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Investigation of combustion gases of Li-ion, Ni–Cd and Pbq batteries

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ORIGINAL RESEARCH PAPER

ABSTRACT

Appliances used in everyday life, like smart phones, notebooks; do-it-yourself machineries usually operate with battery instead of power supply. It means comfort to users however; they expose them to different dangers. In the last few years, several fire cases happened in connection with these appliances while charging and usage, which have driven the attention to the dangers of battery technology. Regarding the actuality of the topic, combustion products developing during the burning process of batteries with 1:1 ratio burning experiments were investigated, experiences and results from that are represented in this paper. The aim of the research is to call the attention to the flammability properties of lithium-ion and other batteries, the possible dangers and in case of fire to support the involved personnel.

KEYWORDS

Li-ion, Ni–Cd, Pbq batteries, burning, experiment, combustion product

1. INTRODUCTION

Out of most rechargeable, also known as secondary electrochemical energy accumulators, Li-ion technology became a pioneer, and nowadays it is a widely spread technology. The explanation behind its popularity can be found in the huge advantage of its technology, since this technology ensures the highest energy density, which nowadays reaches, strictly at the level of battery cells, 250 Wh/kg specific value [1]. These days, the so-called second generation Li-ion batteries that include graphite anode and Li-transition metal-oxides or lithium-iron-phosphate cathode are spreading. According to prognoses, in third generation Li-ion batteries, graphite anodes will be changed to silicon (Si), firstly just in a part (graphite/nano silicon mixture), later the anode would be clearly silicon based. The nowadays used Li-ion batteries include cells that are made from liquid-electrolyte [2, 3].

A Li-ion battery can contain significant active electrodes with flammable electrolyte, thus heat can be generated inside the cell in case of extraordinary circumstances, like excessive charging or internal shortcut, that can result in dangerous over-temperature in worst case [4, 5]. Weight loss, temperature and speed of heat release are used for deep reaction analysis of burning behavior. Several researches have been done on the mechanism of thermal overrun of batteries. The researchers came to the conclusions if the battery exceeds a given critical value in temperature reactions take place in a sequence [6, 7]. As an effect of heat, the following reactions happen in a battery: solid electrolyte interphase degradation for the carbon based anode, melting of the separator, the reaction of the negative material and the electrolyte, the degradation of the electrolyte, the reaction of the positive material and the

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electrolyte. These reactions do not take place in this given order, rather a mutual interaction was experienced among them [8, 9].

According to the experiences up to date, flame and heat radiation became the main phenomena among the elements. As soon as one of them gets out of thermic control, the surrounding cells bear strong heat effect and consequently further reactions start off. Continuous burning or explosion, moreover the formation of toxic gases threatens the safety of the whole battery system. That is the reason why the advanced knowledge of burning behavior is necessary to have adequate safety instructions both for lithium-ion and for the further developed other batteries. The dynamic parameters investigated during the burning process of batteries included weight loss, the temperature of surface and flame, also the speed of heat release to characterize the burning behavior of lithium-titanate battery [10]. This can be also the case regarding Li-ion batteries.

It is important to mention, that fire cannot only occur in appliances using battery technology, but also can spread in their environment over to appliances as well. The investigation of recent fire cases show experiences, that the burning phenomena are totally different in case of batteries and their appliances, as in other fire cases. In case of cathodes thermal degradation occurs and since oxygen develops during reaction, it gets uncontrollable during burning. According to fire experiences, at the measured temperature, chemical degradation processes take place in the cells. This results in intense pressure increase and explosion. As a result of metallic burning, extremely high temperature can evolve. Fire experiments with the previously mentioned facts taken into account were prepared and carried out [11, 12].

2. PREPARATION OF EXPERIMENTS

During the preparation of the experiment place, first the emphasis is put on safety, since general knowledge about the burning behavior of batteries is incomplete at this state. Experiments were therefore done in a special device for this purpose. To achieve the proper chimney effect, a 200-liter-capacity metal vessel with 400 × 200 mm dimensions was used, with a hole cut into its lower side. A gas burner was driven throughout this hole, above which a metal beam was built in, on which batteries were placed during the experiments. As heat source propane was used. The beam was placed in the vessel so that the base temperature of the batteries laid on it, was 650 °C. Different battery samples that are represented in Fig. 1, were placed on the sample holder above the gas burner. The configuration of the investigator experimental device is represented in Fig. 2.

Smoke, formed during burning, escaped controlled from the device and its content was examined with certified gas sensors. Eight different type batteries were examined from eight manufacturers; their technical data is represented in Table 1. Batteries were placed on the beam before the ignition. After this, the gas burner was ignited. Afterward the ignition of the gas burner 5 min (300 s) burning time was determined, time was measured with two stopwatches at once. Meanwhile burning, continuous measurements were done about the gas composition with the following devices, these were the followings:

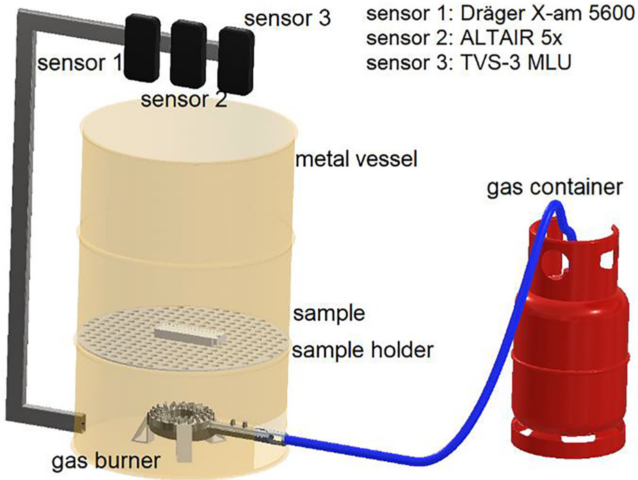

Fig. 2. The experiment setup (*Source*: edited by Authors)

Fig. 1. Different battery types, in the top row from left to right: ASUS BTY-M66, Lenovo VL09c6Y02, Toshiba PA3817U1PRS, Dell M5Y1K, in the second row from left to right: Makita NiCd, Pbq 2.6-12, Sony Ericsson BST-30, Sony 12W29 (*Source*: photos by Authors)

Table 1. Data of batteries used in the experiment and the temperature results experienced during burning

Battery type	ASUS BTY-M66	Lenovo VL09c6Y02	Toshiba PA3817U1PRS	Dell M5Y1K	Makita NiCd	Pbq 2.6-12	Sony Ericsson BST-30	Sony 12W29
Absolute temperature [°C]	620	711	711	671	640	652	488	362
Ignition time [s]	55	60	30	30	20	41	80	80
Burning time [s]	295	216	279	145	252	289	185	149

Source: edited by Authors from measured data

- Dräger X-am 5600 gas detector;
- ALTAIR 5X - multipurpose gas sensor;
- TVS-3 MLU mobile monitoring station;
- Dräger UCF 9000 thermal imaging camera.

Dräger X-am 5600 can measure 5 different substances: CO_2, CH_4, O_2, NO_2 and Hydrogen-Cyanide, (HCN). Altair 5x is suitable for the measurement of CO, CO_2, NH_3, H_2S and Cl_2. TVS-3 MLU type can detect several substances like NO, NO_2, SO_2, CO, H_2S, Cl_2, NH_3, CH, HCl, H_2, H_2CO and HF. In the measurements all of the substances were monitored, where data do not contain any values at the different substances, it means that it could not be detected as it was not present during the fire.

3. ANALYSIS OF THE COLLECTED INFORMATION FROM BURNING

During the experiments three phases of the burning process of the batteries were observed.

1st phase: beginning of overheating

Thermal overrun is due to the overheating of the battery system, in this presented case with the help of the gas burner set-up to 180 °C. In the initial phase, as an effect of intense heat load, the outer plastic shell of the battery melted and after it, burning happened along with flame. At the upper part of the examination device, which is in 1 m distance from the beam, 80–90 °C temperature was measured.

2nd phase: heat accumulation and gas release process

By the beginning of 2nd phase, the internal temperature was increasing rapidly and the outflow of electrolyte in batteries started. The gases detected during the continuous measurement are included in Table 2.

3rd phase: burning and explosion

As the 3rd phase burning process started, the compound of gases indicated maximum value and moreover maximum temperature was reached. In the 2nd and 3rd phases, exothermic reactions took place in more or less adiabatic circumstances. Temperature stagnated due to the inflowing air, but thermal overrun reaction can be uniformly stated to be around 200 °C. Above this temperature, solid electrolyte interphase disintegrates which triggers other exothermal chemical reactions for instance the cell loses stability, swelling, venting and ruptures occur, also all remaining thermal and electrochemical energy can be released into the surroundings.

The speed of self-heating increases, which leads to thermal release (in case the speed of self-heating >10 °C min^{-1}) and it also leads to electrolyte burning. The data about temperature and time changes measured during burning are included in Fig. 3.

The compound of combustion products, which formed during the burning of batteries, were monitored with the above represented gas composition monitoring apparatus. Atmospheric data was measured with an installed weather station, these were the followings:

- Average temperature: 17.1 °C;
- Relative humidity: 69.3%;
- Wind force: 6.13 km h^{-1}, wind direction: in the burning period it changed several times, which was monitored between 53.2 and 353.5 °C taking northern 0 °C as base by TVS-3 weather station.

The Hungarian accepted boundary values regarding air pollutants occurring in air are regulated in [13, 14] legislations. In Fig. 4 the measured values can be observed.

Gas emission measurements of fire experiments represent the fact, that electric devices with batteries in households, release health damaging poisonous materials that exceed the given boundary values. Similar conclusions were drawn by other research works as well [15]. It can be read from the compiled table, from Table 2 that the following substances exceeded the boundary values:

- HCN (hydrogen cyanide);
- CO (carbon-monoxide);
- Cl_2 (chlorine);
- CH_2O (formaldehyde).

4. DESCRIPTION OF TOXIC VAPORS

HCN also known as prussic acid, is colorless in general circumstances, it is an easily evaporating liquid. Its gases are severely poisonous. It is an inorganic chemical material, it compounds unlimitedly with water, alcohol, and ether. Its molecule is strongly polar. In liquid state it is present as $(HCN)_2$ dimer, among hydrogen-cyanide molecules hydrogen bonding can be found. It is a weak acid, in

Table 2. Measured values with gas composition monitoring apparatus, values indicated with "*" sign exceeded the limits, samples from 1 to 8 are in the following order respected: ASUS BTY- M66, Lenovo VL09c6Y02, Toshiba PA3817U1PRS, Dell M5Y1K, Makita NiCd, Pbq 2.6-12, Sony Ericsson BST-30, Sony 12W29

Sample	1	2	3	4	5	6	7	8	Limit (ppm)
Dräger X-am 5600									
CO_2	20*	0	0.12	1.8*	0.12	0.08	0.08	0.36	0.5–1
CH_4	5	0	3	3	0	3	3	3	10–20
O_2	20.9	20.9	20.9	20.9	20.9	20.9	20.9	20.9	19.5–23
NO_2	0	0	0	3	0	1.2	0.9	2.7	5–10
HCN	0	0	1.1	6.2*	1.2	0	1.7	4.8*	1.9–3.8
MSA Altair 5x									
CO	65*	55*	70*	40*	103*	71*	25	110*	30–60
CO_2	0	0.56*	0.18	0.25	0.1	0.33	0.25	0.26	0.5–1
NH_3	0	0	0	0	0	0	0	0	25–50
H_2S	0	0	0	0	0	0	0	0	5–20
Cl_2	0	0.85*	0.43	0.5*	0	0.4	0.75*	0.75*	0.5–1
TVS-3									
NO	4.5	4.1	2.5	1.4	0.8	1.1	0.7	0.1	25–75
NO_2	0	0	0	0	0	0	0	0	5–15
SO_2	0	0	0	0	0.3	0.2	0.1	0	2–6
CO	5.2	1.4	0.9	1.1	1.4	2.3	2.1	5.6	30–60
H_2S	0	0	0	0	0	0	0	0	10–30
Cl_2	0	0	0	0	0	0	0	0	0.5–1.5
NH_3	0	0	0	0	0	0	0	0	20–60
CH	0	0	0	0	0	0	0	0	ARH 20–60%
HCl	10.5*	0.5	0	0.2	0.1	0	0	0	5–15
H_2	0	0	0	0	0	0	0	0	0–8,000
H_2CO	0.5*	0.2*	0.1*	0.6*	0.1*	0	0	0	0.05–1.0
HF	0	0	0.2	0.1	0.1	0	0	0	3–9

values indicated with "*" sign exceeded the limits, samples from 1 to 8 are in the following order respected: ASUS BTY- M66, Lenovo VL09c6Y02, Toshiba PA3817U1PRS, Dell M5Y1K, Makita NiCd, Pbq 2.6-12, Sony Ericsson BST-30, Sony 12W29
Source: edited by Authors from measured data

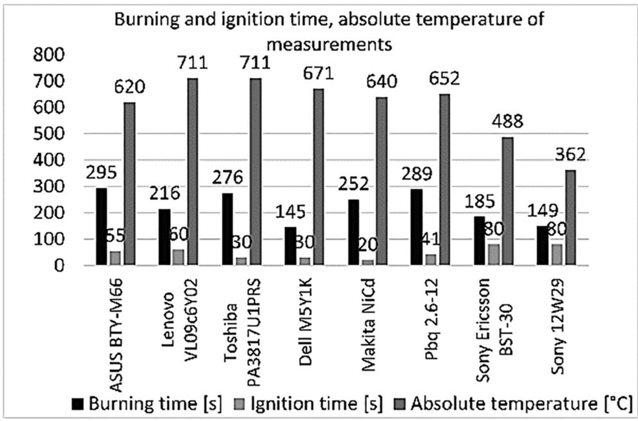

Fig. 3. Data about value changes in the fire (*Source*: edited by Authors from measured data)

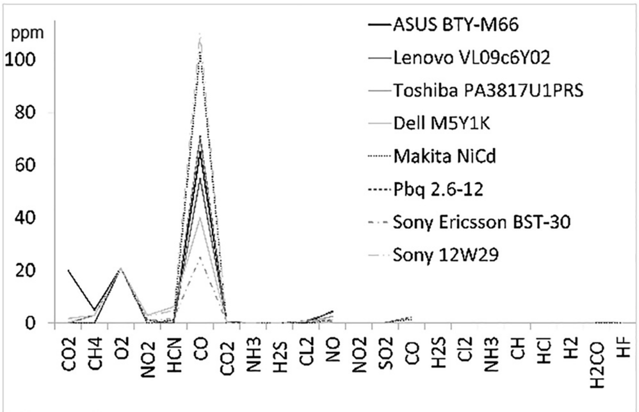

Fig. 4. Diagram about the different measured values by gas detector (*Source*: edited by Authors from measured data)

aqueous solution it dissociates in small extent, during its dissociation cyanide ions (CN−) form. It can be considered as the nitrile of formic acid. CO color- and odorless, it is produced from imperfect burning, during the burning of every carbon-contented solid, liquid or gas stated material. These can be natural gases, derivatives of petroleum, liquefied petroleum gas, coal or even wood. Carbon-monoxide is a severely poisonous gas. Its poisonous effect can be explained so, that it forms a stable complex in the hemoglobin of blood, with this process it prevents the oxygen intake and oxygen supply of the body. Cl was used in World War I as chemical warfare, at standard pressure it is yellowish green in color, it is a strongly poisonous gas, it belongs to halogen group. Chlorine is the second strongest oxidizing agent after fluorine in the halogen group. It is able to oxidize bromides and iodides to elemental state, meanwhile it turns to chloride. During inhalation it is strongly irritating, it develops coughing effect. CH_2O is an organic compound, it is in gasous state at room temperature, colorless, it has inconvenient, sharp odor. It dissolves well in water, its aqueous solution is used for disinfection. Formaldehyde is the intermediate compound forming during the oxidation of methane and other organic compounds; it forms during the burning of different materials. It has severe health damaging effects [13]. Gas emission measurements of fire experiments represent the fact, that electric devices with batteries in households, release health damaging poisonous materials that exceed the given boundary values.

From the experiments that were carried out, it can be reported that commercially available and in the everyday life frequently used Li-ion, Ni–Cd, Pbq batteries emit a significant amount of harmful material during their burning process. It can be stated, that fire can occur due to heat or as a consequence of some mechanical action, however there is no difference between the poisonous combustion residuals that formed during burning.

It was determined that during thermal escape, the high heat of a malfunctioning cell in the battery spreads to the next cells that also caused heat stability. As a result of this a chain reaction started, in which every cell disintegrates. The coverage perished in a short period of time. It is inevitable to mark, that type Dell M5Y1K battery suddenly exploded at the end of the 145 s burning time. There was no experienced relation between the burning time and absolute temperature. Regarding the released poisonous materials, type Sony 12W29 phone battery seemed to be the most dangerous. In case fire occurs in an enclosed area, in which devices assembled with the batteries mentioned above are involved, harmful concentration from combustion residuals that are dangerous to human health can develop.

The value of HCN in case of Dell M5Y1K was the highest, the second highest was at Sony 12W29. HCN is a very dangerous material, it can cause the paralysis of olfactory nerve, but in long-term it leads to death. CO was present in all cases in a high extent. CO has a greater tendency than oxygen to connect to the hemoglobin of blood. Through the bronchi it enters our blood stream and changes oxygen molecules and thus decreases the blood oxygen level.

Cl_2 usually forms during the combustion process of plastic materials, the so-called Polyvinyl Chlorides (PVC). Consequently, hydrochloric acid forms in the air during combustion. If wet human tissue (eyes, upper respiratory tract) gets into contact with Cl_2, it forms hydrochloric acid with the water content of it that irritates the mucous and also can cause caustic harms on that area. Only a small amount of this inhaled gas can cause immediately burning feelings in the nose or in the throat and it can trigger voluntary coughing. It develops a burning, stabbing pain in the eyes and itching skin. CH_2O was detected higher than the boundary value. This substance severely irritates the eyes and skin. Gas severely irritates the respiratory tracts, if high extent is inhaled, it can cause pulmonary edema. In long-term, it triggers skin sensibility and chronic inflammation of upper respiratory tract. It is carcinogenic [15].

From the conducted experiments, it can be reported that commercially available and in the everyday life frequently used Li-ion, Ni–Cd, Pbq batteries emit a significant amount of harmful material during their burning process. It can be stated, that fire can occur due to direct heat or some mechanical cause, however there were always some kind of poisonous combustion residuals present that formed during burning.

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5. CONCLUSION

The results of the experiments about Li-ion, Ni–Cd and Pbq batteries called the attention to the risk of the spreading technology of which users most of the time are not aware. In case fire occurs in an enclosed area, in which devices assembled with the batteries mentioned above are involved, harmful concentration from combustion residuals that are dangerous to human health can develop. During the experiments and measurements, it was enabled to reveal the harmful combustion residuals formed during the burning of different batteries, whose amount exceeded even in open area the boundary values given in the applicable legislation. It is remarkable that the volume of the released gases formed in atmosphere, was not possible to be measured in open space, but the measured values regarding the different residuals are very high even in this case, considering them to be harmful to human health. Further experiments are necessary to be carried out. The open space burning represented in the article should be extended to enclosed space experiment as well.

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