Review

Large-Scale Li-Ion Battery Research and Application in Mining Industry

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Abstract: The lithium-ion battery (LIB) has the advantages of high energy density, low self-discharge rate, long cycle life, fast charging rate and low maintenance costs. It is one of the most widely used chemical energy storage devices at present. However, the safety of LIB is the main factor that restricts its commercial scalable application, specifically in hazardous environments such as underground coal mines. When a LIB is operating under mechanical and electrical abuse such as extrusion, impact, overcharge and overheating, it will trigger thermal runaway and subsequently cause fire or even an explosion. According to the relevant requirements in IEC60079, the explosion-proof protection of LIB can be adapted to the working environment of high dust and explosive gas environments such as in the mining face of coal production. This paper presents an overview of the LIB-relevant technology, thermal runaway, safety and applications in the general mining industry with implications to establish a theoretical and technical basis for the application of high-capacity LIBs in the industry. These then promote intelligent, safe and efficient production not only for the coal mine industry but also for non-coal applications.

Keywords: lithium-ion battery; thermal runaway; battery safety; large-scale energy storage; explosion-proof electric vehicles; mining industry

1. Introduction

The lithium metal battery was first proposed by Gilbert n. Lewis in 1912. In 1970, M.S. Whittingham proposed and began to study LIBs and patented the Li//TiS$_2$ batteries in 1974. In 1991, the first commercial LIB came out [1]. After more than 100 years of development, the LIB has gradually become one of the most widely used chemical energy storage methods because of its high energy density, low self-discharge rate, long cycle life, fast charging rate and low maintenance costs [2].

LIBs are mainly used in 3C products, electric vehicles (EVs), communication base stations, energy storage renewable integration and other fields, especially in the field of heavy traction. Many countries around the world regard the development of EVs as an important strategic measure to deal with climate change and optimize the energy structure. The scale of the EV market increases year by year, exceeding 1 million in 2017 and 2 million in 2018. In 2020, as the global automobile market was shrinking, the EV market grew against the trend, with sales increasing by 41.6% year-on-year to 3.07 million vehicles, and a penetration rate reaching 4%. In the mining industry, 30–50% of the total mining energy usage is related to diesel used by the major mining vehicles that have a number of
undesirable characteristics, which will likely disappear from the domestic market within the next few decades. EVs injected new energy into the world’s economic growth. EV power batteries are mainly composed of ternary lithium battery (NCM) and lithium iron phosphate (LFP), accounting for 62.5% and 39.2%, respectively [3], and the proportion of LFP batteries is growing rapidly, mainly because LFP batteries have a large thermal stability range and stable discharge rate, which can ensure no explosion in malignant traffic accidents. Based on the technical requirements for the safety of LIBs for mining (Trial) issued and implemented by the Chinese National Center for safety standards in 2012, it is required that only LFP batteries are allowed to be used for all underground LIB power supplies in coal mines, and the battery enclosure needs to be an explosion-proof design [4,5].

In recent years, with the wide use of EVs, although mining explosion-proof EVs have also been preliminarily applied, the traditional explosion-proof diesel vehicles still dominate the market. The diesel-powered vehicles, among other disadvantages such as high exhaust emission, high noise, high failure rate, high operation cost and low efficiency, also cause considerable detrimental health effects to the mining workers, particularly in confined areas such as an underground coal mine that has limited ventilation [6,7]. The mining explosion-proof EVs can effectively avoid the shortcomings of explosion-proof diesel trucks, improve the underground working environment and realize the efficient utilization of mining vehicles [8,9].

Further applying and popularizing explosion-proof EVs requires the following challenges to be solved urgently: First, the restrictions by industry standards. At present, only LFP batteries are allowed to be used, and the maximum permissible capacity of a single battery is 100 Ah, resulting in a short mileage range of mining explosion-proof EVs with an average travel distance of only 80 km for a typical machine, which cannot meet the needs of multiple coal seams, multiple panels and the long travel distance of large production mines. Second, the long charging time, with an average of up to 4 h for every machine, and the strict national mine safety regulations for charging requirements underground have considerably restricted the mass adoption of mining EVs. Third, the low temperature in certain coal mines presents various challenges and complications in operating the lithium-battery-powered machine and subsequently reduces the likeliness of adopting the technology. Last but not least, the risk and consequences of thermal runaway of LIBs working in underground coal mines, especially in a concentrated gas environment, are not fully investigated. At present, to the best of the authors’ knowledge, there are no effective countermeasures and solutions.

This paper presents an overview of LIB technology and its safety implications for the application in the mining industry. In particular, the contents deeply focused on the analysis of the LIB thermal runaway mechanism and prevention methods for the anticipation of establishing a theoretical and technical basis for the application of high-capacity LIBs and subsequently promote the intelligent, safe and efficient production in the coal mine industry.

2. LIB Cathode Material

In the last decade, the LIB has been rapidly adopted in most of the 3C products and EV market due to its high energy density, long cycle life, fast charging rate, wide operation temperature range, no memory effect and lack of pollution to the environment. The chemistries are mainly divided into four types.

2.1. Lithium Cobalt Oxide (LCO)

The chemical formula of the LCO battery is LiCoO$_2$, and it is a layered inorganic compound. Compared with other types of LIBs, LCO has the highest theoretical energy density and volume specific energy [10]. In addition, the LCO battery also has the advantages of simple fabrication processes, a stable working voltage, good cycle stability and high compaction density [11]. As the market demand has grown, the research on the LCO battery has been continuously improved with working voltage increases from 4.2 V to
4.45 V. The specific capacity of LCO in production has reached 185 mAh/g, and is rapidly moving towards its theoretically specific capacity of 274 mAh/g [12]. The main application field of LCO is 3C electronic products.

The reactions of LCO electrodes are as follows:

During the charging process, Li-ion is detached:

\[ \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \]

During the discharging process: Li-ion is embedded:

\[ \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2 \]

LCO has a spinel structure and a layered structure. The layered structure has the best chemical properties. Li ions between CoO layers are continuously detached and embedded during the charge-and-discharge process, and LCO can keep the layered structure stable without collapse, as shown in Figure 1 [13,14]. However, the capacity of the LCO battery will gradually decrease during the charge-and-discharge cycle, mainly due to the continuous expansion and contraction of the lithium cobaltate crystal structure during the charge-and-discharge process, resulting in crystal defects [15–17]. The crystal structure will also be changed, resulting in a grain fracture and structure collapse [18]. The cathode material decreases, the internal resistance increases, and the specific capacity decreases. Kazuhiro Kawashima et al. [19] show that the quality of the cathode thin films (phase purity, crystallinity, and orientation) is essential for thin-film battery research.

![Figure 1. Crystalline structure of layered LiCoO₂][13].

![Figure 2. Crystalline structure of spinel LiMn₂O₄][13].
2.2. Lithium Manganate Oxide (LMO)

The cathode chemical formula of the LMO battery is $\text{LiMn}_2\text{O}_4$, which has a cubic spinel crystal structure, as shown in Figure 2 [13]. One cell contains 56 atoms (8 lithium atoms, 16 manganese atoms and 32 oxygen atoms). Lithium ions (green) can be freely detached and embedded in the lattice.

The reactions of LMO electrodes are as follows:

During the charging process, Li-ion is detached:

$$\text{LiMn}_2\text{O}_4 \rightarrow \text{Li}_x\text{Mn}_2\text{O}_4 + (1 - x)\text{Li}^+ + (1 - x)e^-$$

During the discharging process, Li-ion is embedded:

$$\text{Li}_x\text{Mn}_2\text{O}_4 + (1 - x)\text{Li}^+ + (1 - x)e^- \rightarrow \text{LiMn}_2\text{O}_4$$

The electrochemical reaction of LMO occurs between 3.0 and 4.5 v, and its theoretical specific capacity is 148 mAh/g. The LMO battery has the advantages of a benign environmental effect, abundant reserves and excellent electrochemical performance [20]. However, in practical applications, the LMO battery has fast capacity attenuation, low specific capacity, low conductivity, low ion diffusion efficiency and large structural changes after the charge-and-discharge process, resulting in the existing materials not being able to meet the current requirements of energy storage, traction applications and cycle life [21]. Wujie Dong et al. constructed a similar 2–3 nm artificial solid electrolyte interphase (SEI) layer, which satisfies the expectations of aqueous lithium-ion batteries toward high energy density, durability, safety, low cost and fast charge/discharge capability [22].

2.3. Lithium Iron Phosphate (LFP)

The cathode chemical formula of the LFP battery is $\text{LiFePO}_4$, which has a regular olivine crystal structure [23], as shown in Figure 3. There are four LFP units in each cell. The oxygen atoms are approximately hexagonally stacked. Lithium ions have two-dimensional mobility and can be freely detached and embedded during the charge-and-discharge process. The $\text{PO}_4^{3-}$-polymer tetrahedron has high stability. LFP has a long platform of the charge–discharge curve and is safer at high temperatures, which is also the reason the LFP battery has the highest safety level among lithium batteries.

The reactions of LFP electrodes are as follows:

During the charging process, Li-ion is detached:

$$\text{LiFePO}_4 - x\text{Li}^+ - xe^- \rightarrow x\text{FePO}_4 + (1 - x)\text{LiFePO}_4$$

During the discharging process: Li-ion is embedded:

$$\text{FePO}_4 + x\text{Li}^+ + xe^- \rightarrow x\text{LiFePO}_4 + (1 - x)\text{LiFePO}_4$$

Figure 3. Crystal structure of LFP cathode [23].
The theoretical electrochemical specific capacity of LFP cathode material is 170 mAh/g. The potential of the lithium metal electrode is approximately 3.45 V, and the theoretical energy density is 550 wh/kg. However, due to the low conductivity of LFP, only 0.6 mol lithium ion can be used for the intercalation and deintercalation cycle at room temperature, and the actual discharge capacity can only reach 113 mAh/g [24]. LFP has good cycle performance. When a lithium ion is deintercalated, the volume is reduced by 6.81% [25], which counteracts the volume change of the carbon anode in the process of discharging, and this greatly increases the cycle life of the LFP battery.

LFP is widely used in EV power battery and energy storage systems because of its high specific energy, stable charging and discharging platform, high safety, long cycle life and moderate cost [26]. Xiao-Guang Yang et al. demonstrate a thermally modulated LFP battery to offer an adequate cruise range per charge that is extendable by 10 min recharge in all climates [27]. In addition, because of LFP’s excellent safety performance, it is widely used in auxiliary transportation vehicles in underground coal mines.

2.4. Lithium Nickel Manganese Cobalt Oxides (NCM)

The cathode material of NCM is generally composed of three chemical elements: Nickel, cobalt and manganese. The chemical formula is LiNi\(_x\)Co\(_y\)Mn\(_z\)O\(_2\), which maintains an \(\alpha\)-NaFeO\(_2\) layered structure [28], transition elements and lithium elements in each layer, as shown in Figure 4. The crystal structure can be regarded as the stacking of the transition metal layer–oxygen layer–lithium layer–oxygen layer [29].

![Figure 4. Crystal structure of NCM cathode. The gray, blue and purple spheres represent Ni, Co and Mn atoms in the transmission metal (TM) layer, respectively, and the red sphere represents O atoms [28].](image)

The typical composition ratio of nickel cobalt manganese in NCM material is 111, 523 and 811, and the numbers correspond to the content of nickel, cobalt and manganese, respectively. With the increase in the proportion of nickel, the specific energy of the NCM battery increases, accordingly; with the increase in the proportion of cobalt, the battery performance is more stable; with the increase in the proportion of manganese, the output voltage of the battery increases accordingly [30–33]. NCM combines the advantages of nickel, cobalt and manganese, so it has a high comprehensive performance, and the theoretical capacity can reach 278 mAh/g.

Nickel cobalt aluminum (NCA) is a cathode material developed simultaneously with NCM. Its structure is similar to the NCM \(\alpha\)-NaFeO\(_2\) layered structure. Because there is no manganese element, the working voltage of NCA is slightly lower than that of NCM. When the ratio of nickel, cobalt and aluminum is 0.8:0.15:0.05, it has the best electrochemical performance [34]. Compared with NCM, NCA only occupies a small market share. Changting Chu et al. studied large-sized nickel–cobalt–manganese ternary...
composite oxide agglomerate microspheres, which reduced the specific surface area of the material, resulting in fewer undesirable interfacial side reactions [35].

NCM has a high specific energy, a long cycle life, stable discharge and good performance at low temperatures, which has accounted for 67.37% of lithium batteries in electric vehicles. However, due to the higher safety risk as compared with the LFP battery, NCM could cause a cascading effect after single-battery thermal runaway, resulting in fire and the explosion of the battery pack. At present, it is not permitted to be used in underground coal mines.

3. LIB Thermal Runaway

3.1. Thermal Runaway Mechanism

Thermal runaway refers to the phenomenon of overheating caused by an exothermic reaction in the battery due to internal or external factors. The probability of fire and explosion after battery thermal runaway is very low, at approximately one in ten million to one in a million. However, the safety of lithium batteries is still a common concern. Therefore, many battery manufacturers recall lithium batteries with problems in the production process [36]. EV power battery accidents are mainly characterized by smoke, combustion and explosion caused by thermal runaway.

A large number of researchers have conducted extensive and in-depth research on the thermal runaway mechanism of LIB. The research shows that when the thermal runaway of LIBs occurs, it can be divided into the following stages according to the temperature distribution, from low to high: The decomposition of the SEI layer, the reaction between the anode and electrolyte (SEI film regeneration), separator meltdown, decomposition of the cathode, decomposition of the electrolyte, the reaction between the anode and binder and burning of the electrolyte [37–39], as shown in Figure 5. Each stage of the thermal runaway reaction does not occur in order, as shown in the figure. With the increase in temperature and the intensification of the reaction, some stages may occur simultaneously.

![Diagram of LIB thermal runaway](image)

**Figure 5.** Exothermic reaction in different stages of LIB thermal runaway [39].
3.1.1. Decomposition of SEI Layer

The first stage is the decomposition of the anode SEI layer due to overheating or physical penetration. The SEI layer is mainly composed of stable substances such as LiF, Li₂CO₃, etc., and metastable substances such as RCO₂, (CH₂OCO₂Li)₂, ROLi, etc. [40-42]. It is generally believed that the reaction begins at 70 °C [43]. As the temperature rises close to 90 °C, the decomposition of the SEI layer begins to accelerate, and the heat released by decomposition causes lithium to react with the organic electrolyte and release flammable hydrocarbon gas. The reactions are as follows:

\[
\begin{align*}
(\text{CH}_2\text{OCO}_2\text{Li})_2 & \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + 0.5\text{O}_2 \\
2\text{Li} + (\text{CH}_2\text{OCO}_2\text{Li})_2 & \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4
\end{align*}
\]

Taeho Yoon et al. [44] studied the thermal decomposition process of SEI of LIB with a Thermal Gravimetric Analyzer (TGA) and pointed out that the SEI layer will undergo a decomposition reaction between 50 °C and 300 °C to produce CO₂ and C₂H₄. Najmus Saqib et al. [45] used infrared thermometry to measure the electrolyte temperature during the heating of an LCO battery. It was found that SEI and electrolyte decomposition occurred when the temperature was higher than 70 °C. The working spectrum collected during the heating process showed that with the occurrence of thermal degradation, the ethylene carbonate (EC) ring was opened, resulting in permanent capacity loss of the battery. Maleki [46] and Ryou [47] observed the SEI layer decomposition process has an exothermic peak at 100 °C. Zhang [48] observed that there was an exothermic peak in the SEI layer at 130 °C. It can be seen that the decomposition of the SEI layer can generally be considered to occur at 60–130 °C, and its accurate decomposition temperature is related to battery chemistry, SEI thickness and SOC state [39].

3.1.2. Reaction between Anode and Electrolyte (SEI Film Regeneration)

The decomposition of the SEI layer causes the lithium intercalation in the carbon anode to be exposed to the electrolyte, which promotes the reaction between the electrolyte and the negative lithium intercalation, so as to regenerate the SEI layer and generate hydrocarbon and alkane gases. The reactions are as follows [36]:

\[
\begin{align*}
2\text{Li} + \text{C}_3\text{H}_4\text{O}_3(\text{EC}) & \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 \\
2\text{Li} + \text{C}_4\text{H}_6\text{O}_3(\text{PC}) & \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_3\text{H}_6 \\
2\text{Li} + \text{C}_4\text{H}_6\text{O}_3(\text{DMC}) & \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_6
\end{align*}
\]

These reactions usually occur at 100 °C, and the gas released by the reaction will increase the internal pressure of the battery. Although the internal high temperature of the battery reaches the ignition point of the gas, it will not cause gas combustion due to the lack of oxygen.

3.1.3. Separator Melt Down

The common LIB separators are polyolefin membranes made from polyethylene (PE) and polypropylene (PP). The main problem of polyolefin membranes is poor thermal stability [49]. When the temperature of the battery rises during operation, the separator material must not shrink significantly and must not wrinkle. E. P. Roth et al. [50] suggested that the melting points of PP and PE are 155 °C and 130 °C, respectively, as shown in Figure 6. When these temperatures are reached, the separator melts, and the internal short circuit of the battery takes place and results in thermal runaway degradation.

There are three main methods to reduce the thermal runaway caused by separator melting. The first method is to close the channel of lithium ion passing through the separator using a multi-layer structure [51], so as to prevent an external short circuit, accidental overcharge or other further aggravation of battery temperature rise. However, at a high current density, this closing mechanism has little protection against a short circuit or rapid overcharge in the battery. When the internal temperature of the battery rises sharply, it will lead to the melting of the separator material. The second method is to mix the polyolefin membrane with inorganic nano materials [52,53]. The additional ceramic
material coating with an ultra-high melting point and good mechanical properties will significantly improve the thermal stability and dimensional stability of the membrane material. In addition, the thermal conductivity and electrolyte wettability of the membrane layer will also increase, which can significantly improve the safety of the battery. The third method is to modify the existing polyolefin separator structure and design functional separator material to eliminate the lithium dendrites generated by overheating [54].

Figure 6. Melting temperature of PE/PP separator material [50].

3.1.4. Decomposition of Cathode

A short circuit occurs inside the battery after the separator has had a meltdown, which will generate a large amount of heat, resulting in an exponential increase in the temperature rise rate of the battery. There are also electrolyte decomposition and a binder reaction alongside the decomposition of the cathode. These reactions are generally considered to accelerate the material reaction in the battery when the internal temperature of the battery is higher than 155 °C after the separator melts and will happen simultaneously. The heat generation rates of various cathode materials are shown in Figure 7 [55].

Figure 7. Comparison of thermal runaway reaction of different cathode materials [55]: (a) Comparison of reaction degrees; (b) comparison of heat generation rates.

According to the measured values in Figure 7, it can be found that the safety of LFP is better than that of LCO, LMO and NCM in terms of the safety of cathode materials. The specific distribution is LFP > LMO > NCM > NCA > LCO. The decomposition of the cathode material will release oxygen. After mixing the hydrocarbon and alkane gas generated by the reaction of the anode electrolyte, a combustion reaction will occur in
the battery, resulting in breaking through the battery safety valve to form a jet fire. The reactions of various cathode materials during decomposition are summarized in Table 1.

<table>
<thead>
<tr>
<th>Cathode Materials</th>
<th>Decomposition Equation</th>
<th>Decomposition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP</td>
<td>2Li$_0$FePO$_4$ → Fe$_2$P$_2$O$_7$ + 0.5O$_2$</td>
<td>190–285 °C</td>
</tr>
<tr>
<td>LMO</td>
<td>Li$_0.2$Mn$_2$O$_4$ → $\frac{1}{2}$LiMn$_2$O$_4$ + $\frac{1}{2}$Mn$_2$O$_4$ 3Mn$_2$O$_4$ → 2Mn$_3$O$_4$ + 2O$_2$ LiMn$_2$O$_4$ → 2LiMn$_2$O$_4$ + $\frac{3}{2}$O$_2$ LiMn$_2$O$_4$ → LiMnO$_2$ + $\frac{1}{2}$Mn$_3$O$_4$ + $\frac{1}{2}$O$_2$ Mn$_2$O$_4$ → Mn$_3$O$_5$ + $\frac{1}{2}$O$_2$</td>
<td>150–400 °C</td>
</tr>
<tr>
<td>NCA</td>
<td>Li$<em>x$(NiCoMn)$</em>{1-x}$O$<em>2$ → $\frac{1+x}{2}$[Li$</em>{\frac{1}{2}}$(NiCoMn)$<em>{\frac{1}{2}}$]O$</em>{1+x}$ + $\frac{1-2x}{2}$O$<em>2$ Li$<em>x$(NiCoMn)$</em>{1-x}$O$</em>{1+x}$ → Li$<em>x$(NiCoMn)$</em>{1-x}$O$_{1+x}$ + $\frac{1-2x}{2}$O$_2$</td>
<td>160–200 °C</td>
</tr>
<tr>
<td>NCM</td>
<td>Li$<em>{0.35}$(NiCoMn)$</em>{0.75}$O$<em>2$ → Li$</em>{0.35}$(NiCoMn)$_{0.75}$O$_2$ + $\frac{1}{2}$O$_2$</td>
<td>175–199 °C</td>
</tr>
<tr>
<td>LCO</td>
<td>Li$_x$CoO$_2$ → xLiCoO$_2$ + $\frac{1-x}{2}$Co$_3$O$_4$ + $\frac{1}{2}$O$_2$</td>
<td>220–500 °C</td>
</tr>
</tbody>
</table>

3.1.5. Decomposition of Electrolyte Solution

The electrolyte is essential in LIB. Its basic function is to act as the transfer medium between the cathode and anode of LIB. Electrolytes can be solid or liquid [49]. The electrolyte is usually an organic solution with LiPF$_6$, and the solvent is mainly a combination of linear and cyclic alkyl carbonate, mainly including Ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and methyl ethyl carbonate (EMC) [59]. Although the carbonate solvent is relatively stable, the addition of the LiPF$_6$ solution will make the organic electrolyte highly volatile and flammable. When battery thermal runaway occurs, the electrolyte will react with the active electrode material to release a large amount of gas and heat. The decomposition reaction of LiPF$_6$ is [60]:

$$\text{LiPF}_6 \rightarrow \text{LiF} \downarrow + \text{PF}_5 \uparrow$$

PF5 is a strong acid, which can lead to the decomposition of EC cyclic carbonate and react with the trace amounts of water in the electrolyte to form HF, which will also lead to further decomposition of the solvent and the generation of gas.

The decomposition of the solvent produces many different kinds of gases, including CO$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_5$F and other products, as shown in the following equation [58]:

$$\text{C}_2\text{H}_5\text{OCOOC}_2\text{H}_5 + \text{PF}_5 \rightarrow \text{C}_2\text{H}_3\text{OCOOPF}_4 + \text{HF} + \text{C}_2\text{H}_4$$

$$\text{C}_2\text{H}_4 + \text{HF} \rightarrow \text{C}_2\text{H}_5\text{F}$$

$$\text{C}_2\text{H}_5\text{OCOOPF}_4 \rightarrow \text{PF}_3\text{O} + \text{CO}_2 + \text{C}_2\text{H}_2 + \text{HF}$$

$$\text{C}_2\text{H}_3\text{OCOOPF}_4 \rightarrow \text{PF}_3\text{O} + \text{CO}_2 + \text{C}_2\text{H}_5\text{F}$$

$$\text{C}_2\text{H}_5\text{OCOOPF}_4 + \text{HF} \rightarrow \text{PF}_3\text{OH} + \text{CO}_2 + \text{C}_2\text{H}_5\text{F}$$

A large amount of gas generated by the above reaction rapidly increases the internal pressure of the battery, and finally opens the battery safety valve. The released gas reacts with O$_2$ generated by the positive active material, which produces smoke and forms a jet fire. The decomposition of different solvents with temperature is shown in Table 2 [59].
Table 2. Boiling point of electrolyte.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>517 K</td>
</tr>
<tr>
<td>DEC</td>
<td>400 K</td>
</tr>
<tr>
<td>DMC</td>
<td>364 K</td>
</tr>
<tr>
<td>EMC</td>
<td>380 K</td>
</tr>
</tbody>
</table>

3.1.6. The Reaction between Anode and Binder

A. Du Pasquier et al. [61] found through experiments that when the internal temperature of the battery is greater than 260 °C, the anode reacts with the polyvinylidene fluoride (PVDF) binder and LixC₆. The PVDF binder can enhance the reaction rate of LCO. When the internal temperature of the battery increases, the formation rate of Co₃O₄ and the dissolution rate of Co ions will accelerate at the interface between the active material and the binder [58]. E. Markevich et al. [62] also found that the presence of the PVDF binder increased the reactivity of LCO and believed that hydrogen bonds were formed after PVDF reaction, so the local concentration of acidic substances near LCO particles increased, which also accelerated the decomposition of LCO. Biensan P [63] found that the initial reaction temperature of the anode with the binder was 240 °C and the peak reaction rate was 290 °C, while Maleki H [46] found that the initial reaction temperature was lower than 200 °C and the reaction peak was 287 °C. The reactions between the anode and PVDF binder are as follows:

\[
-CH₂ − CF₂ → -CH = CF − + HF \\
-CH₂ − CF₂ + Li → LiF + -CH = CF − + 0.5H₂
\]

3.1.7. The Burning of Electrolyte and Gas Release

The burning of the electrolyte will be accompanied by the release of a large amount of gas. Many researchers have performed many experiments to collect the gas released by thermal runaway. SEE K W et al. [64] heated seven different types of prismatic LFP batteries with a constant power of 640 W until the surface temperature of the battery and the internal pressure of the container suddenly increased and the battery voltage dropped sharply. Then, the gas was collected by the gas collection bag on the sealing cover of the device, and the gas composition was analyzed by a gas chromatography device. The experimental equipment is shown in Figure 8, and the released gas components are shown in Table 3. Hydrogen accounts for the highest proportion, accounting for more than 50% of the released gas, followed by CO₂, accounting for 20%, and hydrocarbon and alkane gases are mainly methane, accounting for 10%.

![Figure 8. Thermal runaway collection device for prismatic LFP battery [64].](image-url)
Y. Fernandes [65] overcharged the 100% SOC commercial LIB, placed the battery in a closed container, extracted the internal gas during and at the end of the experiment, and then analyzed and identified the gas composition by gas chromatography, mass spectrometry and FTIR spectroscopy. He found that the gas release of thermal runaway mainly has three stages: The first stage releases DMC, EMC, CH₄, CO and CO₂. At this stage, less gas is released, mainly filling the internal volume of the battery, so it mainly leads to an increase in the internal pressure of the battery. In the second stage, the battery shell is cracked, and the battery surface temperature is higher than 110 °C, and a large number of new gases such as CH₃OCH₃, CH₃OCHO and C₂H₄ are generated. In the third stage, the battery begins to cool down, the generation of CH₃OCH₃, CH₃OCHO, CH₄, CO and CO₂ decreases and the generation of HF increases. The gas composition of the thermal runaway is shown in Figure 9.

### Table 3. Composition of thermal runaway release gas [64].

<table>
<thead>
<tr>
<th>Gas Composition</th>
<th>M1-72 Ah V₃, %</th>
<th>M1-100 Ah V₃, %</th>
<th>M1-180 Ah V₃, %</th>
<th>M2-90 Ah V₃, %</th>
<th>M2-280 Ah V₃, %</th>
<th>M3-120 Ah V₃, %</th>
<th>M3-202 Ah V₃, %</th>
</tr>
</thead>
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<td>CO₂</td>
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<td>7.99</td>
<td>11.95</td>
<td>5.69</td>
<td>14.18</td>
<td>6.69</td>
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<tr>
<td>C₂H₄</td>
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<td>4.18</td>
<td>5.88</td>
<td>0.85</td>
<td>2.30</td>
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<tr>
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<td>0.65</td>
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<td>0.56</td>
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<tr>
<td>C₃H₈</td>
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<td>0.37</td>
<td>N.A</td>
<td>0.20</td>
<td>0.1</td>
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<td>5.74</td>
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<tr>
<td>O₂</td>
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<td>0.45</td>
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<td>11.04</td>
<td>3.36</td>
<td>0.58</td>
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<tr>
<td>N₂</td>
<td>67.91</td>
<td>61.64</td>
<td>45.23</td>
<td>75.52</td>
<td>36.79</td>
<td>72.14</td>
<td>48.06</td>
</tr>
<tr>
<td>CH₄</td>
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<td>2.12</td>
<td>3.35</td>
<td>0.26</td>
<td>2.56</td>
<td>1.02</td>
<td>2.64</td>
</tr>
<tr>
<td>CO</td>
<td>2.89</td>
<td>2.66</td>
<td>4.04</td>
<td>0.73</td>
<td>5.33</td>
<td>1.34</td>
<td>3.7</td>
</tr>
</tbody>
</table>

**Figure 9.** Thermal runaway gas composition of LIB [65].

### 3.2. Thermal Runaway Inducements

There are three main factors leading to battery thermal runaway: Mechanical abuse (penetration, impact, collision, vibration), electrical abuse (overcharge, short circuit) and thermal abuse (overheating) [66]. Mechanical abuse is caused by the distortion of the battery due to collision and squeezing, resulting in the rupture of the internal separator of the battery and the internal short circuit, which will generate a large amount of heat and trigger thermal runaway. Electric abuse is caused by the external short circuit, the fast charging and discharging speed and overcharge of the battery. Eventually, the internal temperature of the battery rises and the separator melts, resulting in an internal short
circuit and a large amount of heat releasing. Thermal abuse is caused when the internal temperature rise rate of the battery is higher than the heat dissipation rate, so that heat accumulates in the battery, which leads to the separator melting and an internal short circuit, so as to release more heat and further aggravate the thermal runaway reaction. It can be seen that the three inducements of thermal runaway are inter-connected with each other, and the common factor is the internal short circuit of the battery. Figure 10 shows the relationship between the three causes of thermal runaway [67].

**Figure 10.** Main factors and internal relationship of thermal runaway inducements [67].

### 3.2.1. Mechanical Abuse

Mechanical abuse refers to the change of the internal structure of the battery caused by an external force, which includes penetration, impact, collision, vibration, etc. Different from electrical abuse and thermal abuse, thermal runaway caused by mechanical abuse is generally a violent reaction that occurs instantaneously. Among the different forms of mechanical abuse, the most serious is nail penetration, which directly leads to the penetration of the internal separator of the battery, resulting in an internal short circuit.

Researchers have conducted in-depth research on the dynamic mechanics of LIB materials. Wei Jen Lai et al. [68] conducted tensile, compression and impact tests on the test piece of a single LIB. Elham sahraei et al. [69] performed CT scanning on cylindrical LIBs and soft-packed LIBs to detect the tension of electrode separator bonding. Elham sahraei et al. [70] established the micromechanical model and carried out the failure sequence of multi-layer and multi-material batteries in combination with experiments. The mechanical properties of different LIB separators were studied in the literature [71–73].

Based on the research on the mechanical properties of battery materials and separators, Takumi Yamanaka et al. [74] developed a new electro-chemical-thermal coupling calculation model. In this model, the needling speed and thermal decomposition reaction are considered, and the “combustion volume” is defined to evaluate the burning risk. The results show that when the nail penetration speed is 10 times slower than that under standard conditions, the risk of battery burning increases. Donal P. Finegan et al. [75] found through experiments that the temperature at the needle part of the battery placed vertically is the highest, but the temperature propagation rate is slower than the battery under nail penetration placed horizontally. Figure 11 shows the heat conduction time after
nail penetration. Shan Huang et al. [76] conducted a slow nail penetration experiment on the 3 Ah soft pack battery, detected that multiple peak temperatures appeared 100 s before the thermal runaway and found that these peak temperatures decreased rapidly after they were higher than the safety limit. They believe that the decrease in the internal short-circuit current is the reason for the decrease in temperature, which is due to the tear of the separator caused by nail penetration, resulting in the increase in contact resistance.

**Figure 11.** Thermal runaway propagation after nail penetration for battery placed horizontally and vertically [75].

Hsin Wang et al. [77] studied the mechanical response of a single cell with a thickness of 6.5 cm and a three-cell stack under compressive load. The indentation depth of the ball with a diameter of 1 inch is limited to 0.245 inches, which is equivalent to 90% of the cell thickness. Through experiments, it is found that the short-circuit probability caused by mechanical indentation increases with the thinning of the separator. Ilya Avdeev et al. [78] carried out mechanical modeling of the cylindrical LIB. The homogenization model accurately captured the mechanical response of battery collision. The team verified the effectiveness of the model through dynamic and static tests and verified the feasibility of single-battery collision by finite element analysis. Wang Wenwei [79] carried out plane, cylindrical and spherical punch loading on the cylindrical battery, recorded the deformation degree of the battery under different SOCs and verified the correlation between the parameters of the battery-equivalent mechanical model and SOC.

### 3.2.2. Electrical Abuse

Electrical abuse is generally caused by overcharge. Excessive lithium intercalation of the anode leads to the formation of lithium crystal branches between the anode and the separator, which pierces the separator, resulting in an internal short circuit, while excessive lithium removal leads to the collapse of the positive crystal structure. An external short
circuit will also cause thermal runaway. When the heat production of the battery is greater than the heat release and the temperature reaches the separator melting temperature, it will lead to a short circuit in the battery.

Mao-sung Wu [80] tested the internal short circuit and external short circuit of 750 mAh lithium batteries with three different separators. The internal short circuit triggered by the nail penetration experiment is more violent than the battery thermal runaway measured by an external short circuit. The maximum temperature of an internal short circuit is 350 °C, while it is 100 °C for an external short circuit. It can be seen that the external short circuit is safer than the internal short circuit. This is because the contact area of the electrode short circuit during an external short circuit is much larger than that of an internal short circuit, and the short circuit current is small.

Junqi Li et al. [81] proposed an impedance-based method to describe the heat released by the battery under an overcharge. It is concluded that the thermal runaway after battery overcharge can be divided into three stages: The temperature rises slowly in the first stage, where the rate of rise is 0.025 °C/s and the rate of voltage and heat rise is low. The second stage is the rapid temperature rise stage. The temperature rise rate is between 0.04 °C/s and 0.1 °C/s. The separator begins to decompose, a small amount of gas is released and the internal temperature of the battery can reach 150 °C or higher. The third stage is the exothermic stage after serious thermal runaway, and the battery bulges. Figure 12 shows the three stages during battery overcharge.

Zhenpo Wang et al. [82] studied the overcharge thermal runaway behavior of LFP and NCM (NCM111, NCM622, NCM811) batteries. It is found that the overcharge resistance of LFP is worse than NCM batteries, and it is more prone to thermal runaway after overcharge. However, in the case of thermal runaway, the maximum temperature of the LFP battery is low, and the thermal runaway is mild. All NCM batteries burn and explode after thermal runaway, while the LFP battery only releases gas and does not cause a fire.

3.2.3. Thermal Abuse

The difference in battery group characteristics will cause inconsistent SOCs during battery charging and discharging, which will result in local overheating in the battery. Although the same batch of batteries is required for the same battery module in EVs, there are still a few batteries that experience short circuits and overheating after a certain number of charge-and-discharge cycles. If the heat dissipation capacity of the battery pack is insufficient, the heat will further accumulate, resulting in the thermal runaway of the single battery and even the thermal runaway of the whole battery pack. Therefore, it is very important to heat the single cell and measure the relationship between its internal temperature and thermal runaway. When the battery temperature exceeds a certain range, a timely early warning mechanism can be established to cut off the battery charge and discharge, so as to avoid battery thermal runaway.

Peter J. Bugrynec [83] studied the thermal runaway of the LFP battery by accelerating the rate calorimeter (ARC) and oven exposure. When the SOC is 100%, the heat release of the cathode and anode decomposition is the main factor causing battery thermal runaway. When the SOC is low, the anode decomposition is the dominant factor. After thermal
runaway in an oven experiment, the battery temperature and temperature rise rate are greater than ARC, indicating that external heating will cause more serious thermal runaway. Zheng Liao [84] heated the NCM batteries with different SOCs to the target temperature of 218 °C and analyzed the thermal runaway reaction and gas composition of the battery. The experimental device and temperature loads are shown in Figure 13. For the gas components released from thermal runaway under different SOCs, the early warning mechanism is realized by gas sensing technology. References [85,86] analyzed the thermal runaway of an LIB through ARC and ISC, established an electric thermal coupling model for simulation calculation and gave the corresponding thermal runaway prevention mechanism.

![Figure 13. Thermal runaway experiment of NCM battery [84]. (a) Test container. (b) Load step.](image)

4. LIB Safety Measures

The standardized test of an LIB is very important to battery safety. In order to reduce the probability of thermal runaway of the LIB, many countries have successively issued corresponding standardized tests, among which the most widely used standard is the LIB standard issued by the International Electrotechnical Commission (IEC), which includes IEC 62133-2 Secondary cells and batteries containing alkaline or other non-acid electrolytes—Safety requirements for portable sealed secondary cells, and for batteries made from them, for use in portable applications—Part 2: Lithium systems [87], IEC 62619 Secondary cells and batteries containing alkaline or other non-acid electrolytes—Safety requirements for secondary lithium cell and batteries, for use in industrial applications [88] and IEC 62281 Safety of primary and secondary lithium cells and batteries during transport [89]. China has also issued a series of standards to regulate the lithium-ion power battery market, such as GB 31241-2014 Lithium ion cells and batteries used in portable electronic equipment-Safety requirements [4] and GB 38031-2020 Electric vehicles traction battery safety requirements [5]. These standards are constantly updated with the development of LIB technology.

The introduction of international and national safety standards for LIBs has pointed out the direction and set the threshold for battery manufacturers in terms of LIB performance.
indicators. Scholars have conducted in-depth research on improving the safety performance of lithium batteries, mainly including the following five aspects: Overcharge protection, overheat protection, a battery management system (BMS), a Battery Thermal Management System (BTMS), and a safety protection device [90], as shown in Figure 14.

![Diagram of safety protection technology of LIB]

**Figure 14.** Active safety protection technology of LIB.

### 4.1. Overcharge Protection

BMS can externally control the charge and discharge voltage of each battery in the battery pack, but it cannot control the chemical changes inside the battery. Adding redox additives is a method to improve battery safety by avoiding excessive internal voltage. When the internal voltage of the battery is higher than the end of charging voltage, redox additives can carry out a reversible redox reaction between electrodes to provide overcharge protection.

J. Wen et al. [66] believe that high-performance redox additives should have the following characteristics: The reaction voltage of the redox agent should be 0.3–0.4 V higher than the charging cut-off voltage; the redox agent reacts reversibly on the positive and negative surfaces of the electrode; additive molecules should have a high diffusion coefficient and solubility and the redox agent should have good chemical stability and can provide long-term charging protection. TEMPO, MPT and DBBB are redox additives used in LFP batteries [91–93].

### 4.2. Overheat Protection

The main method to improve the safety of LIB is to improve the characteristics of the LIB electrode, binder, electrolyte, diaphragm and other materials.

To improve the safety of cathode materials through element substitution, researchers have replaced Al with CO, Ni and Mn, and increased the proportion of Mn and reduced the proportion of Ni in an NCM battery, which can increase the stability of the battery [94,95].

The surface of the cathode material can be coated with a protective coating, which is a thin layer of a lithium-ion conductive compound, which mainly protects the cathode surface from direct contact with the electrolyte, enhances the structural stability and prevents side reactions. For example, fluoride coating has inert characteristics to reduce reaction heat generation, and phosphate coating has a strong covalent bond to improve material stability [90].

The battery separator implements a three-layer structure, such as a PE layer sandwiched between two PP layers, or high safety separators. By means of ceramic coating, the thermal shrinkage of the separator is reduced and the separator collapse temperature
is increased. Expensive membranes such as polyethylene terephthalate (PET) [96] and polyimide (PI) [97] are still under research.

The main characteristics of a flame retardant are the higher flash point than the organic solvent, the inertness and the lack of effect on battery performance. Solid polymer electrolytes, ionic liquid and electrolytic salt are mainly used to improve the thermal safety of electrolytes [98].

4.3. Battery Management System (BMS)

In addition to the improvement of the materials of each component of the battery, BMS is essential in the safe working process of an LIB. In addition to the basic functions of monitoring the battery voltage, temperature and current, BMS also provides a charge equalization scheme to ensure that each battery in the battery pack has the same charge and discharge rate, so that the SOC of the battery is at the same level. Table 4 shows the current SOC monitoring technology.

Table 4. SOC estimation techniques.

<table>
<thead>
<tr>
<th>SoC Estimation Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Measurement</td>
</tr>
<tr>
<td>Book-Keeping Estimation</td>
</tr>
<tr>
<td>Adaptive System</td>
</tr>
<tr>
<td>Hybrid Methods</td>
</tr>
<tr>
<td>• Open circuit voltage (OCV)</td>
</tr>
<tr>
<td>• Terminal voltage</td>
</tr>
<tr>
<td>• Impedance spectroscopy</td>
</tr>
</tbody>
</table>

State of health (SOH) describes the aging degree of the battery during operation. When the battery runs to a certain number of cycles, aging will occur, resulting in the decline of battery capacity. Therefore, BMS must evaluate SOH to quantify the battery discharge depth and remaining cycle life. SOH depends on SOC and battery internal resistance, so it is very challenging to estimate. Table 5 shows the main techniques for estimating battery SOH.

Table 5. SOH estimation techniques.

<table>
<thead>
<tr>
<th>SoH Estimation Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Methods</td>
</tr>
<tr>
<td>• Impedance measurement</td>
</tr>
<tr>
<td>• Internal resistance</td>
</tr>
<tr>
<td>• Capacity level</td>
</tr>
<tr>
<td>• Incremental and differential of capacity and voltage</td>
</tr>
</tbody>
</table>

4.4. Battery Thermal Management System (BTMS)

The battery thermal management system adjusts the temperature in the battery pack under different external environments to keep the battery temperature at a suitable working temperature, avoid overheating and improve electrochemical performance. Battery pack thermal management can generally be classified as (i) an air cooling method, (ii) liquid cooling method, (iii) refrigerant-based cooling, (iv) phase change material (PCM) cooling and (v) hybrid method [99–102]. Battery cooling is complicated by the thermal resistance of the electrolyte and plastic components in the battery, which limits the heat transfer to the battery surface. Air cooling is the simplest form and energy-saving method, but the efficiency is low. It is generally not recommended for high-power or high-energy battery packs. Liquid cooling has the highest efficiency and provides good uniformity, taking into account energy consumption, complexity and weight. More advanced methods include
PCM cooling, a thermoelectric module or hybrid cooling, which are easy to integrate, compact and efficient. However, the implementation cost is high, and in some cases, will significantly increase the complexity of the maintenance of the whole battery pack system.

4.5. Safety Protection Device

A thermal fuse is a type of overheat protection device, which is made of wires with a special alloy. When the preset current is exceeded, the wire will fuse. When the battery has short-circuited, excessive joule heat will be generated. When the set temperature of the thermal fuse is reached (generally 30–50 °C), the thermal fuse will be broken [67].

The positive temperature coefficient element (PTC) is an element of the protection circuit whose resistance increases with the increase in temperature. The device mainly prevents overcurrent and overheating of the LIB due to an external short circuit. PTC is made of a polymer conductive material, with a heat resistance temperature of 72–90 °C, and can work at a 6–20 A current and high voltage at room temperature [90].

The main function of the current interrupt device (CID) is to cut off the power supply and ensure the safety of the battery when the battery is in a bad condition or the charging device malfunctions. Sometimes gas will be generated in the sealed shell, resulting in a rise in the internal pressure. If the pressure inside the sealed shell rises to an abnormal state, it will cut off the power supply to ensure the safety of the battery. This technology has been applied to a variety of LIBs, including cylindrical 18,650 LCO batteries, which can effectively inhibit the occurrence of thermal runaway caused by overcharge.

When PTC or CID fails or there is a short circuit inside the battery, it will cause more serious electrochemical reaction, resulting in the decomposition of the separator inside the battery and the reaction between the anode and electrolyte to generate a large amount of gas. In order to prevent the explosion caused by the high internal pressure of the battery, the safety valve will be torn, so as to release the internal high pressure and reduce the harm caused by thermal runaway. However, in some cases, the internal pressure of the battery rises too fast, resulting in the failure of the safety valve to respond in time, which will lead to the bulging of the battery. When the internal temperature of the battery is too high, it will even eject jet fire from the safety valve. Therefore, researchers have studied the opening size of the safety valve, the setting of the bursting pressure and the design of the auxiliary safety valve to some extent [103,104].

5. Research and Application Status of Large-Scale LIB in Mining Industry

5.1. Research of Large-Scale LIB in Mining Industry

Table 6 lists the recent progress for large-scale LIB applications in mining industry.

<table>
<thead>
<tr>
<th>Time</th>
<th>Research Group</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>Kuchta, J.M.</td>
<td>Observed the lowest spontaneous combustion temperature of CH₄</td>
</tr>
<tr>
<td>2005</td>
<td>MSHA</td>
<td>The ignition temperature of coal dust cloud is 440 °C to 640 °C</td>
</tr>
<tr>
<td>2017</td>
<td>MPSACC</td>
<td>Studied LIB safety performance requirements, chassis design, body structure,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>automatic protection and monitoring system, etc.</td>
</tr>
<tr>
<td>2018</td>
<td>MPSACC</td>
<td>Conducted short circuit and overcharge experiments on 60 Ah LFP battery</td>
</tr>
<tr>
<td>2020</td>
<td>CCTEG</td>
<td>Analysis on explosion—proof techniques and standards for lithium—ion battery</td>
</tr>
<tr>
<td></td>
<td></td>
<td>power supply used in underground coal mine</td>
</tr>
<tr>
<td>2020</td>
<td>NIOSH</td>
<td>Measured TR pressures of LFP cells as a function of free space within sealed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>enclosures and observed an inverse power relationship.</td>
</tr>
<tr>
<td>2021</td>
<td>Binbin Mao</td>
<td>Conducted 300 Ah large-scale LFP batteries under external heating. TR can</td>
</tr>
<tr>
<td></td>
<td></td>
<td>be divided to 4 stages.</td>
</tr>
<tr>
<td>2022</td>
<td>CCTEG</td>
<td>Conducted nail penetration test for 202 Ah large-scale battery under</td>
</tr>
<tr>
<td></td>
<td></td>
<td>encapsulation protection.</td>
</tr>
</tbody>
</table>
Thomas H. dubaniewicz et al. [108] studied 18,650 and 26,650 cylindrical LIBs, analyzed the morphology and composition of battery anode, cathode and separator with a scanning electron microscope and then sealed LFP units in different free spaces in the ARC device for steady-state heating until battery thermal runaway occurred. Because the safety performance of the LFP battery is better than 18,650 battery and 26,650 batteries, the relationship between the free space and maximum pressure during LFP thermal runaway is studied and fitted by measuring the maximum pressure that the LFP battery can reach. It takes about 34 times the volume of free space of the LFP unit to meet the thresholds of 18,650 and 26,650.

Binbin Mao et al. [110] conducted a series of thermal runaway tests on a 300 Ah large-scale LFP battery under external heating. The experimental rig of LIB combustion tests is shown in Figure 15. Figure 15a presents a combustion chamber (1.8 m × 1.8 m × 2 m) as well as some monitoring apparatuses. Figure 15b shows the gas analysis and exhaust system. After externally heating the battery to thermal runaway, the safety valve opens, and an aggressive cylindrical flame is observed. Four stages were divided during battery external heating processes: (i) Constant heating until the safety valve deformed and swelled; (ii) the safety valve cracked and heat is released; (iii) combustion and aggressive thermal runaway; (iv) abatement and extinguishment. However, the flaming combustion accelerates the occurrence of TR but has little influence on the peak surface temperature.

Kuchta [105] indicated the lowest spontaneous combustion temperature of CH$_4$ is 600 °C in their experiment, and the ignition temperature of methane in air is 1040 °C. Even if the external heating LFP battery is under thermal runaway, the maximum temperature reached by the battery is 450 °C, which cannot reach the temperature of CH$_4$ detonation. The ignition temperature of coal dust measured by Kuchta ranges from 160 °C to 220 °C. During coal mining or processing, coal dust accumulates into the explosion-proof shell of the battery. MSHA [106] requires that the outer surface temperature of the explosion-proof shell shall not exceed 150 °C. The ignition temperature of the coal dust cloud is 440 °C to 640 °C. If the temperature of gas released by LFP is higher than 440 °C, it is possible to detonate external CH$_4$, resulting in an explosion.

Lei Wo et al. [107] conducted short-circuit and overcharge experiments on a 60 Ah LFP battery and studied the influence of the LFP battery after thermal runaway on a CH$_4$ explosion. The experimental results show that under the condition of an external short circuit, the appearance of the battery is intact, there is no combustion, explosion, leakage and pressure relief and the battery voltage is reduced to 0 V. The battery was seriously damaged after overcharge, and the battery underwent a combustion explosion and pressure relief, but it did not cause a secondary CH$_4$ explosion; however, the internal pressure of the explosion-proof shell reached 4 MPa, exceeding its design pressure. It is verified that the LFP battery will not cause a secondary explosion even under the condition of a high concentration of CH$_4$ after thermal runaway; however, the release of gas could potentially
lead to excessive pressure in the explosion-proof shell and further cause catastrophic events. Hence, it is necessary to design a pressure relief technique for the battery enclosure.

Yong Zhang [8] interpreted the LIB vehicle in terms of vehicle operating conditions, LIB safety performance requirements, chassis design, body structure, automatic protection, monitoring system, etc. In terms of battery safety performance, all on-board electrical appliances are required to meet the requirements of the GB 3836 explosive environment [112] series standards: (i) The temperature of the battery surface shall not exceed 150 °C; (ii) the capacity of the LFP battery for mining shall not exceed 100 Ah; (iii) the connection mode of the single battery shall adopt a low-resistance design to avoid heat accumulation; (iv) the LIB shall be placed separately in an explosion-proof chamber with a pressure of 1.5 MPa, and a pressure relief valve shall be installed; (v) the protection grade of the LIB shell shall not be lower than IP55; (vi) when the LIB is fully charged, the braking regenerative energy shall be completely consumed and absorbed by the special device without overcharging the battery pack [113,114].

The authors presented a thorough analysis and experimental results on the effect of encapsulation on the lithium cell that undergoes nail penetration thermal runaway. Regarding the nail penetrating the cell, the rising temperature and voltage profile of the cell’s thermal runaway behavior are shown in Figure 16 [111]. Each battery was installed with 3 sensors, located in the cell’s left wide face, safety valve, and negative terminal respectively, total 30 sensors. Sensor 31, 32 and 33, as shown in Figure 16c, were installed in the upper space enclosure to measure the ambient environment above the encapsulated cells. Note that the instantaneous drop of the cell’s voltage at the onset of thermal runaway shows that the cell short-circuited internally through the nail penetration. Temperature sensors T25, T26 and T27 are recorded for the triggered battery. In Figure 16b, the voltage dropped to 0 within 3 min. The temperature of the safety valve (T26) increased faster than T25 and T27 due to the reaction gasses and electrolyte breaking through the safety valve. The highest temperature of the cell’s wide surface (T25) occurred after 5 min of the triggering, and reaches up to around 490 K. The heat released from the thermal runaway battery dissipated quickly through the heat conduction of the encapsulation and blocked transmission by resin separator. The investigations illustrated that the encapsulated cells have exceptional advantages in providing the required protection to a large number of series-connected battery cells, particularly for a high-capacity cell.

Table 7. Relationship between protection type and equipment protection level.

<table>
<thead>
<tr>
<th>EPL</th>
<th>Protection Type</th>
<th>Sign</th>
<th>Group</th>
<th>Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘Ma’</td>
<td>Intrinsically safe</td>
<td>‘ia’</td>
<td>I</td>
<td>GB 3836.4 &amp; IEC 60079.11</td>
</tr>
<tr>
<td></td>
<td>Encapsulation</td>
<td>‘ma’</td>
<td>I</td>
<td>GB 3836.9 &amp; IEC 60079.18</td>
</tr>
<tr>
<td></td>
<td>Special</td>
<td>‘s’</td>
<td>I</td>
<td>GB 3836.24 &amp; IEC 60079.33</td>
</tr>
<tr>
<td></td>
<td>2 independent EPL Mb</td>
<td></td>
<td>I</td>
<td>GB 3836.23 &amp; IEC 60079.14</td>
</tr>
<tr>
<td>‘Mb’</td>
<td>Intrinsically safe</td>
<td>‘ib’</td>
<td>I</td>
<td>GB 3836.4 &amp; IEC 60079.11</td>
</tr>
<tr>
<td></td>
<td>Explosion-proof</td>
<td>‘d’</td>
<td>I</td>
<td>GB 3836.2 &amp; IEC 60079.1</td>
</tr>
<tr>
<td></td>
<td>Increased safe</td>
<td>‘e’</td>
<td>I</td>
<td>GB 3836.3 &amp; IEC 60079.7</td>
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<tr>
<td></td>
<td>Positive-pressure</td>
<td>‘p’/‘px’</td>
<td>I</td>
<td>GB 3836.5 &amp; IEC 60079.2</td>
</tr>
<tr>
<td></td>
<td>Encapsulation</td>
<td>‘m’/‘mb’</td>
<td>I</td>
<td>GB 3836.9 &amp; IEC 60079.18</td>
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<td></td>
<td>Sand filling</td>
<td>‘q’</td>
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<td>GB 3836.7 &amp; IEC 60079.5</td>
</tr>
<tr>
<td></td>
<td>Special</td>
<td>‘s’</td>
<td>I</td>
<td>GB 3836.24 &amp; IEC 60079.33</td>
</tr>
</tbody>
</table>

The LFP battery has a large thermal stability range and is safer than other types of LIBs in faulty conditions such as short circuits and fire [109]. However, the thermal runaway heat generation of the LFP battery will also cause a sharp increase in temperature and may be accompanied by the release of high-temperature gas. The explosion-proof design must be adopted, and the internal pressure of the explosion-proof container must meet the static pressure of 1 MPa. There are three explosion-proof protection technologies for LIB vehicles: Explosion-proof (Ex’d’), intrinsically safe (‘ia’/’ib’) and encapsulation (Ex ‘ma’/’mb’). At
the same time, the increased safety type (Ex ‘e’) or the combination of several protection technologies may also be considered to achieve the required protection level. Table 7 shows the relationship between the protection type and equipment protection level (EPL).

**Table 7**

<table>
<thead>
<tr>
<th>Protection Type</th>
<th>Equipment Protection Level (EPL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>EPL 1</td>
</tr>
<tr>
<td>Type 2</td>
<td>EPL 2</td>
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<tr>
<td>Type 3</td>
<td>EPL 3</td>
</tr>
<tr>
<td>Type 4</td>
<td>EPL 4</td>
</tr>
</tbody>
</table>

**Figure 16.** Large-scale LIB pack thermal runaway experiment: (a) Model of encapsulated cell pack in enclosure; (b) experimental measurement of temperature, voltage vs. time; (c) front view of battery pack sensor installation position; (d) top view of battery pack sensor installation position.

5.2. Application of Large-Scale LIB in Mining Industry

The South African mining health and safety bureau defines engineering mobile machinery for mining operations as “any self-propelled machine used for mining, transportation or related operations underground or on the mine surface, including any mobile device that is driven by wheels, slides, rails, machinery or installed on the machine”. With the progress of battery technology, the trend of replacing diesel-driven trackless vehicles with EVs is becoming more and more prominent. Although EVs are more expensive than gasoline or diesel vehicles and require fixed charging equipment, the working efficiency of the motor is much higher than that of the traditional internal combustion engine, and the braking energy can be recovered. When EVs are implemented in mining projects, their operating costs are much lower than diesel vehicles. Figure 17 compares the operating costs of diesel vehicles and EVs in detail [115].

In 2019, the carbon emissions of commercial vehicles in Australia accounted for 38% of the total emissions. Commercial vehicles mainly include light commercial trucks, light and medium trucks, waste-disposal vehicles, mining and multipurpose vehicles and customized and special vehicles. Furthermore, 84% of freight vehicles in Australia are light commercial vehicles. The transformation of light and medium fuel vehicles can significantly reduce carbon emissions.
Australia’s mining industry is also prone to using EVs. Replacing heavy mining vehicles and light multipurpose vehicles with EVs brings great benefits to workers and operators in open-pit mines and underground mines. As with all electric vehicles, electric mining vehicles provide quiet and stable driving, can output higher torque and generate less heat. They have irreplaceable advantages under the mining conditions of sharp turns and limited space operation. They are not affected by ventilation and have no quantity restrictions on underground operation. In addition, electric vehicles can carry out regenerative braking in complex terrain, greatly reducing energy waste [116].

European Sustainable Intelligent Mining Systems for the global mining industry proposes the creation of a digital mine in a three-year plan [115]. With a total investment of nearly US $20 million, the project aims to establish a connected, efficient, safe and attractive workplace, which has been successfully demonstrated in Germany, Poland, Sweden and Finland. The project includes the use of an LIB drilling rig and an auxiliary transportation system to improve the underground air pollution caused by diesel engines, as shown in Figure 18.

The global mining guidelines Association (GMG) and the mining Innovation Council of Canada issued proposed methods for EVs in underground mining environments in 2018 [117]. The guide focuses on seven parts, explaining the basic knowledge and application of EVs, mine design, EV design, energy storage system, charging system, operation precautions and performance standards, which provided application guidelines for global mining companies and equipment manufacturers.
Table 8. Test standards for energy-storage systems.

<table>
<thead>
<tr>
<th>Recommended Industry Standard</th>
<th>Topic</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>E/ECE/324/Rev.2/Add.99/Rev.2</td>
<td>Safety requirements of vehicle electric power train</td>
<td>United Nations, 2013</td>
</tr>
<tr>
<td>ST/SG/AC.10/11/Rev.5</td>
<td>Criteria, test methods and procedures for classifying dangerous goods</td>
<td>United Nations, 2019</td>
</tr>
<tr>
<td>J2288_200806</td>
<td>Standardized test method to determine the expected life cycles of BEV battery modules</td>
<td>SAE International, 2008</td>
</tr>
<tr>
<td>UL 1642</td>
<td>Requirements to reduce the risk of and injury from fire or explosion when lithium batteries are used or removed from a product and discarded</td>
<td>UL, 2012b</td>
</tr>
<tr>
<td>UL 2580</td>
<td>Evaluates the ability of the electrical energy storage assembly to safely withstand simulated abuse conditions and prevents exposure of persons to hazards as a result of the abuse</td>
<td>UL, 2013</td>
</tr>
<tr>
<td>CAN/CSA-E62660-1:15</td>
<td>Performance and life testing of rechargeable lithium-ion cells for propulsion of BEVs and hybrid electric vehicles</td>
<td>CSA Group, 2015a</td>
</tr>
<tr>
<td>CAN/CSA-E62660-2:15</td>
<td>Test procedures to observe the reliability and abuse behavior of rechargeable lithium-ion cells for propulsion of BEVs and hybrid electric vehicles</td>
<td>CSA Group, 2105b</td>
</tr>
<tr>
<td>IEC 62133–2:2017</td>
<td>Requirements and tests for safe operation of portable sealed rechargeable lithium cells and LIBs containing non-acid electrolyte</td>
<td>International Electrotechnical Commission, 2017</td>
</tr>
<tr>
<td>IEC 61508:2010</td>
<td>Aspects to be considered when electrical/electronic/programmable electronic systems are used to carry out safety functions</td>
<td>International Electrotechnical Commission, 2010</td>
</tr>
<tr>
<td>Canada TDG</td>
<td>Transportation of dangerous goods regulations</td>
<td>Transport Canada, 2016</td>
</tr>
<tr>
<td>IATA Dangerous Goods Regulations</td>
<td>International Air Transport Association Dangerous Goods Regulations</td>
<td>International Air Transport Association, 2018</td>
</tr>
<tr>
<td>ISO 14990–1:2016</td>
<td>General safety requirements for electrical equipment and components incorporated into earth-moving machines as defined in 1506165:2012</td>
<td>International Organization for Standardization, 2016a</td>
</tr>
<tr>
<td>ISO 6165:2012</td>
<td>Terms and definitions and an identification structure for classifying earth-moving machinery</td>
<td>International Organization for Standardization, 2012a</td>
</tr>
</tbody>
</table>

The rechargeable LIB in the energy storage system is at the core of the operation of electric vehicles. The battery capacity and energy density determine the operation range of a single charge of EVs. Energy-storage materials with small volume, light weight, high efficiency,
low price and high energy density promote the development of the battery industry. These excellent characteristics are more critical in mining, because mining vehicles have a larger volume and weight and higher energy consumption. However, with the increase in the energy density of a single battery, the safety of the battery decreases. GMG proposed three main approaches to battery safety: First, limit the number of active materials to achieve a balance between energy density and safety. Second, add safety mechanisms inside the battery, such as CID, a safety valve, etc. Third, add an electronic guaranteed circuit to the battery pack. The test standards of the energy-storage system have multiple criteria. Table 8 summarizes international standards related to the energy-storage system [117].

China’s EV industry has developed rapidly in recent years, with nearly 6 million in use, accounting for more than 50% of the world. The intelligent electrification of vehicles has penetrated the whole auto industry, and the development of EVs can be divided into three stages: (i) From 1995–2000, EVs were mainly used for passenger cars; (ii) from 2001–2020, the number of EV passenger cars, buses and logistics vehicles increased sharply; (iii) after 2020, special EVs will become a new growth engine of the market. Through structural innovation, BYD, an EV company, invented blade batteries, which are designed by skipping the module when they are grouped. Compared with the modular battery pack design, the weight-specific energy density of blade batteries can reach up to 180 Wh/kg. Depending on the particularity of the shape of the blade battery and the stability of the material, the densely arranged blade battery can act as a simple structural part, and the space utilization rate is increased from 40% to 60%. Moreover, the blade battery also improves the disadvantage of the low-temperature resistance of lithium iron phosphate. Even in a severe cold environment of minus 20 degrees, the discharge capacity of the blade battery is at least 90% of that at room temperature. It can still maintain the stability of the battery performance in the low-temperature environment, thus better improving the problem of low-temperature endurance attenuation of the lithium iron phosphate battery [118]. The new battery technology accelerates the development of the EV industry.

In the coming period of time, auxiliary transport vehicles for coal mines will change from diesel engines to electric engines to a large extent. There are 2403 auxiliary transportation vehicles in use in the Shendong Coal Group, including 456 LIB vehicles. Zhongtian Hechuang Energy Co., Ltd. has 218 explosion-proof auxiliary transportation vehicles, including 36 LIB vehicles. It can be seen that LIB vehicles have been preliminarily applied in some companies, and there is a great space for their development in the future.

6. Conclusions and Prospects

High-capacity LIBs have been widely used in EVs and electrochemical energy storage, which reaches 300 Ah, while in underground coal mines, the capacity of the LIB needs to be less than 100 Ah [119]. With the increase in the capacity of a single battery, its energy density increases accordingly, which leads to an increase in the severity of the thermal runaway of a single battery and the probability of thermal runaway of battery packs. Battery safety is particularly important. This review introduced the cathode materials of LIBs, analyzed the occurrence conditions of internal chemical reactions after thermal runaway, compared the severity of decomposition and heat release of different cathode materials when thermal runaway occurs and came to the conclusion that the temperature rise rate of LFP is slower than that of LMO, LCO and NCM when thermal runaway occurs. This review performed a detailed analysis of the causes of battery thermal runaway. Regardless of mechanical abuse, electrical abuse and thermal abuse, the inducing factors of thermal runaway are attributed to the fierce chemical exothermic reaction caused by the internal short circuit of the battery, and the excessive temperature rise in the battery could potentially cause fire and an explosion. Therefore, in order to ensure the intrinsic safety of the battery pack, one strategy is to select safer cathodes and anodes, electrolytes and separator materials, and the other is to take away the heat of the thermal runaway battery in time, so as not to cause the spread of thermal runaway. For battery safety, this review analyzes five dimensions: Overcharge protection, overheating protection, BMS, BTMS and battery safety protection
device. Finally, this review summarized and analyzed the latest research results on the application of high-capacity batteries in coal mines and introduced the design requirements of IEC 60079 and GB 3836 series standards for electrical equipment used in an explosive environment, and considered that, after encapsulation, even if the internal battery is under thermal runaway, it is cooled by encapsulation materials and buffered in the internal space of the explosion-proof chamber. Hence, it will not further cascade to the explosive environment that will potentially lead to fire or explosion accidents.

To summarize, high-capacity LIBs are qualified for application in underground vehicles and equipment in coal mines; however, increasing the single battery capacity without conducting thorough thermal runaway studies may bring new potential safety hazards. Therefore, various meticulous tests must be carried out to verify that the high-energy-density LIB will not cause a cascade of effects after thermal runaway. High-energy-density lithium batteries should be used to make breakthroughs from new materials, such as lithium sulfur batteries and lithium oxygen batteries, for which the theoretical energy density can reach up to 2600 and 3500 Wh/kg, respectively [120,121]. However, sharp decay, poor cycling stability, low coulombic efficiency and serious safety hazards impede their practical application [122–125]. The Fe$_7$S$_8$/SiO$_x$/nitrogen-doped carbon anode exhibited a superior discharge capacity of 1060.2 mA h g$^{-1}$, which demonstrates great potential in electrochemical energy storage [126]. In the composition of a battery pack, new thermal insulation and heat transfer materials should be applied to prevent the thermal runaway propagation of a single battery. A full operation life cycle battery management system shall be developed to ensure battery charge and discharge consistency and overcharge and discharge protection. The application of LIBs in mining auxiliary transportation vehicles is still in its initial stage and has broad market prospects. It can gradually replace explosion-proof diesel vehicles in the future, so as to ensure safe, efficient and sustainable mining operations.

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Abbreviations

3C Computer, communication, and consumer electronics
ARC Accelerating rate calorimeter
BMS Battery management system
BTMS Battery thermal management system
CCTEG China Coal Technology Engineering Group
CID Current interrupt device
DBBB 2,5-Di-tert-butyl-1,4-bis benzene
DEC Diethyl carbonate
DMC Dimethyl carbonate
EC Ethylene carbonate
EKF Extended Kalman filter
EMC Methyl ethyl carbonate
EPL Equipment protection level
EV Electronic vehicle
GMG Global mining guidelines
IEC International electrotechnical commission
ISC Internal short circuit
KF Kalman filter
LCO Lithium cobalt oxide
LFP Lithium iron phosphate
LIB Lithium-ion battery
LMO Lithium manganese oxide
MPSACC Mining products safety and certification center
MPT Methylphenothiazine
MSHA Mine safety and health administration
NCA Nickel cobalt aluminum
NCM Lithium nickel manganese cobalt oxide
NIOSH National institute for occupational safety and health
OCV Open circuit voltage
PCM Phase change material
PE Polyethylene
PET Polyethylene terephthalate
PI Polyimide
PP Polypropylene
PTC Positive temperature coefficient element
PVDF Polyvinylidene fluoride
RLS Recursive least squares filter
SEI Solid electrolyte interphase
SOC State of charge
SOH State of health
TEMPO 2,2,6,6-tetramethylpiperidinyl-oxide
TGA Thermal gravimetric analyzer
TM Transmission metal
TR Thermal runaway
UKF Unscented Kalman filter

References

2. Zhu, X.; Wang, Z.; Wang, C.; Huang, L. Overcharge investigation of large format lithium-ion pouch cells with Li(Ni0.6Co0.2Mn0.2)O2 cathode for electric vehicles: Thermal runaway features and safety management method. J. Electrochem. Soc. 2018, 165, 3613–3629. [CrossRef]

34. Watanabe, S.; Kinoshita, M.; Nakura, K. Capacity fade of LiNi1-x-yAlxO2 cathode for lithium-ion batteries during accelerated calendar and cycle life test. I. Comparison analysis between LiNi1-x-yAlxO2 and LiCoO2 cathodes in cylindrical lithium-ion cells during long term storage test. J. Power Sources 2014, 247, 412–422. [CrossRef]


36. Wang, Q.; Ping, P.; Zhao, X.; Chu, G.; Sun, J.; Chen, C. Thermal runaway caused fire and explosion of lithium-ion battery. J. Power Sources 2012, 208, 210–224. [CrossRef]

37. Liu, C.; Li, H.; Kong, X.; Zhao, J. Modeling analysis of the effect of battery design on internal short circuit hazard in LiNi0.8Co0.1Mn0.1O2/SiOx-graphite lithium ion batteries. Int. J. Heat Mass Transf. 2020, 153, 119590. [CrossRef]

38. Kim, G.-H.; Pesaran, A.; Spotnitz, R. A three-dimensional thermal abuse model for lithium-ion cells. J. Power Sources 2007, 170, 476–489. [CrossRef]


41. Zhao, L.; Watanabe, I.; Doi, T.; Okada, S.; Yamaki, J.I. TG-MS analysis of solid electrolyte interphase (SEI) on graphite negative-electrode in lithium-ion batteries. J. Power Sources 2006, 161, 1275–1280. [CrossRef]

42. Wang, Q.; Sun, J.; Chen, C. Thermal stability of delithiated LiMn2O4 with electrolyte for lithium-ion batteries. J. Electrochem. Soc. 2007, 154, 263. [CrossRef]

43. Ren, D.; Hsu, H.; Li, R.; Feng, X.; Guo, D.; Han, X.; Lu, L. A comparative investigation of aging effects on thermal runaway behavior of lithium-ion batteries. Transportation 2019, 2, 100034. [CrossRef]

44. Yoon, T.; Milien, M.S.; Parimalam, B.S.; Lucht, B.L. Thermal decomposition of the solid electrolyte interphase (SEI) on silicon electrodes for lithium-ion batteries. Chem. Mater. 2017, 29, 3237–3245. [CrossRef]


49. Yuan, M.; Liu, K. Rational design on separators and liquid electrolytes for safer lithium-ion batteries. J. Energy Chem. 2020, 43, 58–70. [CrossRef]


51. Deimele, V.; Elmasides, C. Separators for lithium-ion batteries: A review on the production processes and recent developments. Energy Technol. 2015, 3, 453–468. [CrossRef]


53. Zhang, S.; Xu, K.; Jow, T. An inorganic composite membrane as the separator of Li-ion batteries. J. Power Sources 2005, 140, 361–364. [CrossRef]


55. Peng, P.; Jiang, F. Thermal safety of lithium-ion batteries with various cathode materials: A numerical study. Int. J. Heat Mass Transf. 2016, 103, 1008–1016. [CrossRef]

56. Spotnitz, R.; Franklin, J. Abuse behavior of high-power, lithium-ion cells. J. Power Sources 2003, 113, 81–100. [CrossRef]


59. Lamb, J.; Orendorff, C.J.; Roth, E.P.; Langendorf, J. Studies on the thermal breakdown of common Li-ion battery electrolyte components. J. Electrochem. Soc. 2015, 162, 2131–2135. [CrossRef]

60. Roth, E.P.; Orendorff, C.J. How electrolytes influence battery safety. Electrochem. Soc. Interface 2012, 21, 45. [CrossRef]

98. Zeng, Z.; Wu, B.; Xiao, L.; Jiang, X.; Chen, Y.; Ai, X.; Yang, H.; Cao, Y. Safer lithium ion batteries based on nonflammable electrolyte. J. Power Sources 2015, 279, 6–12. [CrossRef]
100. Bandhauer, T.M.; Garimella, S.; Fuller, T.F. A critical review of thermal issues in lithium-ion batteries. J. Electrochem. Soc. 2011, 158, 1–25. [CrossRef]
110. Mao, B.; Liu, C.; Yang, K.; Li, S.; Liu, P.; Zhang, M.; Meng, X.; Gao, F.; Duan, Q.; Wang, Q.; et al. Thermal runaway and fire behaviors of a 300 Ah lithium ion battery with LiFePO4 as cathode. Renew. Sustain. Energy Rev. 2021, 139, 110717. [CrossRef]
111. Meng, L.; See, K.W.; Wang, G.; Wang, Y.; Zhang, Y.; Zang, C.; Xie, B. Explosion-proof lithium-ion battery pack–In-depth investigation and experimental study on the design criteria. Energy 2022, 249, 23715. [CrossRef]
113. Safety Requirements for Mining Lithium Ion Battery (Trial); China Mining Products Safety Approval and Certification Center: Beijing, China, 2017.
114. Safety Requirements for Mine Flameproof (Inntrinsically Safe) Lithium ion Battery Power Supply (Trial); China Mining Products Safety Approval and Certification Center: Beijing, China, 2020.


