SAFETY ASSESSMENT OF LITHIUM-ION BATTERY BASED ON FMEA METHOD

Jin-quan XUAN, Xiao-Hong WANG, Li-Zhi WANG

School Of Reliability And System Engineering, Beihang University
Rd. Xueyuan, No.37, Beijing, China, 100191,
Email: xjq304@163.com

Lithium-ion batteries have been widely used in many fields, while their safety issues have aroused increasing concern at the same time, particularly in electric vehicle applications. In order to assess the safety state of lithium-ion batteries, firstly, the potential safety hazards and harmful factors generated by a lithium-ion battery's heat balance mechanism and constituent material have been studied and analyzed based on the deep analysis of its composition and structure. Secondly, Failure Mode and Effect Analysis (FMEA) and Risk Analysis were applied to evaluate the lithium-ion battery's safety level. Finally, the results of the lithium-ion battery's safety risk assessment and then the methods for its risk management were obtained. The research results of this paper can be used to prevent and avoid safety accidents caused by lithium-ion batteries, and to guide the design, maintenance and protection of lithium-ion batteries and their application system as well.

I. INTRODUCTION

The greenhouse effect and environmental pollution brought about by increasing consumption of petrochemical energy make people become more aware of the importance of new and renewable energy development and utilization. Lithium-ion battery has been widely used in electronic communications, electric vehicles, aerospace and other fields because of its high voltage and specific energy, long cycle life and non-pollution (Ref. 1). The lithium-ion battery have even been applied to the Spirit Mars probe and the Opportunity Mars probe as power sources (Ref. 2). However, due to its properties of high energy density and voltage output, the lithium-ion battery itself can easily lead to thermal runaway, which will therefore cause safety accidents like fire and explosion taking a toll on people and properties. In this sense, its safety issues have become a main obstacles standing in the way of lithium-ion battery's large-scale commercial application. According to the survey data, one in every one million batteries will cause an accident (Ref. 3). But with the wider application of lithium-ion battery and the augment of battery energy density, the probability and danger of its accidents will both be greatly improved. Fire and explosion accidents caused by lithium-ion batteries have been reported frequently, especially for the electric cars in the last few years, as shown in Table I (Ref. 4). These accidents have become a huge obstacle for the wider application of lithium-on battery in the aerospace, especially in the military fields.

TABLE I. Examples Of Lithium-ion Battery's Safety Accidents

No	Time	Accidents and Places	Causes
1	2014.07	Tesla EV burned, Los Angeles	Crash
2	2014.06	Nikon recalled batteries, China	Deformation, fire
3	2014.05	Millet mobile power spontaneous combustion, hina	Burning, overcharge
4	2014.03	Lenovo recalled battery, China	overheat
5	2013.04	Samsung cell-phone battery explosion, China	Overheat, overcharge
6	2013.03	Mitsubishi EV got fire, Japan	Overheat
7	2013.01	Boeing 787 aircraft caught fire, Boston	Overheat
8	2012.10	Fisker Hybrid EV caught fire, New Jersey	Explosion, immersion

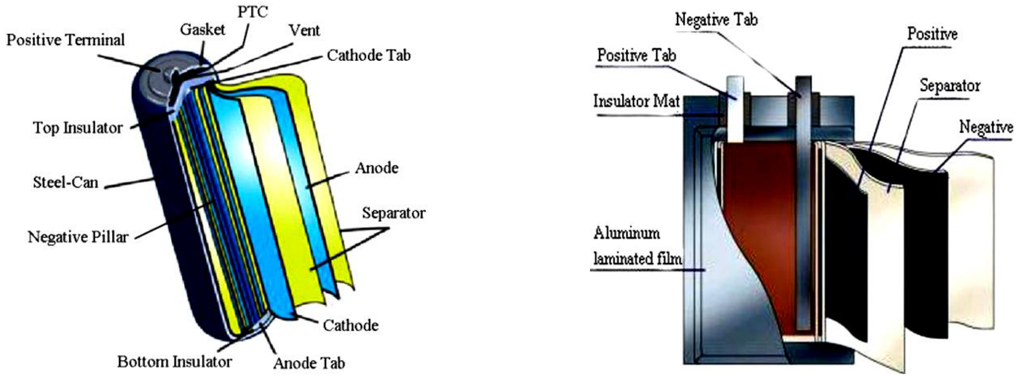
Plenty of researches have shown that two aspects have to be considered before solving the safety problem of lithium-ion battery: safety design and accident prevention (Ref. 5-8). In this paper, FMEA and Risk Assessment were used to evaluate the safety level of lithium-ion battery from the above two aspects, which will in turn prevent and avoid safety accidents caused by lithium-ion batteries, and then guide the design, maintenance and protection of lithium-ion battery and its application system.

II. THE STRUCTURE AND PRINCIPLE OF LITHIUM-ION BATTERY

The battery is a system, in which chemical energy can be directly converted into electrical energy by electrochemical reaction. According to its usage frequency, batteries can be divided into one-time batteries and rechargeable batteries. Lithium-ion battery is a typical rechargeable battery.

II.A. Structure of Lithium-ion Battery

Lithium-ion batteries are either cylindrical or square in terms of their shapes. Its common structure was shown in Fig 1 (Ref. 1-8).



（a）　　　　　　　　　　　　　　　　　　　　（b）

Fig. 1. Lithium-ion Battery's structure. (a)cylindrical lithium-ion battery; (b)prismatic lithium-ion battery

A square lithium-ion battery and a cylindrical one are similar in structure which are composed of the positive, the negative, the electrolyte, the shell and other components. When the electrolyte is liquid, the shell is made from steel; When the electrolyte is the polymer, the shell is made from plastic packaging materials (Ref. 7). The positive temperature coefficient (PTC) and Safety Vent in the picture are safety components. PTC is a thermal resistor, and its resistance is proportional to its temperature. When the battery's temperature is abnormally increased, it would block current to prevent temperature rise. Safety Vent is a vent, it will open when the battery's inside pressure accumulates to a certain high level to maintain the inside pressure under a safety level, thus avoiding explosion from excessive pressure.

II.B. Operating Principle of Lithium-ion Battery

Lithium-ion batteries' operating principle can be described as: When charging, Li^+, removed from the cathode, went through the separator by the transmission of electrolyte, and then embedded itself into the negative pole. At the same time, electron transferred to the negative electrode through the external circuit. When discharging, Li^+, removed from the anode, returned to the cathode through the separator. And by the external circuit, electron transferred to the positive electrode. As the process of charging and discharging is achieved by the transfer of Li^+, the battery is therefore called Lithium-ion Battery. In addition, lithium-ion battery is also formerly known as Rocking Chair Battery because Li^+ migrated back and forth between the positive and negative poles in the process (Ref. 6-8). The operating principle of lithium-ion battery can be expressed by the following formula.

$$\text{Positive reaction:}\quad LiMO_m \xrightleftharpoons[\text{discharge}]{\text{charge}} Li_{1-x}MO_m + xLi^+ + xe^- \qquad (1)$$

$$\text{Negative reaction:}\quad LiMO_m + C_n \xrightleftharpoons[\text{discharge}]{\text{charge}} Li_{1-x}MO_m + Li_xC_n \qquad (2)$$

$$\text{Total reaction:}\quad C_n + xLi^+ + xe^- \xrightleftharpoons[\text{discharge}]{\text{charge}} Li_xC_n \qquad (3)$$

III. HAZARD ANALYSIS OF LITHIUM-ION BATTERY

The safety issues of lithium-ion battery are mainly related to fire and explosion. The internal defects or improper use of lithium-ion batteries (such as overcharge/discharge, short circuit, etc.) will lead to internal generation of heat and gas, which will cause thermal runaway and finally fire and explosion accidents. Because there are safety risks no matter in what kind of situations, the in-depth safety analysis therefore must be carried out to eliminate these safety hazards form the designing process. Many analyses show that the thermal equilibrium failure is the main cause of lithium-ion battery safety accidents. Therefore, the thermal equilibrium mechanism of lithium-ion battery is deeply analyzed in this section to study the safety hazards of its composition and abuse behaviors.

III.A. The Mechanism of Lithium-ion Battery's Heat Balance

Many researches indicate that the main exothermic reactions in the lithium-ion battery include: the reduction reaction of the electrolyte in the cathode, the decomposition reaction of the electrolyte, the oxidation reaction of the electrolyte in the cathode, the thermal decomposition reaction of the cathode, etc (Ref. 1,3,4,5,10). Battery temperature (T) can be obtained by the following formula:

$$dT/dt = (W_e+W_i)/C_b - W_d/C_b = (W_e+W_i)/C_b - k(T - T_0) \qquad (4)$$

Where, W_e is for external energy (J/s)； W_i for internal heat generation (J/s)； W_d for the heat loss (J/s)； C_b for heat capacity of Battery[(J/s) / T; t for time(s)； k for heat dissipation constant(1/s); T_0 for external temperature (k).

In Ref. 10, Jung-Ki and Park proposed to describe battery's safety performance with simulation diagram, as shown in Fig 2. Under normal operation, the process of charge/discharge is controllable, but when it is abused, the rapid conversion of energy will produce a harmful by-product.

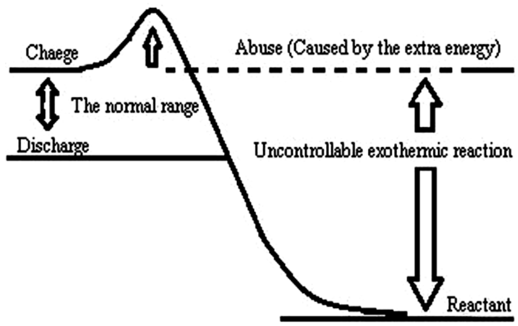


Fig. 2. Battery safety performance simulation diagram

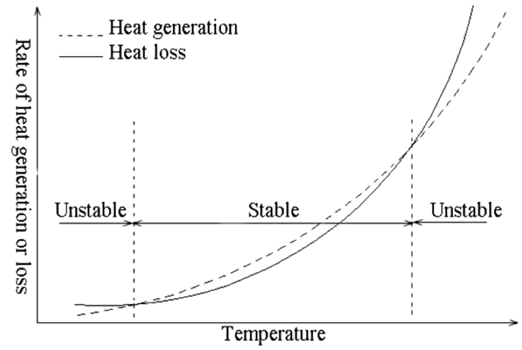


Fig. 3. Battery's relationship diagram of safety and heat balance

The temperature of the battery is largely determined by its heat generated inside and the heat loss to the external environment. Averagely, when the temperature is higher than 60~80℃, the exothermic decomposition reaction will give rise to more decomposition reaction along with the generation of self heating, which would then cause thermal runaway. If the heat dissipation rate is higher than that of the generation rate, the thermal runaway can be avoided and the battery will be stable; otherwise, it will cause energy accumulation, and the battery temperature will be not safe as time goes by. The relationship between the heat dissipation/generation and the safety performance of the battery was shown in Fig 3. For commercial lithium-ion battery, thermal safety must be guaranteed at around 60℃. If the temperature continues to increase, a self heating reaction will take place in the battery and then the exothermic reaction will be accelerated, which leads to thermal runaway that causes serious safety problems.

III.B. Hazard Analysis of Lithium-ion Battery's Constituent Materials

Lithium-ion battery is mainly composed of the positive and negative poles, electrolyte and separator materials, etc. Those materials help with electrochemical reaction in Lithium-ion battery to realize the conversion of chemical energy and electric energy. Only when the material composition and its potential safety hazards are fully understood, safety analysis can be carried out specifically. The safety hazard analysis of the lithium-ion battery composition is shown in Table II.

III.C. Hazard Analysis of Lithium-ion Battery's Abuse Behavior

Accidents caused by lithium-ion battery mainly relates to the abuse behaviors, it is ,therefore, necessary to analyze the potential safety hazards concerning the abuse behaviors. In this section, the safety hazard analysis was carried out from five typical abuse behaviors, namely, overcharge, over discharge, acupuncture/impact, thermal shock, and water inlet, as shown in Table III.

IV. FMEA ANALYSIS OF LITJIUM-ION BATTERY

Failure Mode and Effects Analysis (FMEA) is a method for analyzing the potential failure modes of a product and their potential impact to the product, as well as for classifying each potential failure mode according to its severity.

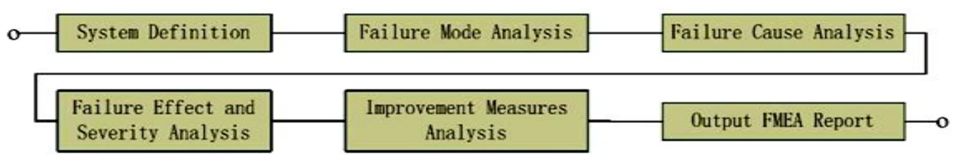


Fig. 4. Main process of FMEA analysis

This method has now been widely used in nuclear power plants, the chemical industry, electronics, machinery and other fields, becoming an important means for safety risk assessment. In this section, the possible failure modes and impacts, the severity, the damage degree of the lithium-ion battery were analyzed by virtue of the FMEA method, and the FMEA analysis table shown in Fig 4.

IV.A. System Definition

System definition, mainly including product function analysis and the drawing of the product block diagram, can be regarded as the first step in FMEA analysis. Its purpose is to make the subsequent analysis better targeted. This paper has already analyzed the function lithium-ion battery in the preceding part, and the following part is mainly focused on the classification of indenture level and the drawing of indenture level diagram and task reliability block diagram.

TABLE II. The Safety Hazard Analysis Of The Lithium-ion Battery Composition

Parts	Materials	Functions	Safety hazards
Positive electrode	$LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$,etc.	Release Li^+ when charging; absorb Li^+ when discharged	• When the temperature is above 50℃, the positive electrode will release large amounts of oxygen, and cause the decomposition of electrolyte, thus causing battery expansion • When the temperature exceeds 200℃, the positive electrode material will breakdown, causing electrolyte exothermic reaction • Overcharge will cause the excessive loss of Li^+, causing electrolyte oxidation, which will produce a lot of heat.
Negative electrode	Lithium, lithium-compound, or carbon material	Absorb Li^+ when charging; release Li^+ when discharge	• When overcharged, Li^+ is easy to accumulate in the cathode to form the lithium-dendrite, piercing separator to cause a short circuit • Charging expanded graphite crystals, causing the swelling of the cell • Lithium metal gets explosion when exposed to moisture • SEI film begins to decompose at 80℃ and be completely decomposed at 100~120℃, causing Li + reaction with the electrolyte , thus generating large amount of heat.
Electrolyte	Composed of the organic-solvent, the lithium-salt-electrolyte like $LiClO_4$, $LiPF_6$	Transport Li^+, conducting current	• Toxic and irritating causing headache, weakness, difficulty breathing , etc after inhaling; • Flammability; risk of a fire hazard in case of fire or heat. • Thermal decomposition reaction occurs at about 200℃ and explosive thermal reaction of the positive electrode will be catalyzed; • When the temperature is below -20℃, viscosity of the electrolyte solvent will decrease and the lithium salt will precipitate, thus stopping the Li + conduction.
Separator	Commonly using polyolefins, such as PE, PP	Separating the positive and negative poles to prevent internal short circuit; to conduct ion	• Flow phenomena occurs when the temperature is above 120℃. Separator melts when temperatures is higher than about 150℃, resulting in a short circuit; • In the case of metal particles or other impurities, Separator is vulnerable to rupture.

(Note: some of the data in the table are referred from Ref. 10).

TABLE III. Safety Analysis Of Lithium-ion Battery's Typical Abuse

Abuse	Occurrence Condition	Safety Risks
Over-charge	• Charging voltage is higher than a predetermined value. • Electrophoresis shock fails the charger. • Charging protection circuit fails. • Charging under high temperature environment.	• Voltage and temperature goes up quickly, and releases oxygen and heat; • Oxidation decomposition of the electrolyte generates more heat, resulting in thermal runaway.
Over-discharge	• Separator broken, causing internal short circuit. • Vibrations cause the short-circuit. • Using under high temperature environment.	• High current makes temperature go up quickly, and causes fire, explosion and other accidents.
Needling/ Strike	• Used or stored in vibration environment. • Drop. • Sharp objects or rigid material shock.	• Cell structure is destroyed, such as terminals broken , solder fall off; • Local high temperature causes thermal imbalance, leading to thermal runaway.
Thermal-shock	• Sudden changes in ambient temperature. • Used or stored under high temperature environment.	• Thermal equilibrium destruction causes thermal runaway, Such as, the exothermic reaction is accelerated under high temperature conditions, and Li^+ deposition at low temperatures.
Water immersion	• Soaking. • Used or stored under high humidity environment.	• Circuit corrosion, causing short circuit; • H_2O is decomposed to produce hydrogen and oxygen, causing a fire or explosion phenomena.

IV.A.1. Classification Of Indenture Level

Indenture level means functional level or structural level of a product, which is classified by the functional relationship or the complexity of the product. The purpose is to identify the analysis object so as to figure out the impact of failure modes from a certain level of products on other levels of products, including the final products. Initial indenture level is the first analysis level for the given product, in which the total and complete product level will be analyzed through FMEA analysis. The lowest indenture level means the lowest level of products, which determines the depth of the FMEA analysis (Ref. 11,12). According to the structural characteristics of lithium-ion battery, the indenture level is divided into three levels in this paper, as shown in Fig 5.

IV.A.2. Definition Of Reliability Block Diagram

Reliability block diagram describes the reliability relationship between the product and its components. It reflects the logic relationship of the failures of the product, which is used to analyze the influence of the product's failures. According to diagram of lithium-ion battery level division, the reliability block diagram of the lithium-ion battery is obtained as shown in Fig 6.

IV.B. Definition of Severity and Possibility

Severe degree refers to the severity of a failure or an adverse event, which is usually estimated by the possible ultimate consequences. Through the analysis of the safety accidents caused by lithium-ion batteries and the general definition of severity degree, the severity level of lithium-ion batteries and its definitions were obtained, as shown in Table IV.

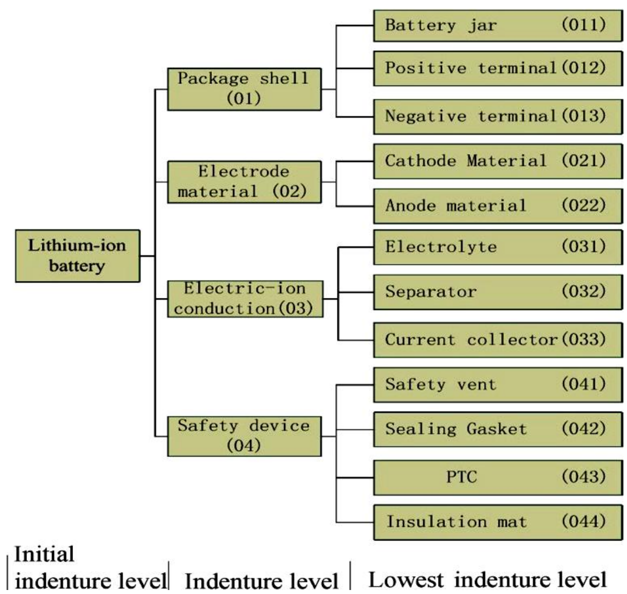


Fig. 5. Diagram of lithium-ion battery level division

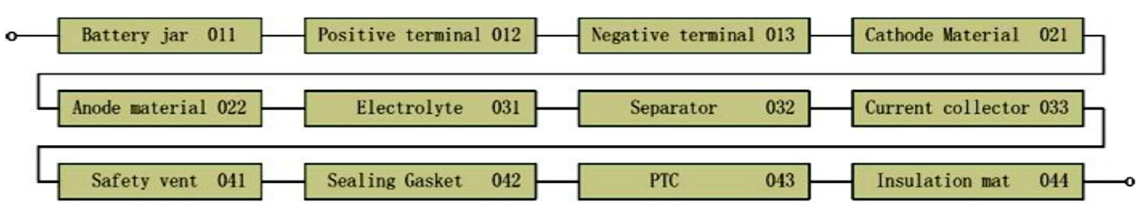


Fig. 6. Diagram of lithium-ion battery mission reliability

TABLE IV. Lithium-ion Battery Severity Levels and Definitions

Level	Value (S)	Definition
Catastrophic	4	Cause death or major economic loss and environmental damage
Fatal	3	Cause serious injury or equipment and batteries destruction, and serious environmental damage
Moderate	2	Cause personal injury or moderate economic loss, or result in mission failure, batteries and moderate environmental damage
Slight	1	Not enough to cause personal injury, or mild economic loss, or the mild damage to the battery and environment, but will lead to unplanned maintenance or repair

The occurrence probability of failure modes (i.e. occurrence degree) refers to the possibilities of a failure or an adverse event. In this paper, the occurrence probability of lithium-ion batteries accidents is creatively defined with Heinrich's law to backward induce the accident rate. According to Heinrich's 300: 1: 29 rule (Fig 7), among 330 adverse events, there are 300 attempted accidents; 29 minor or failure accidents; 1 serious or major accident causing death or severe injury.

Heinrich's law is actually the reflection of a general law between the accidents frequency and the severity of accident consequences. Originated from mechanical production accidents, it has been widely used in the safety analysis of many fields. For different processes, the types of accidents will be different. This law indicates that there will be a major casualty from the numerous accidents in the activity (Ref. 13). This law is also true to lithium-ion battery accidents, so this paper explores the feasibility of Heinrich rule to backward induce the accidents probability. Statistics data shows that there are thousands of lithium-ion battery safety accidents worldwide every year, and based on the Heinrich law, the higher the accident severity is, the lower the probability of the accident is, as shown in Table V.

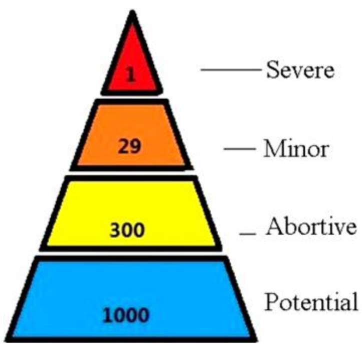


Fig. 7. Model of Hain's safety pyramid theory

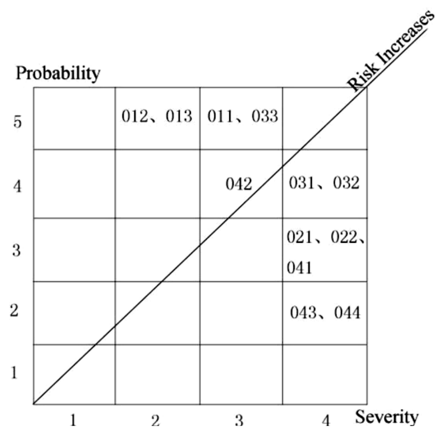


Fig. 8. Risk matrix of lithium-ion battery

TABLE V. Possibility of Lithium-ion Battery Accidents and Definitions

Level	Value (P)	Definition
Frequently	5	More than 1000 accidents occur each year
Probably	4	300 to 1000 accidents occur each year
Occasionally	3	30 to 299 accidents occur each year
Seldom	2	1 to 29 accidents occur each year
Impossible	1	Less than 1 incident occurs each year

Based on the above definitions of severe degree and occurrence degree, the risk matrix of lithium-ion battery was obtained, which is a way of combining qualitative or semi-quantitative consequences with the possibility of generating a certain level of risk or risk levels. Through the risk value calculation in Eq. 5, the risk matrix of lithium-ion battery was shown in Table VI.

$$R = S \times P \tag{5}$$

Where R is for the risk value (or damage degree), S is for the severity of the value, P is for the occurrence possibility.

TABLE VI. Risk Matrix of Lithium-ion Battery

$R = S \times P$		Severity			
		4	3	2	1
Possibility	5	20	15	10	5
	4	16	12	8	4
	3	12	9	6	3
	2	8	6	4	2
	1	4	3	2	1

According to the risk matrix, the risk levels of lithium ion battery can be divided into 4 grades, namely, I, II, III, IV. Grade I indicates "Intolerable" with the risk value in 12~20; grade II indicates "Do not want to happen" with the risk value is 8~10; grade III indicates "Tolerable under the control measures," with the risk value in 4~6; grade IV indicates "Tolerable" with the risk value in 1~3.

IV.C. FMEA Table

TABLE VII. FMEA Analysis Of Lithium-ion Battery

No	Function sign	Function	Failure Mode		Failure Cause	Failure Effect	Risk Level	Improvement Measures
01	Pack shell	Protect structure, connect circuit	011	Shell broken	·Lack of strength ·External damage ·Internal pressure or corrosion	·Battery damage ·Corrosion equipment	I	·Increase shell material strength ·Strengthen maintenance management
			012 013	Deformation and fall off	·Package defects ·Mechanical stress damage ·Internal corrosion		II	·Improve the packing process quality ·Strengthen maintenance management
02	Electrode-material	Electrochemical reaction release Li^+	021	Thermal-decomposition	·High voltage charge ·High environmental temperature ·Internal chain reaction	·Thermal runaway causes fire or explosion ·Equipment damage ·Casualties	I	·Avoid battery abuse ·Select the material of high thermal stability
			022	Generate lithium-dendrite or flammable-	·Over charge ·Lithium-dendrite or external stress pierces separator causing		I	·Avoid battery abuse; ·Adding polymer or inorganic material to make Li stable
03	Electric-ion Conduction	Conduct Li^+ and e^-	031	Release flammable and toxic gas,burn	·Over charge; ·PTC failure ·the temperature is too high	·Thermal runaway leads to fire or explosion ·Equipment damage ·Casualties	I	·Avoid battery abuse; ·Choose the good performance of PTC components and electrolytes
			032	Broken ,dissolution	·Not uniform separation ·Lithium-dendrite ·Internal exothermic reaction ·PTC failure		I	·Avoid battery abuse; ·Select good performance PTC components and separator materials
			033	Corrosion , fracture	·Active substance accumulates and stress corrosion occurs due to the not uniform metal foil	·Cell destruction ·Equipment corrosion	II	·Improve the battery manufacturing process
04	Safety Devices	Prevent accidents	041	Deformation and block	·Mechanical stress damage; ·The external environment pollution	·Over-pressure explosion ·Equipment destroyed ·Casualties	I	·Avoid battery abuse ·Strengthen maintenance management
			042	Crack, deformation,or leak	·Low temperature freezing burst ·Rubber aging	·Solution spillover ·Equipment corrosion ·Injuries	I	·Select seal ring of good performance ·Avoid battery abuse ·Strengthen the maintenance
			043	Short-circuit breakdown and sealing layer crack	·Resistance layer and electrode layer bonding strength is low ·Sudden change in	·Fire, explosion caused by thermal runaway ·Equipment destroyed	II	·Choose PTC of good performance ·Avoid battery abuse ·Strengthen the maintenance
			044	Crack and bubble	·Low temperature freezing burst ·Rubber aging ·Impurities	·Fire, explosion caused by short circuit ·Equipment destroyed	II	·Choose insulation pads of good performance ·Avoid battery abuse ·Strengthen the maintenance

Through the analysis of severe degree, occurrence degree and risk matrix, the FMEA analysis of lithium-ion battery was obtained, which is shown in Table VII..

IV.D. Safety Analysis

Through the analysis of the failure effects of indenture levels in the FMEA, the risk matrix of lithium-ion battery components of was obtained, as shown in Fig 8. By analyzing the risk matrix, the failure modes of lithium-ion batteries can be mainly described as thermal runaway, air or liquid leakage, current collector corrosion, safety device failure, etc. According to the "4M elements" (that is, Man-Machine-Medium-Management) in the safety science, the causes of lithium-ion battery accidents can be divided into: A. human factors: false charge/discharge, using at high temperatures, water immersion, and high strength of the collision, etc.; B. machine factors: component quality defects, production process defects and design defects, etc.; C. medium factors: high temperature, humidity and vibration, etc.; D. management factors: inadequate maintenance, delayed replacement of hazardous batteries, etc.

According to above accident reasons, the key points for safety design and accident prevention of lithium-ion batteries are listed as follows:

- *Key points for safety design: A.* selecting electrode materials with high thermal stability; *B.* avoiding the use of toxic, hazardous, flammable and explosive raw materials or reaction products; *C.* high safety and reliability of the design of safety protection devices and its components.
- *Key points for accidents prevention: A.* avoiding the storage or use of lithium ion batteries in harsh conditions, such as high temperatures, humidity or turbulence, and the recommended temperature for lithium-ion batteries use or storage is at range of -20~60; *B.* strengthening the maintenance management work and avoiding contamination, puncture or impact, etc. *C.* strict compliance with the usage regulations of lithium-ion batteries and prohibiting unsafe acts like overcharge or over-discharge in the high pressure or the continued work of failure batteries, etc.

V. CONCLUSION

Based on the deep understanding of lithium-ion batteries' composition and structure, this paper analyzed their thermal balance mechanism and the safety hazards and risk factors of their component materials on the one hand, and studied their failure modes, effects and perniciousness by FMEA. Finally, after analyzing the lithium ion battery risk matrix, the main failure modes of lithium ion batteries was obtained, and the reasons for the accident were explored according to the "4M Elements", thus putting forward key points for the safety design of lithium-ion batteries and suggestions for their accident prevention. The research results of this paper are beneficial to the prevention and avoidance of safety accidents caused by lithium-ion batteries, as well as to guiding the design, maintenance and protection of lithium ion batteries and their application system.

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