elektrycznego waha się od 2500 do 6000 litrów. Tak duże zapotrzebowanie w wodę może powodować, że do ugaszenia takiego pożaru nie wystarczy tylko jeden pojazd pożarniczy. Ilość promieniowania cieplnego w odległości półtora metra od modelu płonącego samochodu z elementami wykończeniowymi waha się od 8,1 do 11,8 kW/m^2. Badania laboratoryjne wody użytej do gaszenia samochodu wykazały obecność w niej chlorowodoru (HCl) oraz fluorowodoru (HF) w stężeniach odpowiednio dwu- trzykrotnie oraz stokrotnie wyższych niż normalne. W próbkach wody nie znaleziono żadnych innych substancji toksycznych lub korozyjnych.
Wnioski: Konieczne jest prowadzenie dalszych prac koncentrujących się na bezpieczeństwie pożarowym w odniesieniu do baterii akumulatorowych pojazdów elektrycznych. Z wykonanej analizy tematu wynika, że istnieje konieczność prowadzenia badań w makroskali w celu określenia najlepszych sposobów gaszenia pożarów baterii akumulatorowych pojazdów elektrycznych. Dodatkowo niezbędne jest przeprowadzenie analizy możliwych do wystąpienia zagrożeń oraz opracowanie optymalnego sposobu gaszenia, a także określenie najskuteczniejszego środka gaśniczego, który może zostać do tego celu użyty. Istotne jest również opracowanie modelu matematycznego akumulatorów litowo-jonowych, który uwzględniać powinien kształt geometryczny baterii akumulatorowej oraz jej skład chemiczny.
Słowa kluczowe: bateria litowo-jonowa, akumulator samochodu elektrycznego, zagrożenie pożarowe samochodu elektrycznego, gaszenie pojazdów elektrycznych
Typ artykułu: artykuł przeglądowy

Przyjęty: 17.05.2018; Zrecenzowany: 15.10.2018; Zatwierdzony: 20.12.2018;
Procentowy wkład merytoryczny: O. Lazarenko – 40%; V. Loik – 20%, B. Shtain – 20%; D. Riegert – 20%;
Identyfikatory ORCID autorów: O. Lazarenko – 0000-0003-0500-0598; V. Loik – 0000-0002-3772-1640, B. Shtain – 0000-0002-2580-406X; D. Riegert – 0000-0001-8003-8452;
Proszę cytować: BiTP Vol. 52 Issue 4, 2018, pp. 108–117, https://dx.doi.org/10.12845/bitp.52.4.2018.7;

Introduction

The development of modern technologies provides great advantages to humanity, even across a short time span of 10 to 20 years, and, as a rule, is intended to foster the improvement and prosperity of our world. However, very often novelties of technical progress fail, especially at their initial stages of operation, which may entail a series of problems and dangers threatening the appropriate handling of emergencies.

Recently, humankind has begun to explore the possibility of harnessing alternative sources of energy that could replace hydrocarbon fuels. One of such striking examples is the rapid growth and development of electric and hybrid electric vehicles, which in the near future will replace cars powered by internal combustion engines [1]. Simultaneously with the advent of new technologies, the threats and dangers to which emergency rescue units should respond are growing in number as well. Electric vehicles represent a similar danger today. Constant changes in the configuration of the placement of batteries in cars as well as the chemical composition of batteries and their capacity determine the specifics of firefighting tactics and emergency rescue operations in electric vehicles [2, 3]. The safety of firefighters and other emergency services depends on the understanding and proper management of these hazards through appropriate training and learning.

Formulation of the problem

Considering the modern design of the electric vehicle, and based on research [4], it can be argued that the main danger both in terms of fire safety and safety of the rescue works, in this mode of transport, stems from high-capacity batteries (about 24 to 85 kW/hours and more, depending on the model of the car).

The main manufacturers of electric cars (Nissan, Tesla, Mitsubishi, Ford, etc.), in the design of accumulator batteries use lithium-ion power supply elements which differ only in the type of elements (Fig. 1.) and their distribution in the accumulator battery itself.

a) b) c)

Figure 1. Example of power supply elements in accumulator batteries of electric cars [4]: a) Example of 18650 cylindrical cells (18 x 65 mm); b) Example of a hard case prismatic cell; c) Example of a soft-pouch polymer cell

In this case, it is worth mentioning that the most common batteries today are the cylindrical batteries (Fig. 1a) found, in particular, in Tesla's electric cars, and the soft-pouch polymer cells (Fig. 1c) which are widely used by other automakers such as Nissan. To obtain the required capacity of the electric car battery and protect the battery from mechanical damage, the battery cells are placed in metal blocks. For example, the Nissan Leaf battery consists of 48 aluminium blocks (each has four packaged polymer batteries), and in the Tesla Model S, there are 16 blocks (444 elements of the 18650 type are installed in each) [5]. Lithium-ion batteries have a number of advantages, including long service life and the ability to quickly charge. However, there are a number of drawbacks too that carry a potential hazards risk both to the vehicle as well as to people.

Since the electrolyte located in the middle of the cell is combustible, it can cause an irreversible thermal reaction, which subsequently leads to the release of flammable and toxic gases, and in some cases, the explosion of the battery [6, 9–15]. An irreversible thermal reaction can occur in the event of a disturbance to the battery's stable mode of work and other reasons can cause the following:

1. Short circuit;
2. Overheating;
3. Overcharge;
4. Mechanical damage.

Accordingly, with the foregoing, the purpose of this paper is to analyze the current scientific results in the field of fire safety with respect to power supply elements in accumulator batteries of electric cars.

 ISSN 1895-8443

a) b)

Figure 2. Example of the distribution of power supply elements in accumulator batteries of electric cars of different manufacturers [5]: a) accumulator battery of Nissan Leaf; b) accumulator battery of Tesla Model S

Main scientific results

In order for the lithium-ion battery to become a source of ignition, three components must be present: oxygen, ignition source and fuel.

Work [6] offers a detailed description of the process during which, with temperatures of 170°C and 74°C, a positive electrode $Li_{0,5}CoO_2$ and a negative electrode $Li_{0,86}C_6$, respectively, decompose and release oxygen products and a large amount of exothermic heat which are then contributed to the combustion triangle.

Additionally, on the basis of the theory by Semenov [7, 8], it was calculated by the authors that when the temperature of the cell is raised above 65.5°C, there is an acceleration of the occurrence of thermochemical reactions which can lead to an irreversible ignition process. Reaching the temperature of 75°C marks a point of no return, after which the subsequent ignition of the battery follows. The general process of ignition and the resulting "domino effect" chain reaction forms a sequence which, according to the authors, could be described as shown in Fig. 3.

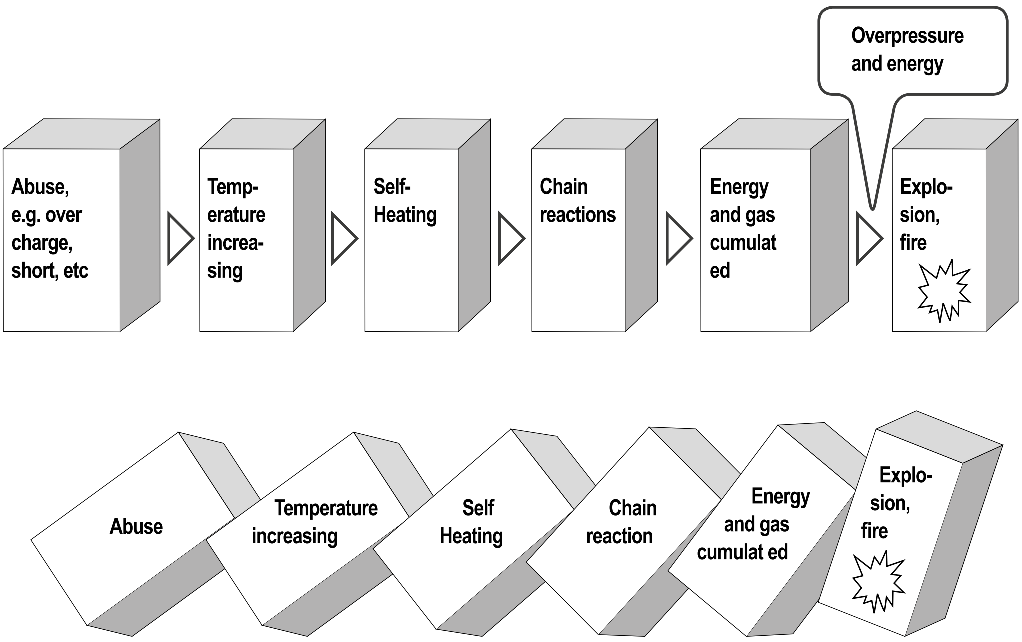


Figure 3. Domino effect of lithium ion battery fire and explosion [5]

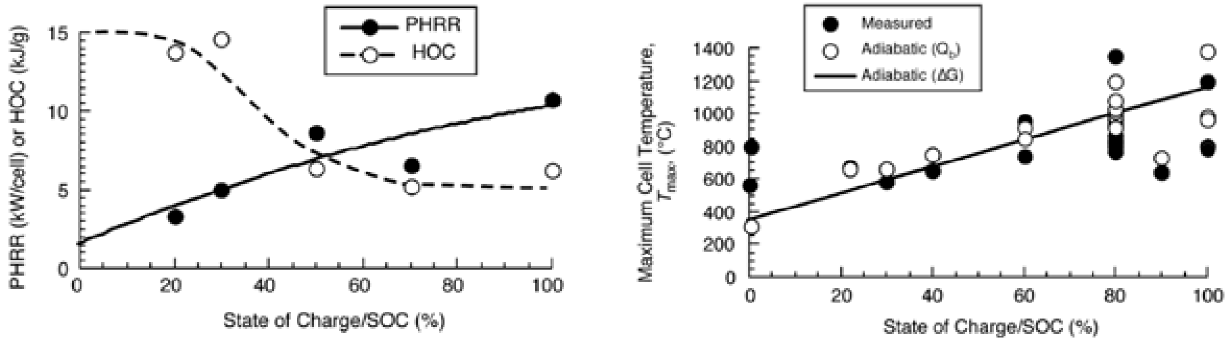
As the thermochemical reaction progresses, a significant amount of thermal energy and hazardous combustion products are released from the lithium-ion power element. These quantities were studied and measured in detail in the following research papers [9–16].

The authors of [9] investigated the order of nine different supply elements among which special attention was paid to cylindrical cells 18650 and soft-pouch polymer cells. The experiment was conducted with the use of submitted power elements, in order to determine the amount of released energy.

For this, a calorimeter was used operating on the principle of oxygen consumption. In these tests, the batteries were exposed to a radiant heat flux from 10 to 75 kW/m^2. Batteries with a different state of charge from 20 to 100% were tested, which also influenced the results of the research.

As a result of the studies, the following data were obtained for the 18650 batteries (Fig. 4).

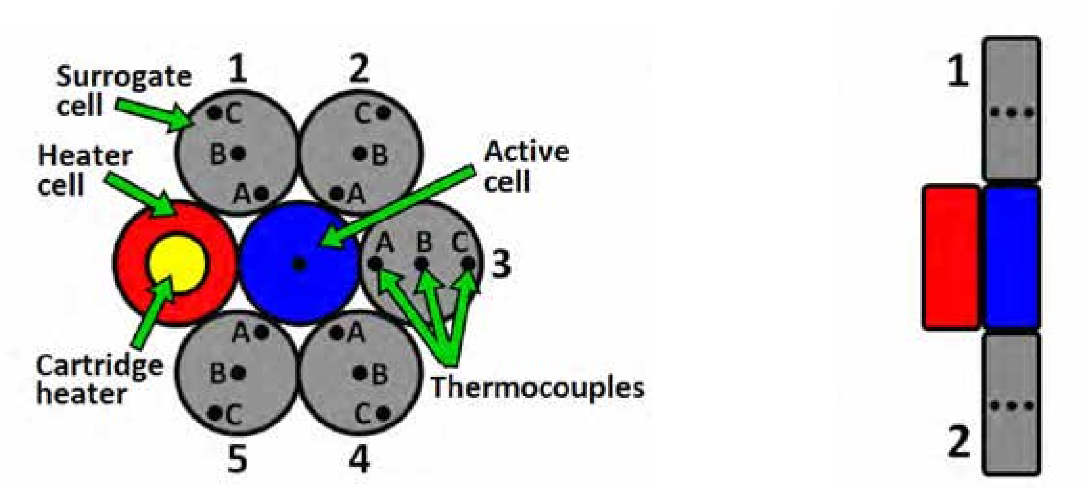
The results of studies for soft-pouch polymer cell were obtained only at a charge value of 50%, where the average value of the HRR was 6.1 kW.



a) b)

Figure 4. Results of studies to determine the dangers of the 18650 lithium-ion batteries [9]: a) The HOC and PHRR vs. SOC for a lithiumi-on 18650 at a heat flux of 50 kW/m^2; b) Maximum surface temperatures of 18650 lithium-ion cell at failure vs. SOC

As part of the studies [10], a number of experiments were carried out to determine the temperature of the 18650 type batteries, depending on the SOC and the type of power elements. For experiments, two options for stacking the batteries were chosen – vertical and horizontal (Fig. 5.). In each of the stacking options, a single cell was placed and heated by being connected to an electrical transformer, and this served as a heat source for another active cell. The rest of the batteries were just an imitation, but at the same time, they were the closest thing to an active cell with built-in thermal sensors.



a) b)

Figure 4. Results of studies to determine the dangers of the 18650 lithium-ion batteries [9]:
a) horizontal or hexagonal;
b) vertically

As mentioned, the experiment was also carried out at a different SOC of the active cell: 30%, 100% and more than 100%. The following results were obtained (Table 1: where: $T^{surface}_{active}$ – the surface temperature of the active cell, $T^{av.}_{adj.\,cell}$ – the average temperature of the adjacent imitation cells):

Table 1. The results of research, depending on the SOC of the battery and their packing [10]

SOC	Horizontal placement of batteries	Vertical placement of batteries
30%	$T^{surface}_{active}$ = 126°C $T^{av.}_{adj.\,cell}$ = 148–236°C	$T^{surface}_{active}$ = 127°C $T^{av.}_{adj.\,cell}$ = 70–75°C
100%	$T^{surface}_{active}$ = 130°C $T^{av.}_{adj.\,cell}$ = 155–236°C – for elements 2, 3, 4; $T^{av.}_{adj.\,cell}$ = 250–418°C – for elements 1, 5;	$T^{surface}_{active}$ = 129°C $T^{av.}_{adj.\,cell}$ = 64–68°C
>100%	$T^{surface}_{active}$ = 141°C $T^{av.}_{adj.\,cell}$ = 114–259°C	$T^{surface}_{active}$ = 107°C $T^{surface}_{active}$ = 805°C – maximum temperature; $T^{av.}_{adj.\,cell}$ = 91–109°C – for elements 1; $T^{av.}_{adj.\,cell}$ = 89–96°C – for elements 2;

It is worth mentioning that when the charge of the active cell was 100% or more, after critical temperatures were reached, abundant spark and gas emission were observed – a signal to finish the experiment.

In addition, worthy of attention is the paper [11] in which the authors carried out a series of experiments, similar to the previous work, with several power cells (5 pieces) of the 18650 type. During the experiment, the amount of heat, the type and amount of hazardous gases released during the burning, depending on the state of their charge, were determined.

The results of the experiment showed that the HRR depends directly on the SOC of the battery (Fig. 6).

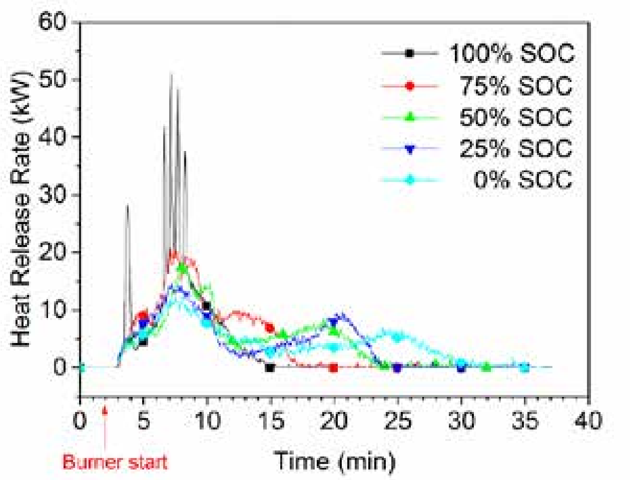


Figure 6. The magnitude of the HRR for the five power elements, depending on their SOC (0–100%) [11]

As mentioned, not only a significant amount of heat, but also substantial amounts of toxic combustion products were released as a result of combustion of lithium-ion batteries, among which the authors [11] isolated hydrogen fluoride (HF) and phosphorus oxyfluoride (POF3). However, because of the accuracy of equipment, the authors failed to measure the concentration and magnitude of POF3, and the production rate of HF depicted in Fig. 7.

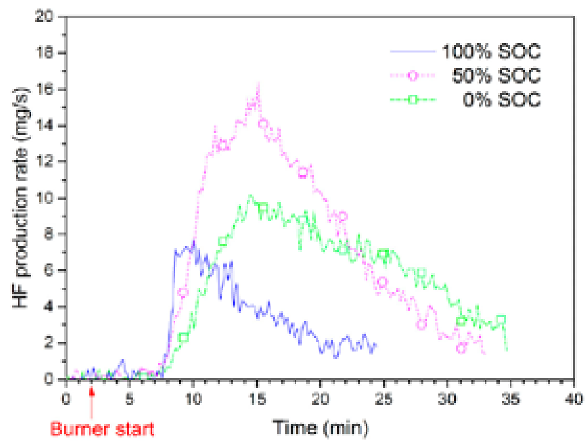


Figure 7. The production rate of hydrogen fluoride (HF) for five cells, depending on the SOC (0–100%) during their burning [11]

It is important to note that the rate of HF release is much higher with SOC of a battery at 50%, and at 100% the indices are the lowest.

The results of the research presented above pertain only to separate battery cells, but as mentioned earlier, the accumulator battery of the electric car consists of 192–7000 thousand of such elements (depending on the car brand). During a fire, such a number of battery cells, based on the results presented earlier, should allocate extremely large amounts of energy, and if we consider this type of fire in terms of its suppression tactics, then extinguishing it would require considerable amounts of fire extinguishing agent. As a result of the full-scale fire testing experiment [12, 13], intended to determine the amount of heat released, during the combustion of a real battery and the tactics of its suppression, we obtained some unique results.

Two types of batteries were used for the experiment. The battery "A" intended for hybrid cars, which contains sealed lithium-ion rechargeable batteries. The accumulator battery with a capacity of 4.4 kWh enclosed in a metal case and rigidly mounting at the bottom of the rear cargo area behind the rear seat (Fig. 8a). The metal case is isolated from high voltage, hidden and separated from the passenger compartment by a moulded plastic cover with carpet covering. The electrolyte used in lithium-ion batteries is a flammable organic electrolyte.

a) Accumulator battery type "A"   b) Accumulator battery type "B"

Figure 8. An example of accumulator batteries for carrying out full-scale fire experiments [12]

The battery "B" intended for electric cars with a capacity of 16 kWh and enclosed in a casing made of fibreglass. The T-shaped form of the battery covers almost the entire length of the vehicle from the rear axle to the front axle and is rigidly mounted under the car's pallet (Fig. 8b).

The first stage of the experiment was aimed to determine the amount of heat released by the battery "B".

The battery was pre-heated by a third-party heat source (propane burners) with a capacity of approximately 400 kW (Fig. 9).

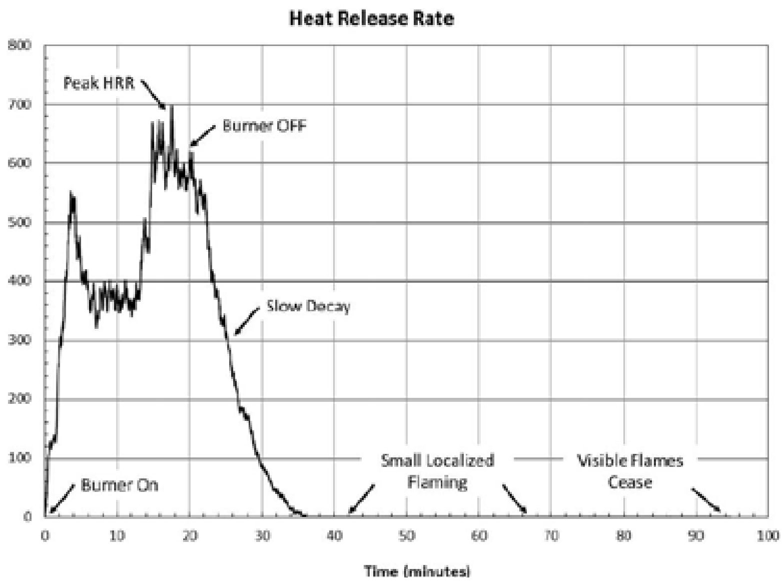


Figure 9. The results of experiments to determine the amount of heat during the combustion of an accumulator battery type"B" [13]

ISSN 1895-8443

Temperature and heat flux measurements were recorded on the outer and inner sides of the battery, as well as at a distance of 1.5 and 3 meters from the battery. Gas samples were collected for the analysis of toxic or corrosive compounds. The experiment was considered complete after a complete, unassisted burnout of the battery.

The maximum value of the HRR was 300 kW (when the propane burner power was subtracted) with a test time of 17 minutes and 30 seconds, and the case temperature from 684 to 1155°C. The maximum temperature at a distance of 1.5 and 3 meters from the battery was 94–110°C and 41–52°C, respectively. At the same time, the maximum value of thermal radiation at a similar distance was from 17.1 to 18 kW/m^2 and 3.7 to 4.7 kW/m^2.

After the burners were switched off, approximately 20 minutes later the values of the thermal radiation gradually decreased. After the 36-minute mark, the flame decreased significantly, and the value of the thermal radiation was practically zero.

Small local fires on the battery continued for about an hour. When the apparent burning stopped, the external maximum temperature of the battery was approximately 400°C. After another three hours, the maximum temperature was about 155°C.

Moreover, during the first stage of the study, fourteen samples of combustion products using Tedlar bags were taken. Sampling was carried out every 5 minutes, starting with 5 minutes of testing. The bags were analyzed for HCl, HF, HBr, HCN, CO_2, CO, NOx, SO_2, acrolein and formaldehyde content using an infrared Fourier transform spectrometer. The results showed only the presence of CO and CO_2. Each spectrum was directly examined for the presence of HCN and HF, but they were not detected. However, the authors acknowledge the possibility of an error which could have affected the final results.

In the second stage of the research, full-scale studies were carried out in order to determine the amount of time and the extinguishing agent (water) which will be necessary for the suppression of fire in the batteries "A" and "B". At the same time, the conditions for placing the batteries were ensured to be as close as possible to the real ones:

- the battery was placed in the body of the car;
- the battery was additionally covered with a metal protective sheet;
- the interior of the car was additionally fitted with decorative elements.

The results of the tests are presented in Table 2.

Table 2. The total results of the amount of water expended during the extinguishing of the batteries in the car [13]

Battery type / test series	Operation Time [min]	Water flow time [min]	Total water flow [l]	Comments
A1	5.88	2.20	1040	Battery only
A2	36.60	3.53	1673	Battery only
A3	49.67	9.77	4012	Battery + Interior Components
B1	26.52	14.03	6639	Battery only
B2	37.60	21.37	9989	Battery only
B3*	13.88	9.32	4410	Battery + Interior Components

* Suppression times and water flow times influenced by the previous experience of one of the firefighters, who extinguished a fire of the Test B2 battery on the previous day. This firefighter acknowledged that he had gained knowledge on the best and most appropriate way to access the battery below the floor pan during the previous test.

Similarly, with the first stage during the second stage, the value of the thermal radiation was measured at a distance of 1.5 meters and thus amounted to 2.1–3.7 kW/m^2 (during the burning of one battery) and 8.1–11.9 kW/m2 (during the burning of the battery with decor elements).

After the termination of each variant of the extinguishing of storage batteries, water samples for the subsequent analysis for the presence of harmful substances were taken. Samples of water collected during the tests indicate the presence of chloride and fluoride (probably in the form of HF and hydrogen chloride HCl). However, the chloride concentration in the solution was only 2–3 times higher than the normal detection levels, while the fluoride concentration was more than 100 times higher. No other corrosive or toxic compounds were found in the water samples.

Discussion of the results

The research results achieved to date as regards lithium-ion cells of accumulator batteries give us a clear understanding that this technical device, simultaneously with positive effects, may also pose a substantial danger for people.

The obtained research results show that the elementary lithium-ion cell can produce from 6 to 10 kW of energy and a rather large amount of dangerous combustion products, especially HF, POF3, during the combustion, although the latter statement requires further studies. Additionally, the shown research results unequivocally confirm that the amount of energy and hazard gases released by the lithium-ion battery depends directly on the degree of its charge.

Full-scale testing results on the investigation of the tactics of extinguishing electric car batteries revealed some unexpected findings regarding the amount of water necessary to extinguish such a fire. Based on the results of the experiment, the average amount of water needed to extinguish such ignition varies from 2,500 to 6,000 litres, which may exceed the volume of water taken by one fire truck. Thus, an urgent need emerges to improve the extinguishing tactics of firefighting and training personnel.

Due to the continuous development and improvement of technologies, the results presented will differ in respect of new types of batteries [16–18]. Therefore, there will always be a need to conduct additional studies in this direction.

Conclusions

Based on the above research results, it is possible to outline the following topics of work in this direction:
- Conduct a full-scale firefighting test of real consumer electric cars to assess the problems of access to batteries and the complexity of their water consumption levels;
- Carry out a full-scale firefighting test of real consumer electric cars to assess the risk of electric shock to personnel from the electric car battery;
- Carry out full-scale testing of firefighting of real consumer electric cars with batteries of other types, e.g. type 18650;
- Develop alternative versions of fire barrels for the extinguishing of electric car batteries;
- Assess the efficiency of extinguishing the batteries using other extinguishing agents.

It is also very urgent to develop a mathematical model for the heating of a lithium-ion battery that takes into account the geometric shape of the element and its chemical composition. The development of such a mathematical model would later enable the calculations to be made to determine the necessary temperature and heat quantity, without the need to conduct costly experiments or develop a variety of new battery options.

List of acronyms

HOC – Heat of combustion
HRR – Heat release rate
PHRR – Peak heat release rate
SOC – State of charge

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