Research Progress on the Safety of LIBs Separators

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Abstract. Over the years, the electrification of transport has forced improvements in energy storage batteries. Lithium-ion batteries (LIBs) are widely used in aerospace, smart devices, electronic communications, and transport because of their high capacity, good cyclability, and environmental friendliness. However, battery safety is a massive issue in people's daily lives. LIBs occasionally suffer from spontaneous combustion and explosion. This is mainly caused by short circuits within the battery. The diaphragm, as the material separating the positive and negative electrodes, prevents the positive and negative electrodes from coming into direct contact, thus avoiding short circuits. The performance of the diaphragm determines the safety of LIBs. Therefore, this paper first introduces the causes of the thermal runaway of lithium-ion batteries and its relationship with diaphragms. Then, this paper presents the essential characteristics and types of high-safety diaphragms. Finally, this paper also summarises the physical and chemical modification methods of diaphragm materials in LIBs. This will help improve the safety of lithium-ion batteries, increase the electrification of transportation, and eliminate concerns about using LIBs.

Keywords: LIBs; thermal runaway; separators.

1. Introduction

LIBs are very efficient and widely used in today's society. These batteries are used to power the electrification of cars. In the past few years, LIBs have improved quality from different parameters, like the cycle life and the driving length for fully charged batteries. The battery has many significant components: cathode and anode, metallic current collectors, sometimes organic liquid electrolytes and maybe other inorganic metal electrolytes, and a porous polymeric separator [1]. There are many places where people use LIBs. For example, people use these batteries for mobile power, electric vehicles (EVs), home appliances, and even in the aviation area [2].

LIBs use the porous separator in the middle with electrolytes at the two sides of the battery; the cathode and the anode are connected with wires [1]. The wires only allow the electrons to move between the battery terminals, and the porous diaphragm accepts the movement of the lithium ions. The anode is lithium oxides, and the other sides contain lithium ions separated with the electrons between many graphene layers. When the battery is charged, the electrons move from the cathode to the anode in the wire, and the ions also move from the cathode to the anode by the porous separator. Then, the ions are volatile at one end. When the battery is discharged, the ions return to the cathode's position with oxides. Figure 1 shows the diagram of the LIBs structure [1]

Lithium-ion batteries are frequently used and are believed by people to be an effective energy storage device that swiftly increases living standards while lowering environmental pollution. The LIBs have many beneficial effects. For example, frequent fire and explosion safety incidents show that the safety of the battery is not very reliable [3]. One of the main reasons why thermal runaway occurs is that a short circuit occurs inside the LIBs under mechanical abuse, electrical abuse, thermal abuse, and so on. When the battery's internal temperature reaches a certain level, the safety valve will open and spew out high-temperature and high-pressure gases. If the ejected gas contains a sizeable combustible gas and meets air or an ignition source, it will satisfy the combustion conditions and cause a fire. An explosion may occur if the combustible gas mixes well and evenly with air in a confined space. The diaphragm is one of the critical components inside the lithium-ion battery, which is located between the positive and negative electrodes and can effectively separate the positive and negative electrodes, preventing them from coming into direct contact, thus avoiding the occurrence of a short circuit. Once the diaphragm is damaged, the positive and negative electrodes will come into direct contact, forming an internal short circuit, generating a large amount of heat and current, exacerbating the thermal runaway process. During the design, manufacture, and use of LIBs, a series of measures need to be taken to ensure the integrity and stability of the diaphragm and improve the battery's safety performance. Therefore, this paper focuses on the progress of high-safety LIBs diaphragms.

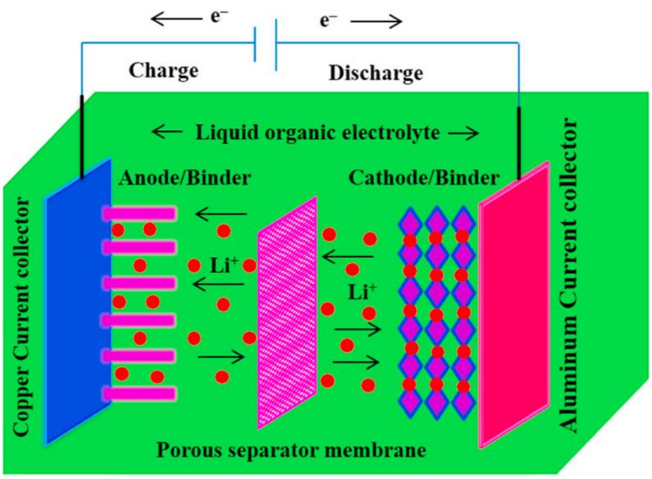

Fig 1. Structure of LIBs [1].

2. Thermal Runaway in LIBs

In daily life, people's safety concerns are the fires and explosions of lithium-ion batteries. The reason for that is mostly the loss of heat control of the battery.

The thermal runaway of the battery is an aspect of that phenomenon. There are a total of three exothermic reactions in the LIBs. The first is the reaction inside the LIBs related to carbon and oxides. These reactions are exothermic, which give out heat. For example, when the battery discharges, the LiC_6 will react with CoO_2 to form C_6 and $LiCoO_2$, which happen at the anode and cathode of the battery, respectively [4]. If the reaction changes to different kinds of metals without cobalt, the compound presented as MO_2, then the reaction becomes $LiC_6 + MO_2 \rightarrow C_6 + LiMO_2$ at discharge time [4]. The enthalpy change of this reaction can be calculated by the enthalpy change of the formation of carbon six plus the $LiMO_2$ subtracted from the reactants.

Table 1. Enthalpies of chemical reactions of batteries discharge [4].

Reaction	Enthalpy of reaction at 298 K(kJ/mol)
$LiC_6+CoO_2 \rightarrow C_6+LiCoO_2$	-351.7
$LiC_6+Ni_{0.33}Mn_{0.33}Co_{0.33}O_2 \rightarrow C_6+LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	-354.3
$LiC_6+Ni_{0.80}Co_{0.15}Al_{0.05}O_2 \rightarrow C_6+LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$	-349.6

From Table 1, it is easy to find that this reaction's enthalpy change is negative and exothermic. Meanwhile, the amount of heat transferred out is not only dependent on this reaction; the electrochemical energy of the batteries and the nominal capacity also contribute a lot [4]. Moreover, the thermal runaway also depends on the amount of lithium in the cathode, which relates to the first reason: the battery's capacity. The second reason is more related to the materials inside the lithium-ion batteries. As the LIBs are used, some nanomaterials will accumulate and form at the layer of lithium oxide, which results in the thermal runaway of the battery since it will react with the active layer of the battery [4].

Despite these, sometimes, effects from other electricity sources will also affect the normal function of the LIBs and cause the thermal runaway of the battery. Some currents beside the LIBs will cause a resonating current, which enlarges the current electromagnetic effect and more easily causes the overheating of the current [5]. The batteries are separated so the heat between the batteries does not accumulate in a complete circuit, which helps to reduce the possibility of thermal runaway of the batteries, increasing the safety for consumers [6].

During the thermal runaway process of lithium-ion batteries, the separator undergoes a series of changes. As the battery's internal temperature increases, the separator may gradually soften, melt, or even crack. These changes will cause the isolation between the positive and negative terminals of the battery to fail, triggering an internal short circuit and releasing a large amount of heat. Eventually, this heat can trigger the battery to smoke, catch fire, or even explode. The separator acts as a physical barrier between the positive and negative electrodes of the battery, and its integrity and stability are critical to prevent short circuits inside the battery. Once the diaphragm is damaged or fails, the positive and negative electrodes will come into direct contact, causing an internal short circuit, generating a large amount of heat and accelerating the occurrence of thermal runaway. In the event of an overcharge or elevated temperature, the high-performance separator separates the positive and negative electrodes of the battery through a closed-cell function, preventing them from short-circuiting due to direct contact. This closed-cell feature helps block current conduction and prevents the battery from overheating or exploding.

The thermal stability of the separator is also an essential factor affecting the thermal runaway of the battery. The diaphragm must maintain sufficient strength and integrity at high temperatures to prevent short circuits due to heat shrinkage or melting. If the diaphragm is not thermally stable enough, it cannot effectively isolate the positive and negative electrodes at high temperatures, increasing the risk of thermal runaway.

3. Feature of Separator Membrane in LIBs

3.1. Structure and Property of the Separator

The separators should have some functional value; for example, they must allow only free ions to move between the battery's terminals. For the safety of the LIBs and to reduce the risk of thermal runaway, the chemical stability of the separator is a very significant issue. They should be stable and inert since if they are reactive, the separator may dissolve inside the electrolyte and cause the electrons and ions to move together; this reaction will directly cause thermal runaway. The thickness of the battery is also critical.

For example, the separator membrane should be thin enough to allow the ions to move freely. However, the thin membrane may break and dissolve, which is also hazardous [1].

The second characteristic is the size of the hole between the terminals of the battery. The pore size is also a significant parameter. The pore should have the same size to perform uniform current inside the LIBs and increase the stability of the battery since the current will have a resonance effect on the average current [1,5].

The third characteristic is the permeability of ions passing through the separator membrane. Permeability is the time for a specific amount of material to flow through a set membrane area. The marvelous permeability of the separator helps the efficiency of the ion movement inside the battery, which may increase the current flow at each moment [1].

Finally, cost is also a significant concern. Better materials should be used to make the LIBs safe. However, the cost is also a very considerable concern when manufacturing. Cost efficiency, which balances cost and safety, is always required. If the LIBs have a meager cost, the material may need to be better and cause a thermal runaway. For example, inferior reactive materials may be used to deal with the separator, but inert material may need to be used here [1].

3.2. Different Types of Separator Membranes

There are many types of separator membranes.

The first one is the Microporous polymer separators, consisting of a single-layered organic membrane with an average pore size of 50 to 100 Å. The examples are polypropylene and polyethylene. These membranes have excellent stability and marvelous strength in physical properties.

For example, the PP membrane has a melting temperature of 160 degrees Celsius [1]. As an example, some high-temperature-resistant polymer composite films are examined. Gao et al. [7] prepared a PAN-PVDF composite nanofiber membrane composed of a polyacrylonitrile (PAN) core and a polyvinylidene fluoride (PVDF) shell by coaxial electrospinning. By comparing the optical images of different separators before and after heat treatment at 170 °C for 1h, it can be found that the PE separator almost disappeared at 170 °C. In contrast, the PVDF, PAN, and PAN-PVDF separators barely changed in size. In addition, the surface morphology of the separator after heat treatment showed that the pores of the PE separator disappeared utterly, and the PVDF and PAN-PVDF separators melted slightly. Hence, the PAN-PVDF separator had excellent thermal stability. Polyimide (PI) has outstanding high-temperature resistance and good thermal stability and can improve the high-temperature safety of the battery.

The second one is the Nonwoven separator membrane. These separators are made of fibrous materials, such as webs and artificial fibers. These products, used as separator membranes, are suitable since it has 200 degrees Celsius to melt and are a hydrophilic material, which attracts the electrolyte [1]. According to Wang et al. [8], the materials of the non-woven separator are mainly glass fiber, synthetic fiber, ceramic fiber, etc., which have good heat resistance and high porosity (up to 60%). The non-woven separator with a three-dimensional pore structure has a high liquid retention rate and can avoid the problem of short circuits caused by lithium dendrites.

The final one is the separators, which consist of inorganic materials. As an example, calcium carbonate is one of the ceramic separators. They have a high surface area, affinity with water, and fantastic performance when dealing with heat, with several 200 degrees Celsius, the same as the nonwoven membrane. Mechanical strength is also guaranteed [1].

4. Modification of Diaphragms in LIBs

Since myriads of problems may highly affect the stability of the LIBs, improving part of the battery is a significant method. In this article, the separator improvement can be a part of preventing thermal runaway. In this section, modifying the LIBs separator membrane is the significant point.

4.1. General Safety

There are some conditions and performances for a safe separator for the LIBs. Firstly, the separator should have a tremendous insulating ability, which prevents contact between the cathode and the anode, which is one of the most common reasons that cause the battery's thermal runaway. Then, as mentioned before, the porosity, the size of the hole in the diaphragm, and the mechanical strength are all the conditions required to keep the battery safe to work individually inside the circuit [8].

4.2. Physical Process

There are some ways of doing different manufacturing processes. The first one is the dry process, which involves melting and extruding polyolefin resin and additives into a film, followed by annealing and other heat treatment processes to obtain a multi-layer structured film, which is then stretched to prepare a porous membrane structure [9].

The second one is the wet process. It is to mix small high boiling point molecules with polyolefin resin by controlling the temperature to form a homogeneous mixture, then lay these mixtures flat on a surface and use the separation principle to reduce the temperature so that the mixture undergoes liquid-liquid or solid-liquid separation. Then, the high boiling point small molecules are extracted through certain volatile solvents and finally subjected to a heat treatment to obtain the membrane [10].

The third one is electrospinning, which is a unique process used to produce fibers involving the long-distance movement of polymer droplets under the action of a strong field. The droplets extend from a spherical tip to form 100-300 nm diameter polymer filaments. Then, by controlling the rapid evaporation of the solution, the filaments solidify to form a nanofiber film [10]. Then, there is a modification method for a better separator membrane for the physical modification. It is the spray method. The spray coating method refers to the process where a surface coating material solution passes through a nozzle, forming a small aerosol at the nozzle, which is then assimilated and treated to cover the surface of the diaphragm [11].

4.3. Chemical Changes

Then, there are some chemical changes in the diaphragm in the LIBs. The first method uses chemical and isoelectric methods. This means the diaphragm introduces a functional group on the surface, which is then connected by the chemical bonds. The other two are the radiation connecting method and the ultraviolet method, which cause the appearance of free radicals to let them connect, form covalent bonds, and reduce the chemical reactivity on the surface of the diaphragm [9].

4.4. Other Ways

Finally, there are other ways to prevent thermal runaway; for example, the diaphragm can be closed while the heat produces too much, preventing the current flow and stopping working. This example is PBS; it is used as a shell material because it has a strong affinity for liquid electrolytes and a suitable melting temperature. As shown in Figure 2, PBS with a low melting point in the composite material will close the partition at a critical out-of-control temperature to prevent lithium ions from passing through. In contrast, the PLA with a high melting point is a stable skeleton that maintains dimensional integrity. Due to its hydrophilic group and sufficient porosity, this dual-functional diaphragm has higher electrolyte affinity and ionic conductivity than the standard diaphragm, thus improving the cyclic stability of the LFP/C battery and showing a broad application prospect [12].

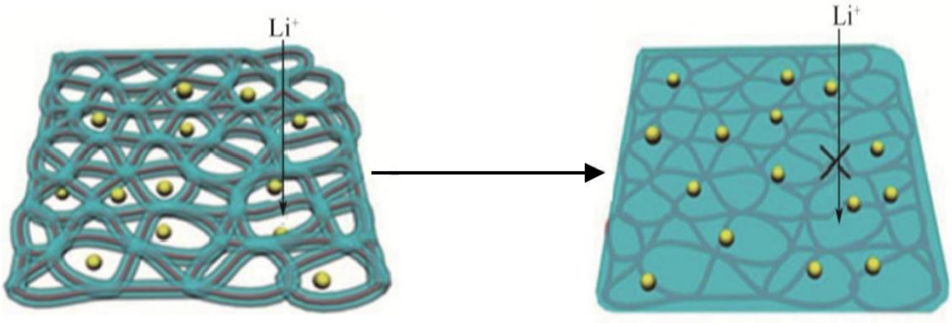

Fig 2. Structure of LIBs [12].

5. Conclusion

This paper discusses the causes of thermal runaway in LIBs and points out that diaphragms play an essential role in LIBs. Based on this, the paper summarises the crucial characteristics of diaphragms in high-security LIBs and introduces different diaphragm materials. In addition, this paper also proposes the chemical modification and physical modification of diaphragm materials.

Although many LIBs diaphragms have a certain degree of stability in high-temperature environments, some diaphragm materials are prone to melt or decompose at high temperatures, leading to a decline in battery performance or even triggering safety issues. Conductivity directly affects the transmission speed of lithium ions, which in turn affects the battery's power density and charging/discharging efficiency. Some diaphragm materials have relatively poor conductivity, limiting the improvement of battery performance. Diaphragms must withstand pressure and compression inside and outside the battery to protect the electrolyte and electrodes inside the battery. However, the mechanical strength of some diaphragm materials is relatively low, and they are susceptible to deformation or rupture due to external impacts.

In the future, new high-temperature-resistant materials, such as ceramic-coated non-woven diaphragms, should be developed to improve the high-temperature-resistant performance of Li-ion battery diaphragms to meet the needs of applications in high-temperature environments, such as electric vehicles and energy storage systems. Develop materials with higher conductivity, such as nanomaterials, conductive polymers, etc., to improve the conductivity of lithium battery separators. Improve the diaphragm's preparation process and structural design to improve its mechanical strength. Optimize the preparation process and equipment to improve production efficiency and reduce material costs. It is believed that with the progress of science and technology and in-depth research, these problems are expected to be solved, and lithium battery technology will be promoted to higher performance, lower cost, and more widely used direction.

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