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A Review on Lithium-Ion Batteries Safety Issues: Existing Problems and Possible Solutions

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Lithium-ion batteries have been considered to be the most competitive power source of electric vehicles (EV), hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV) and energy storage of green grid. However, as a solution to high energy density storage, lithium-ion batteries have been seriously plagued by the safety issues. In this paper, several key facts and corresponding mechanisms of battery safety issues, including overcharge, thermal runaway, lithium dendrites, current collector dissolution and gas evolution are detailed discussed. Additionally, based on the discussed safety issues, a few of efficient solutions to preventing safety issues, including redox shuttle, flame-retardant (FR) electrolyte additive and positive temperature coefficient (PTC) device, are introduced in brief. This review aimed to achieve deeper understanding the safety issues of lithium-ion batteries based on material chemistry and further develop corresponding positive strategy to these occurred issues.

Keywords: Lithium-Ion Batteries, Safety, Overcharge, Thermal Runaway, Redox Shuttle.

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1. INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used for popular power sources in portable electronic device in the past decades.[1,2] Recently, development of green energy technology have promoted the lithium-ion batteries into an extensive applying in the field of electric vehicles (EV), hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), green grid energy storage.[1,3] One of the key requirements for these batteries is numerous batteries in series or parallels to obtain high energy and high power. However, high energy and high power also bring more safety issues of lithium-ion batteries, which have seriously restricted the development of large-scale LIBs.[4–6]

The safety issues associated with LIBs may arise under abnormal abuse conditions. These abuse conditions include mechanical abuse behaviors (crush, nail penetration, drop, vibration etc.), electrochemical abuse behaviors (overcharge, over-discharge, short circuits of full or half charged batteries, gas generation etc.) and thermal abuse (external heating, flame attack, hot combustion gases from a fire etc.). In terms of the abnormal conditions, the mechanical abuse under the damaged conditions (crush or penetration) is significantly likely to cause immediate failure leading to cell thermal runaway. The electrochemical abuse, including forced overcharge, over-discharge or short circuits, will result in the considerable formation of dendritic lithium on the anode, dissolution of current collector, exothermic

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decomposition of electrolytes thus gas generation and heat generation and ultimately a thermal runaway reaction of the whole battery system. Also, the batteries experiencing external heating abuse will directly suffer heat attack and more rapidly undergo thermal runaway.

Under above abuse conditions, the safety issues of lithium-ion batteries usually associate forced increasing of internal material chemistry parameters, such as high voltage (HV) (overcharge), high temperature (HT) (thermal runaway), high pressure (HP) (gas generation) and high current (HC) (dendritic lithium short-circuit). Therefore, from the point of material chemistry view, the key technology to address safety issues of LIBs is to control the internal voltage (V), temperature (T), pressure (P) and current (I) in a normal range.

Currently, tremendous techniques and methods have been used to control these parameters (V, T, P, C) to prevent occurring of the LIBs safety issues with external or internal protection mechanism. The external protection mechanism usually used some of the system hardware devices, including electronic device, temperature senor and pressure valve, to protect the normal operating of LIBs. However, the failures of external hardware occur occasionally and become more likely in the abnormal conditions. Hence, developing the reliable internal protection mechanism combined with external protection system is particularly necessary for the safety of commercial LIBs. The developed internal mechanisms now are mainly focused on the safety improving of individual component, including cathode materials, anode materials, current collector, electrolytes, based on material chemistry.

In this paper, several key facts and corresponding mechanisms relative to safety issues of lithium-ion batteries will be given a detailed discussion based on material chemistry, to take a deeper understanding the safety issues of LIBs. The facts are mainly focused on overcharge, thermal runaway, dendritic lithium formation, current-collector dissolution, gas evolution and so on. In addition, the recent development of a few of solutions to safety protection of lithium-ion batteries will be introduced in brief.

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Jianwu Wen received his M.S. degree in Material Science & Engineering from University of Science and Technology of China (USTC) in 2007. He is currently undergoing his Ph.D. work in the same university. His research area deals with materials for energy storage and energy conversion. He is currently engaged in the research of key material and new method for lithium-ion batteries combining excellent electrochemical performance and safety.

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2. KEY FACTS AND MECHANISMS OF SAFETY ISSUES OF LITHIUM-ION BATTERIES

The popular positive 4 V intercalation compounds, such as $LiCoO_2$, were initially introduced by Goodenough in 1980.[7] Meanwhile, layer graphite material was found to be highly reversible Li-intercalation at a low voltage versus Li/Li^+ (0.2 V).[8] The Sony Corporation used this first $LiCoO_2$/C lithium-ion battery to the telephone cell to achieve the commercialization of lithium-ion batteries. The electrochemical energy storage reaction is finished as following:[1,9]

During the charging process, lithium-ions are removed or deintercalated from layered oxide compounds as cathode (positive electrode) and migrate towards the anode (negative electrode) into the graphite layers. Meanwhile, charge balancing electrons transfer charge from the cathode through the external circuit into the anode of the battery to achieve the electrical energy storage (Fig. 1). During discharging, the same process occurs but in the opposite direction. Once an external load circuit is completed electrons pass back from the anode to the cathode and the Li ions travel back to the anode.

Therefore, the whole system of commercial lithium-ion batteries are usually composed of Li-contained oxide cathode (e.g., $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$), layered anode compounds for Li-intercalation (e.g., graphite C), liquid electrolyte, polymer separator (polypropylene (PP) or polyethylene (PE)), current collector (Cu, Al foil) and some additional attachment (electronic circuits, tabs and shells). The liquid electrolytes usually consist of lithium salt ($LiPF_6$) and a mixture of nonaqueous organic alkyl-carbonate solvents (ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl-methyl carbonate (EMC)), which are highly flammable compounds.

The safety issues of the lithium-ion batteries are mainly caused by the failure of individual components (cathode, anode, electrolytes or current collector) and the whole system of battery in some abuse conditions, including overcharge, thermal runaway, dendritic lithium growth, current-collector dissolution, gas evolution and so on.

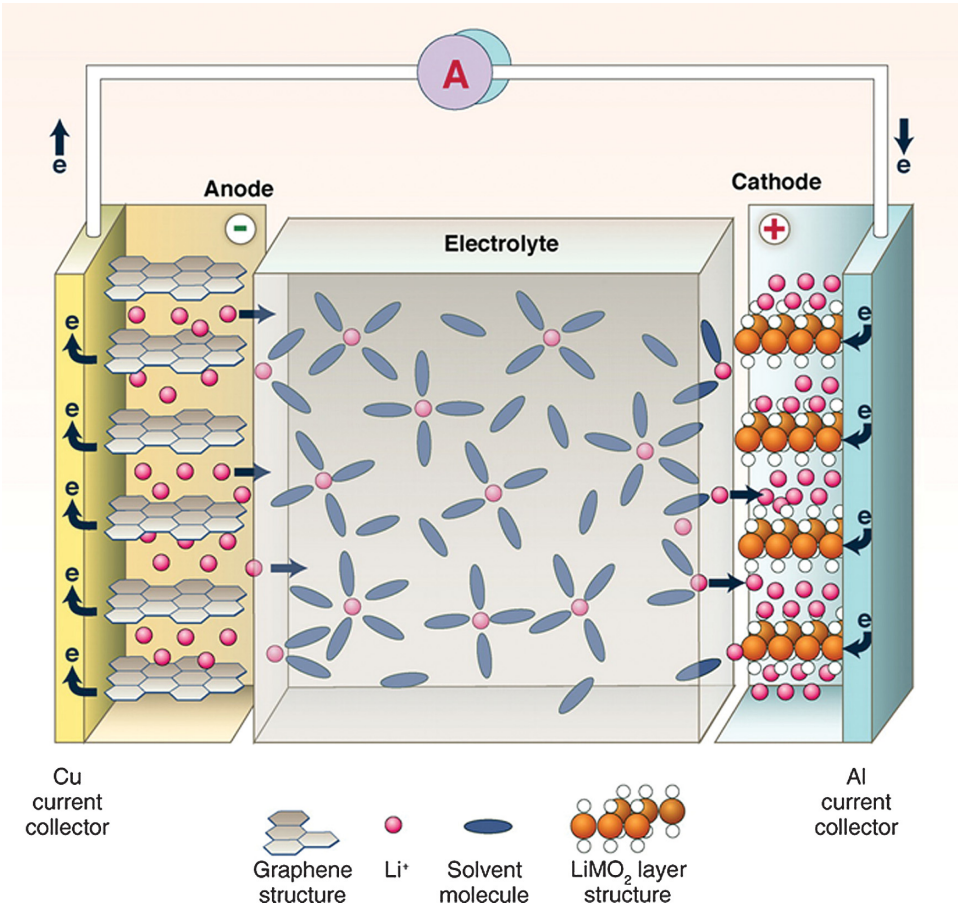

Fig. 1. Schematic model of a lithium-ion battery (LIB). It is commonly composed of layered oxide cathode, graphite anode material, organic flammable liquid electrolyte. Both of the electrodes materials are able to reversibly insert and remove lithium-ion. Reprinted with permission from [1], B. Dunn et al.; Electrical energy storage for the grid: A battery of choices; *Science* 334, 928 (**2011**). © 2011, Science.

Review

2.1. Overcharge

Overcharge, often caused by failure and malfunctions of the cell charger, is one of the most important safety issues for the state-of-the-art lithium-ion batteries. Overcharge can lead to thermal runaway and ultimately to fire or explosion of the batteries. Therefore, it is necessary to understanding the real mechanism of LIBs under overcharge conditions to prevent it efficiently.

By definition,[10] overcharge is a state when electricity flow is forced through the cell after its designed capacity is already full. Based on the $LiCoO_2$/$LiPF_6$-EC-DEC/C (graphite), the whole overcharge process of lithium-ion batteries can be roughly divided into the following stages:
(1) At the first stage, normal charge process (2.8–4.2 V), lithium ions deintercalated from cathode material ($LiCoO_2$) will migrate towards the anode material (graphite), when charge process occurs within the normal up-limit voltage (4.2 V). At the same time, the positive and negative potential will increase and decrease respectively, thus the battery voltage, calculated by the difference between positive and negative electrode potential, reaches the end of the maximum in the limited voltage range when the charge is completed. The normal working potential of lithium-ion batteries is mainly related to the crystal structure and Gibbs free energy changing of Li-intercalating/deintercalating from the electrode materials.[11] Hence, the normal voltage range is different for different positive electrode materials in terms of negative electrode fixed for the graphite material. To maintain the high reversibility of lithium intercalating and de-intercalating, the voltage is designed to be in normal range according to reversibility of crystal structure and phase transition. For $Li_{1-x}CoO_2$ cathode material, in order to maintain the stability of the crystal structure of the compounds and provide efficient reversible capacity, the reversible de-intercalated lithium from the layers is only 50% ($x = 0.5$), the corresponding voltage upper limit to which is about 4.2 V. Generally, charge and discharge within the normal voltage range (2.8–4.2 V) only cause minor changes of interlayer spacing of $LiCoO_2$, and can not destroy the crystal structure of the compounds.[12] The batteries in this period can operate safely.
(2) At the second stage, the battery voltage will increasingly exceed the designed up-limited voltage with charging process continued, namely overcharge occurs. Overcharge will result in excess of lithium de-intercalation of $Li_{1-x}CoO_2$, until lithium is removed near 100% ($x \approx 1$). Excess of lithium de-intercalation ($x > 0.5$) will cause the irreversible phase transitions and then the collapse of the $Li_{1-x}CoO_2$ crystal structure, evidenced by Co deposition on the anode surface,[13,14] and will be responsible for the large mounts of the irreversible capacity.[12] The $Li_{1-x}CoO_2$ will experience a series of phase transitions (H1, H2, M1, H2, M2 and O1) and two two-phase coexistence regions (H1 + H2 stage for $0.1 < x < 0.22$ and H2 + M2 stage for $0.75 < x < 0.85$),[15–17] ultimately $Li_{1-x}CoO_2$ converts to CoO_2[18] which decomposed to Co_3O_4 with O_2 generation.[19,20] Meanwhile, overcharge will cause lithium deposition (mossy or dendritic type) on anode surface when Li-intercalating in graphite exceeds designed value. The formation of lithium dendrites are more likely to lead to large internal short-circuit and then produce high current (HC) hazard (detailed in 2.3 Section).[21]
(3) As nearly all of the lithium ($x \approx 1$) are removed from $Li_{1-x}CoO_2$, the voltage is suddenly increased to higher value.[14] During this higher voltage process, some new oxidation-reduction reactions will occur on the surface of cathode to maintain the excess current. In this condition, the reactions include the release of O_2[19,20] and the decomposition of organic flammable electrolytes.[19,22] The exothermic decomposition of the electrolytes will release large mounts of gases, such as CO_2, CO, H_2, CH_4, C_2H_6 and C_2H_4,[19,22] resulting in the internal high pressure (HP). Meanwhile, a lot of heat generation will lead to internal high temperature (HT) triggering the thermal runaway thus serious safety problem, such as fire even explosion.

From the point of scientific view, overcharge is a comprehensive problem, which is related to intrinsic stability of materials (electrode materials and electrolytes), interface reactions, thermodynamic and kinetic properties and so on. Overall, overcharge often results in high voltage (HV), which is one of the most important factors to arise high temperature (HT), high pressure (HP) and high current (HC), associating serious safety problems. Therefore, maintaining the voltage within the designed normal range is the fundamental solution to solve the overcharge safety problem.

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2.2. Thermal Runaway

Thermal runaway is usually related to temperature rise mainly originating from the external or internal heat generation during the abnormal abuse.

Based on Li-ion battery with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode and MAG-10 graphite anode in 1.2 M EC:EMC (3:7 by wt.) electrolyte,[20] thermal runaway process of externally heated LIBs can be described as a three stages:
(1) low-rate anodic reactions initially occurred at 90 °C and were steadily accelerated with temperature rise. Solid electrolyte interphase (SEI) layer breakdown occured by 120 °C, leading to large electrolyte reduction at the surface of lithiated graphite anode.
(2) Exothermic reactions of cathode materials started at 140 °C, which were dependent on the composition and charge state of cathode materials.
(3) the cathode materials generated O_2 and triggered the interfacial oxidation of the electrolytes at above 180 °C, leading to high-rate thermal runaway with the temperature rise as fast as 100 °C/min.

Thermal stability of the individual components (cathode, anode and electrolytes) and the whole system of battery is an important factor to the heat generation during the external heating.[5, 23–30] In terms of the safety choice of numerous cathode materials ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ etc.), MacNeil et al.[26] took a detailed investigation on the thermal stability comparing of several cathode materials, including $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiNi_{0.7}Co_{0.2}Ti_{0.05}Mg_{0.05}O_2$ and $LiFePO_4$. From their results, $LiFePO_4$ have the best thermal safety, even though it has the largest specific surface areas due to carbon coating. The thermal behaviors of anode, electrolytes or coexistence of both have been given a detailed discussion.[23–25, 30]

The internal heat generation has a close relationship to the overcharge abuse of the battery. During overcharge process, the DC resistance rapidly increases at the 100% charge state, meanwhile, the sharp rise of the temperature occurs due to joule heat. In the low-temperature state, generated heat is almost proportional to charging current.[31, 32] Thermal behavior of the overcharged batteries during high temperature conditions is analogous to the one under external heating condition. Above 150 °C, autocatalytic exothermic reaction of Li_xCoO_2 occurs and melting of deposited lithium metal on the graphite anode during overcharge takes place at 180 °C, which leads to a strongly exothermic reaction with electrolyte.[33] Additionally, it is noted that the heat generation during overcharge is mainly related to the cathode interface rather than anode interface.[32] Sustained overcharge process will result in internal temperature and pressure increasing leading to thermal runaway and ultimately rupture of batteries.

In conclusion, the thermal runaway during continued heat-generation conditions should be related to continued self-generated heating, which is commonly caused by crack of SEI layer, improved O_2 generation from cathode oxide materials,[20] charge state of the batteries, the species of the electrode materials[26] and autocatalytic thermal decomposition reaction of the electrolytes ($LiPF_6$ dissolved in EC, DEC, DMC solvents).[28] Also, the heavy and rapid heat generation can be caused by the internal or external short-circuit accidentally. Short circuits often result from the dendritic lithium plated on the anode surface during overcharge, which will be discussed in the following section (2.3 Section).

2.3. Dendritic Lithium

The formation of dendritic lithium is one of the most common and important factors leading to internal short circuits of lithium-ion battery. Dendrite lithium grown on the surface of anode will puncture the polymer separator and connect the positive and negative electrode, leading to short circuits of batteries. Considerable efforts have been devoted to deeper understanding the existence of lithium dendrites, formation mechanism and influencing factor to prevent its formation on anode surface on the various conditions of battery cycling.[21, 34–48]

Orsini et al.[34] performed *in situ* scanning electron microscopy (SEM) observation of Li morphology on the anode interface with bellcore-type $LiMn_2O_4$/Li batteries and investigated the influence of the current density on the morphology of the lithium. They found that dendritic lithium growth occurred on the surface of anode at 4.5 V with 1 C charging current (Fig. 2), while only mossy lithium layer formed at 4.5 V with C/5 charging current. Hence, it can be concluded that there is a close correlation between Li-dendrite formation and the current density. The larger amounts of dendritic Li often occur at the higher current densities.

Kim et al.[36] investigated the lithium-dendrite growth difference between Li foil and Li powder compacted electrode as working electrode in organic $LiPF_6$/EC-DMC electrolytes. Using compacted Li powder as anode electrode materials, dendritic Li growth was restricted due to more lithium crystal boundaries, which provided more high-diffusivity paths of Li^+ in SEI film and efficiently reduced the localization of the charging current. The explanation was well confirmed by the results that compacted electrode with smaller size Li powder showed less dendritic Li growth under the same charge condition.

Brissot and Rosso et al.[35, 39] performed the dendritic Li growth evolution process with *in situ* Charge Coupled Device (CCD) camera technology in symmetrical Li/polymer/Li cells under galvanostatic condition. The polymer electrolyte consists of poly(ethylene oxide) (PEO) and a $LiN(SO_2CF_3)_2$ lithium salt (LiTFSI). Their experiments well showed the evolution of dendritic Li with time (Fig. 3(a)). The evolution of the cell potential reflected the evolution of the dendrites, which further confirmed the

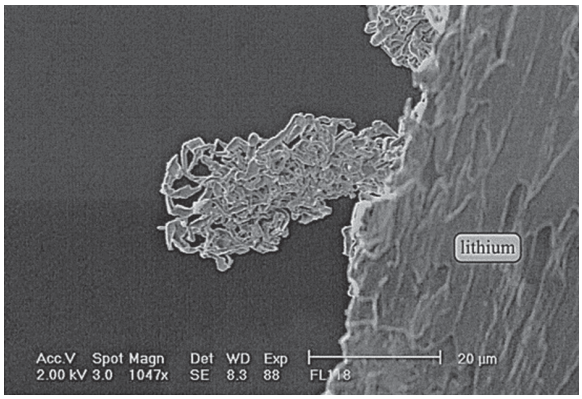

Fig. 2. Lithium dendrite formed on the anode surface of bellcore-type $LiMn_2O_4$/Li battery after first charge at 1C (2.2 mA/cm^2). Reprinted with permission from [34], F. Orsini et al.; *In situ* scanning electron microscopy (SEM) observation of interfaces within plastic lithium batteries; *J. Power Sources* 76, 19 (**1998**). © 1998, Elsevier.

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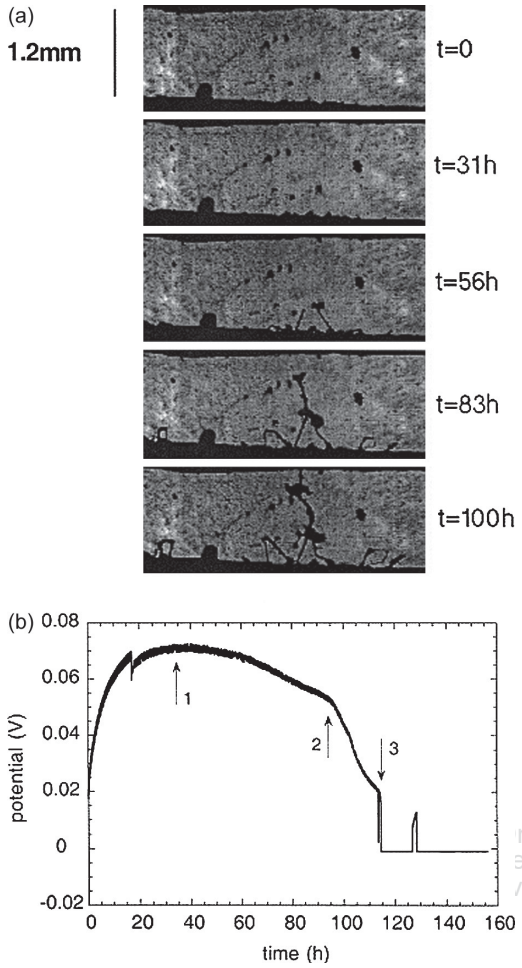

Fig. 3. Time variation of the dendrites observed in the inter-electrode space while polarizing the cell with $J = 0.05$ mA/cm^2, with symmetrical Li/PEO-LiTFSI/Li cells under galvanostatic condition. (a) SEM observation of lithium dendrites with time. Dendrites are seen to be needle-like. (b) The evolution of the cell potential reflects the evolution of the dendrites. Reprinted with permission from [35], C. Brissot et al.; Dendritic growth mechanisms in lithium/polymer cells; *J. Power Sources* 81–82, 925 (**1999**). © 1999, Elsevier.

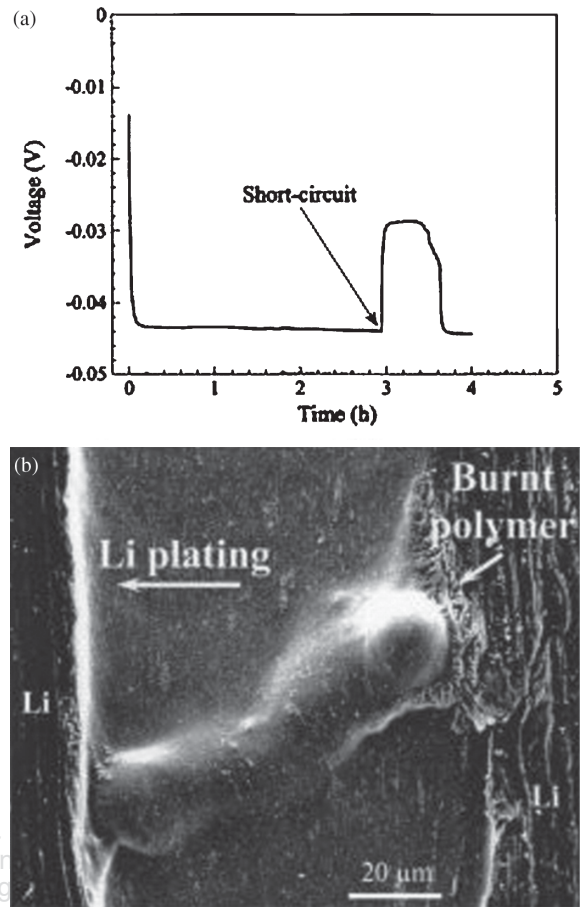

Fig. 4. SEM experiment for symmetrical Li/PEO-LiTFSI/Li cells under galvanostatic polarization condition: (a) Voltage profile of a symmetric cell upon polarization with time and (b) Symmetric cell cross section just after the accident in the voltage profile (short-circuit). Reprinted with permission from [37], M. Dolle et al.; Live scanning electron microscope observations of dendritic growth in lithium/polymer cells; *Electrochem. Solid-State Lett.* 5, A286 (**2002**). © 2002, The Electrochemical Society.

mechanism of short-circuit process. The process consisted of three steps:

(1) The dendritic Li growth was hardly observed during the initial potential evolution over a long period of time (Fig. 3(a) $t = 0$ h to 38 h). The potential varied slightly with the growth of Li dendrites (Fig. 3(b) arrow 1);

(2) Single Li dendrites reached the opposite electrode (Fig. 3(a) $t = 100$ h) and caused the decreasing of potential (Fig. 3(b) arrow 2);

(3) The potential exhibited sharp decreasing and strong short-circuit occurred finally (Fig. 3(b) arrow 3).

In addition, they performed SEM observations just after a short-circuit occurred with the same Li/PEO-LiTFSI/Li polymer symmetric cells.[37] When the cell potential displayed a sharp decrease (Fig. 4(a)), a grown lithium dendrites went across the polymer from left to right and touched the surface of opposite electrode, resulting in short circuits (Fig. 4(b)). More interestingly, the polymer was different at the dendritic extremity, as if it had burnt when the dendrite short-circuited the cell. The observation further confirmed the existence of thermo-fusible effect on the tip of the Li dendrites.

In addition, Li fiber growth on the tip of SnO_2 nanowires[44] and Si nanorods[43] were also observed during *in situ* charging with nano-lithium-ion-battery equipments inside a transmission electron microscope (TEM) microscope. The tip growth of lithium fiber was attributed to strong electric field enhancement on the sharp tip of nanowires or the end of nanorods.

Therefore, the generation of lithium dendrites is frequently encountered in a variety of conditions. Dendritic lithium formation has close relationship to the local current density, diffuse channels of lithium ion (kinetics properties) and stable solid electrolyte interphase (SEI) film on the surface of anode. The safety hazards caused by

lithium dendrites should be prevented from in terms of the above aspects, among which, the SEI film-forming additives should be an efficient solution because it can promote formation of SEI film of electronic insulation to cut off electronic channels of lithium dendrite growth reaction.[4]

In order to prevent the presence of lithium dendrites more efficiently, developing more tools or methods to study lithium dendrites is also very important. Currently, some available experimental methods, including the *in situ* TEM[44] and SEM,[34] have been established to make a qualitative research of lithium dendrites. From the aspect of theoretical modeling the dendritic lithium growth, a few of the studies taken so far are mainly focused on the morphology (the size, shape and growth) of dendritic lithium.[21,38] However, it is necessary to develop some efficient quantitative experimental methods, such as *in situ* NMR,[41] to make a deeper and more detailed understanding the mechanism and negative impacts of lithium dendrites.

2.4. Current-Collector Dissolution

Short-circuit of lithium-ion batteries is an important safety issue, because of its ability to instantly generate a huge current, leading to the rapid increasing of heat generation and temperature, consequently leading to the safety problems.

The internal short circuits of lithium-ion batteries are usually due to the local existence of the highly conductive metal substance, which will establish local current channels between cathode and anode electrode in the internal battery. The conductive metals triggering the internal short circuits may mainly include Al, Cu and Fe, for the components of state-of-the-art lithium-ion batteries.

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Al is extensively accepted as the cathode electrode current collector (Fig. 1) for commercial lithium-ion batteries. Generally, Al is chemically stable in air and aqueous conditions due to its natural surface oxide film, Al_2O_3. Under alkylcarbonate electrolyte solutions containing $LiPF_6$ salt, a stable and dense passivation layer is achieved by the formation of top layer AlF_3 on the Al_2O_3 layer of the Al metal surface (Fig. 5), which has been efficiently observed and proved by extensive efforts.[49–53] The bottom Al_2O_3 passivation layer is easily formed in air, while the formation of stable AlF_3 layer on top is caused by following reaction:

$$Al + 3F^- \rightarrow AlF_3 \quad (1)$$

The F^- is produced by the hydrolysis reaction of $LiPF_6$ with the inevitable trace water impurity often contained in the $LiPF_6$ electrolytes. Under the normal operating voltage (>2.5 V), the double passivation layers containing AlF_3 and Al_2O_3 on the surface of Al current collector provide a stable protection to prevent the persistent corrosion of $LiPF_6$ at least to some extent.

However, the stability of this passivation layer is remarkably dependent on the species of Li salts and

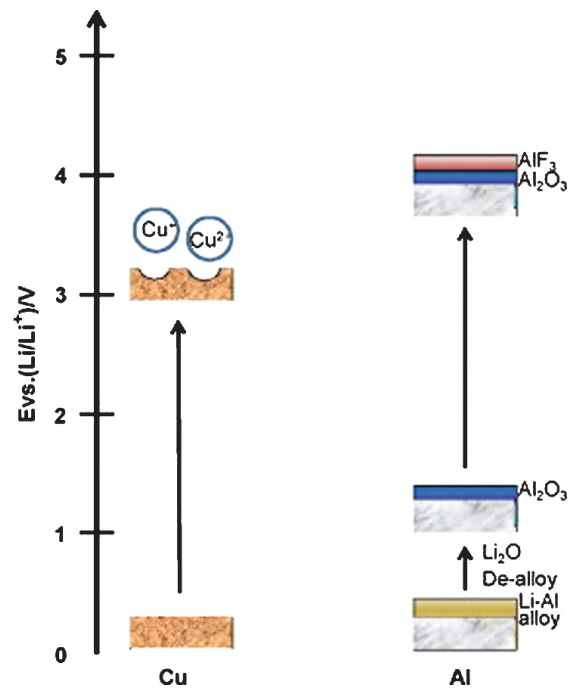

Fig. 5. Schematic drawings of electrochemical reaction of Cu and Al as current collector under a non-aqueous alkyl carbonate solution containing $LiPF_6$ salt. Reprinted with permission from [53], S. T. Myung et al.; Electrochemical behavior of current collectors for lithium batteries in non-aqueous alkyl carbonate solution and surface analysis by ToF-SIMS; *Electrochim. Acta* 55, 288 **(2009)**. © 2009, Elsevier.

organic solvents in electrolytes. The electrolytes containing $LiN(SO_2CF_3)_2$ (LiTFSI)/EC are highly corrosive against Al metal.[51] In addition, during the longtime cycles (Fig. 6), the severe corrosion occurred not only for $LiMn_2O_4$ (Fig. 6(a)) but also $LiFePO_4$ (Fig. 6(b)), although corrosion of Al surface for $LiFePO_4$ was better than $LiMn_2O_4$, due to the lower operating voltage for $LiFePO_4$.[54]

For Al current collector, the corrosion and dissolution effect is an important factor leading to micro-short-circuit of lithium-ion batteries. It is because of the following factors:

(1) The dissolution of Al current collector may cause formation of some dendritic Al deposited on the anode edge or surface resulting in micro-short-circuit;

(2) The corrosion of Al current collector will bring about the random diffusion of Al fragments, which will lead to a short circuits between the positive and negative electrode when Al fragments diffuse to the positions easily touching both of the two electrodes.

(3) Serious corrosion will also lead to crack extension and the detachment of the active materials, consequently result in the performance degradation and even failure of the whole battery.

In addition, at the potential close to 0 V, the Li–Al alloy process can occur leading to the pulverization of Al foil.[53]

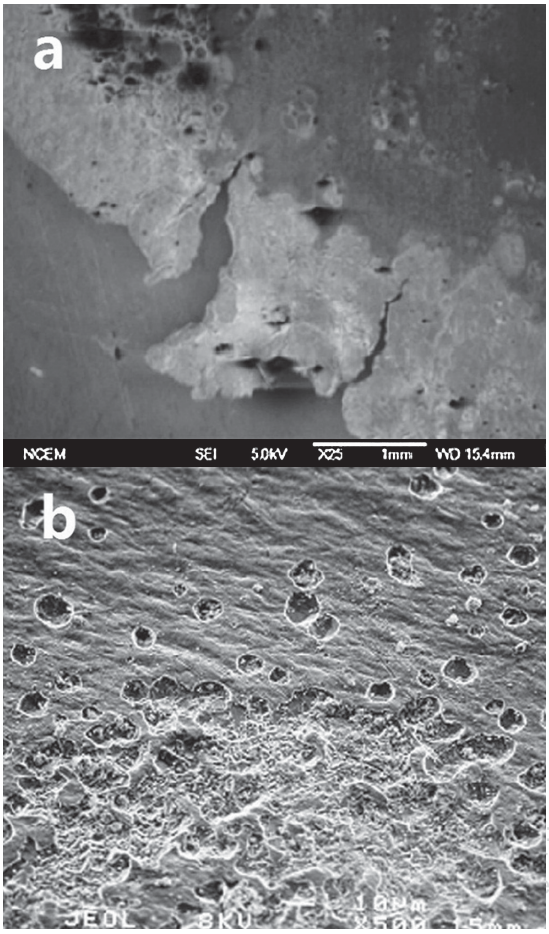

Fig. 6. (a) SEM of severe corrosion that occurred at the edge of the Al current collector of cells with $LiMn_2O_4$ positive electrode material after cycles; (b) Low magnification SEM of Al current collectors after extensively cycled $LiFePO_4$ material. Reprinted with permission from [54], X. Y. Zhang et al.; Corrosion of aluminum current collectors in lithium-ion batteries with electrolytes containing $LiPF_6$; *J. Electrochem. Soc.* 152, B448 (**2005**). © 2005, The Electrochemical Society.

Nevertheless, it is still generally accepted as a stable positive electrode current collector because of commonly far higher positive potential than Li–Al alloy.

Compared with Al foil, Cu foil, generally as negative current collector in LIBs (Fig. 1), is relative stable in a lower voltage range (<3 V). However, when the battery is overdischarged, the relative high potential (around 3 V versus Li/Li^+) at anode will occur leading to the dissolution of Cu metal (Fig. 6). The dissolution of Cu will be deposited on the surface of negative electrode, causing the safety problems due to short circuits.[55]

Therefore, overcharge or over-discharge of batteries will result in the corrosion and dissolution of Al or Cu current collector thus triggering the safety issues of lithium-ion batteries. Based on the fact that electrolyte salts anion have some negative effects to Al passivation layer, some electrolyte salts, such as LiBOB or LiODFB, have been selected to prevent the corrosion of Al foil.[56, 57]

In addition, Fe metal impurity should be primarily considered for the lithium-ion batteries based on $LiFePO_4$ cathode material. In terms of restrictions due to necessary reducing atmosphere or carbon during synthesis process, for $LiFePO_4$, a small amount of Fe metal impurity phase is difficult to avoid. However, the presence of a small content of Fe is likely to result in the micro-short-circuit, even high short-circuit giving rise to serious degration of performance or safety problems of LIBs, especially serious for large-scale LIBs.

2.5. Gas Evolution

In fact, the gas evolution is a commonly encountered phenomenon in the aqueous Ni–Cd or Ni–MH cells. In Ni–Cd or Ni–MH systems, the generated gas (e.g., O_2) under overcharge condition can diffuse to counter electrode then be reduced to the OH^-, so-called "O_2 cycle".[58] However, for lithium-ion batteries, this natural consuming-gas mechanism is not existed.

As described above, the electrolytes generally accepted in the lithium-ion batteries are mainly composed of organic and flammable liquid electrolytes containing a lithium salt ($LiPF_6$) and a mixture of organic alkylcarbonate solvents, such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC). With a voltage of around 4 V level in common lithium-ion batteries, almost no electrolyte is thermodynamically stable towards each electrode. Hence, interface reactions will occur between the surface of electrolytes and electrode all the time. Gas generation in lithium-ion batteries is remarkably relative to these interface reactions between the organic solutions and positive or negative electrode.

Lithium-ion batteries can generate gas under following conditions: the normal cycling, normal storage, overcharge and high temperature due to the internal or external heat. The mechanisms of gas generation in various conditions of battery have been detailed investigated.[5, 14, 19, 20, 22, 28, 30, 59–66]

For one fresh lithium-ion battery, the first charge process usually associates the phenomenon of small amount of gas generation, which is related to the formation of SEI film.[22, 60, 65] The evolved gases associating the first charge were mainly composed of H_2, C_2H_4, and CO. It was confirmed that the C_2H_4 and CO were exclusively formed from EC reduced on anode.[63, 66] In fact, for one fresh lithium-ion battery, it usually has experienced the battery formation to vent gas before its application. After this treatment, the problem of gas generation caused by the formation of SEI layer has been solved.

During the normal cycling within the designed voltage range, the gas is generated mainly due to ester exchange reactions.[19] The detected gas species may include CO_2, CO, CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. Among the gases,

CO_2 is generated by oxidation of the electrolytes on the cathode surface and the hydrocarbons (CH_4, C_2H_4, C_2H_6) and CO are produced from the anode surface by the reduction of the electrolytes (DEC, DMC and EC). It was also found that the species of the gas during normal cycling is not related to the type of cathode materials ($LiCoO_2$, $LiMn_2O_4$ or $LiFePO_4$),[22] further implying the fact that the gas under normal cycling is produced from the electrolytes. Although the species of gases are more, it is noted that the amount of the gas products during the normal cycling is very little.[19]

During the overcharge conditions, for $LiCoO_2$ batteries, the species of the generated gas are the same as the normal cycling, but the amount of gases increases with the rising of charging voltage. More CO_2 were generated for $LiCoO_2$ batteries due to its stronger oxidation ability than $LiFePO_4$. The generation of CO_2 has close relationship with the oxidation of electrolytes due to the O_2 generation from the over-delithiated $LiCoO_2$ compounds.[19,22] Ohsaki et al. designed an H-type glass cell to collect gases produced from cathode and anode respectively. Their results showed that carbon oxide gases (CO and CO_2) were chiefly generated at the cathode. As for the anode, H_2 gas was the main component of the evolved gas, containing small amounts of hydrocarbons (CH_4, C_2H_4, C_2H_6), CO and CO_2.[14] These results further proved that stronger oxidation ability and reducing ability were exhibited on cathode and anode respectively under overcharge conditions than normal conditions. However, by comparing, more C_2H_2 were produced in $LiFePO_4$ batteries, implying its weaker oxidation than $LiCoO_2$.[22] In addition, O_2 generation might be present during the first charge to 4.5 or 4.6 V versus Li/Li^+ in Li-rich composites (e.g., Li_2MnO_3), which should be related to the recent discovered oxidation of oxygen anions.[64] This kind of mechanism of O_2 release was not paid enough attention in the past.

Under over-discharged condition, electrolytes mainly undergo reduction reaction and generally generate mainly hydrocarbons for $LiCoO_2$ batteries.[19]

Under high-temperature storage conditions, according to Onuki's results, for $LiNi_xCo_yAl_{1-x-y}O_2$/graphite batteries,the generated gas species during storage are CO_2 and CO, both of which are mainly from the reduction of EC.[63] And the CO_2 evolution occurs from the cathode surface, but the CO evolution occurs from both of the cathode and anode surface. The results indicate that EC is more easily reduced on anode than DEC.[59,63]

Additionally, the generation of gas often associates thermal runaway or the increasing temperature of batteries. When the temperature reaches to the thermal decomposition conditions (85–100 °C), the electrolytes will generate highly toxic compounds such as alkyl fluorides and the fluorinated phosphorous compounds, alkyldifluorophosphate (OPF_2OR) and dialkylfluorophosphate ($OPF(OR)_2$), by the autocatalytic reaction.[28,61,65]

In conclusion, gas generation in lithium-ion batteries mainly originates in the interface reactions between the organic solutions and positive or negative electrode in various conditions of batteries operating. The amount of the gas under normal conditions is very little and more gas will be generated in abuse conditions, including overcharge, over-discharge and thermal abuse. More gas generation will lead to the increasing of the internal pressure of the batteries thus explosion once the pressure reach a critical point. Currently, safety valve is a relative efficient method to prevent the explosion under high pressure by opening the valve in advance. Additionally, as we know, the stable SEI film is helpful to preventing gas generation during cycling or storage. It is interesting that the battery with $Li_4Ti_5O_{12}$ anode material, a typical one without the SEI-layer formation due to its working potential range is higher than SEI formation potential (0.8 V), did not generate any gaseous decomposition products during the high temperature storage (100 °C for 12 h) compared with the graphite-based batteries.[62] It should be related to its higher potential than the decomposition potential of the electrolytes, which will need further detailed investigation to be proved.

Generally, the safety issues mentioned above often occur synchronously. In fact, for example, overcharge usually associates thermal runaway,[31,32] gas generation[14] and short circuits,[41] corresponding to high temperature (HT), high pressure (HP) and high current (HC) respectively. These associated safety problems practically originate in high voltage (HV) and high temperature (HT) of lithium-ion battery during overcharge. Therefore, several possible methods to avoid these safety issues should be considered, including redox shuttle additive, flame-retardant (FR) additive, positive temperature coefficient (PTC) device and so on, which are all based on the efficient response to the HV or HT.

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3. SOLUTIONS TO SAFETY ISSUES FOR LITHIUM-ION BATTERIES

3.1. Redox Shuttle Additive

From the above demonstration, overcharge abuse is one of the most common and dangerous safety issues with commercial lithium-ion batteries now. During the overcharge process, high voltage (HV) often occurs firstly thus leading to the other safety issues, such as thermal runaway, gas generation and short circuits. Therefore, voltage controlling within the designed range to prevent HV is the key point to solve the overcharge safety problem.

Currently, the voltage of lithium-ion batteries is commonly controlled by the external electronic circuits with the senor touching each individual cell of the battery pack.[67] For the large battery packs used in EV or HEV, the full electronic system of pack protection is usually referred to battery management system (BMS). The external electronic circuit system can achieve accurate controlling to

the electrical and thermal parameters of the LIBs, including voltage. This method is relatively effective for overcharge protection in most cases for LIBs.

However, the external electronic circuits system can lead to obvious increasing of weight, volume and cost of lithium-ion batteries, especially for the large-scale battery packs on EV or HEV. Beyond that, the failures of external hardware occur occasionally and become more likely in the abnormal conditions. In addition, the fact should be especially noted that the internal chemical environments of individual components of lithium-ion battery are constantly changing during the various aspects of battery cycling, such as impedance increasing, interfacial phenomenon, current-collector corrosion and so on. However, the external electronic circuits can not achieve intelligent perception and efficient responding to these complex internal chemistry changes. Hence, voltage controlling only through the external electronic circuits is not very reliable for commercial lithium-ion batteries. Developing some internal overcharge protection mechanisms is essential to solve the safety problems of the LIBs.

The redox shuttle (O/R), as an internal overcharge protection mechanism, is one of the economic and efficient methods to avoid the voltage overcharge. The redox shuttle is an electrolyte additive which can produce reversible oxidation/reduction at a defined voltage slightly higher than the end-of-charge voltage to prevent the voltage increasing due to overcharge.

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The redox shuttle chemistry is achieved by following mechanism:

$$\text{Cathode electrode: } R \rightarrow O + ne^- \quad (2)$$

$$\text{Anode electrode: } O + ne^- \rightarrow R \quad (3)$$

During overcharge of LIBs, the oxidation reaction of the redox shuttle firstly occurs, rather than oxidation and decomposition of the electrolyte, on the surface of cathode (Eq. (2)). And then the oxidized state (O) of shuttle quickly diffuses to anode and is reduced to original state (R) (Eq. (3)). The opposite diffusion from anode to cathode and reoxidation of reduced state (R) on cathode accomplish the reversible shuttle reaction. In this reaction, an intrinsic consuming excess charge mechanism is established in the internal battery, and the potential of cathode is locked at the oxidation potential of the redox shuttle molecules.

To achieve efficient overcharge protection, appropriate redox shuttle (O/R) should have the following characteristics:[68, 69]

(1) The oxidation potential of the shuttle should be slightly higher than the end-of-charge potential of the cathode, and lower than the oxidation and decomposition potential of electrolyte. Otherwise, it will lead to incomplete charging of the battery or decreasing efficiency to inhibiting the oxidative decomposition of electrolyte.

(2) The redox shuttle reaction should be highly kinetic reversible on the positive and negative electrodes.

(3) The solubility and diffusion coefficient of the shuttle should be as high as possible.

(4) The shuttle should have enough chemical and electrochemical stability to offer longtime overcharge protection.

In terms of overcharge protection at high current density, the shuttling limiting current (I_{max}) (Eq. (4)) should be considered, described as following:[69]

$$I_{max} = nFADC/L \quad (4)$$

Where n is the number of the charges carried by the shuttle molecule; A is the electrode area; C is the concentration of the shuttle molecule in the electrolyte; D is the diffusion constant of the shuttle molecule; F is Faraday's constant; L is the interelectrode distance.

In the past two decades, quite a few efforts have been executed to search appropriate redox shuttle additives suitable for commercially used lithium-ion battery system.[10, 68, 70–84] Generally, most of the additives were selected mainly based on their redox potential.

For early 3 V level of lithium-based batteries, the potential of the redox shuttle should be in the range of 3.2–3.5 V. Accordingly, the first generation redox shuttle additive concept initially proposed by Abraham[85] was based on I^-/I_2 shuttle, the redox potential of which could be around 3.2 V.[70, 71] Similarly, lithium bromide was also proposed.[72] However, this set of halide-based redox shuttle additive were found to be impractical because of the volatility and reactivity of their oxidized forms (halogen).[86]

In the later studies, some novel redox shuttles compounds were proposed, including metallocene family compounds (ferrocene and ferrocene derivatives),[73, 87] aromatic species compounds (tetracyanoethylene, tetramethylphenylenediamine etc.),[88] a series of substituted aromatic or heterocyclic compounds,[89] and dihydrophenazine derivatives bearing either 2-hydroxypropyl or ethyl substituents on both N atoms.[75] These compounds have a redox potential ranging from 2.8–3.5 V, so they are suitable for low voltage lithium-based batteries.

However, with the commercialization of the 4 V cathode materials, such as $LiCoO_2$, $LiMn_2O_4$, the potential of the corresponding redox shuttle additives should be increased. For 4 V class LIBs, substituted aromatic compounds and some organometallic complex compounds offered more promising redox shuttle candidates with high voltage (near 4.0 V). Now, a few possible redox shuttles have been investigated, including 2,5-di-tertbutyl-1,4-dimethoxy (3.96 V)[77] and 10-methylphenothiazine (MPT, 3.74 V),[90] which are possibly suitable for lithium-ion batteries based on $LiFePO_4$ cathode material.

In addition, several non-aromatic redox shuttles have been investigated to offer proper overcharge protection. 2,2,6,6-tetramethylpiperidinyl-oxide (TEMPO) can act as

a typical one, which have a reversible redox reaction at 3.52 V versus Li/Li^+ and is also available in the overcharge protection for $LiFePO_4$-based lithium-ion batteries.[80]

For the higher-voltage (>4.2 V) redox shuttles for $LiCoO_2$ or $LiMn_2O_4$, lithium borated cluster salts, $Li_2B_{12}F_{12-x}H_x$ ($x = 1, 2, \ldots, 12$), the redox potential of which ranges from 4.2 to 4.7 V versus Li/Li^+ depending on the degree of fluorination,[69,91] are promising redox shuttle. The kind of additives ($Li_2B_{12}F_{12-x}H_x$) can act not only as overcharge additive but also available lithium salts for electrolytes of LIBs.

Recently, Amine and his group[84] proposed a redox shuttle additive of high voltage up to 4.8 V, tetraethyl-2,5-di-tert-butyl-1,4-phenylene diphosphate (TEDBPDP). The redox shuttle additive can provide overcharge protection for high potential positive electrode materials, such as $LiCoO_2$, $LiMn_2O_4$. Beyond that, based on density functional calculations, Amine and his group developed another novel redox shuttle additive, 2, 5-di-tert-butyl-1,4-bis (2-methoxyethoxy) benzene (DBBB), which displays a reversible redox potential at 3.9 V suitable for the $LiFePO_4$-based batteries.[10]

In the past decades, the means of search for suitable additive mainly relied on trial-and-error mode. However, the developing in quantum chemical calculation software will significantly accelerate the search process.[10,81] Additionally, developing several high-potential redox shuttle additives has become increasingly important, as the more utilizing cathode materials of high working potential currently, such as 4.9 V required by the lithium-enriched cathode materials from Amine group.[92,93]

On the other hand, polymerizable monomer additives are also a class of electrolytes additive to prevent overcharge.[94–96] The mechanism of the method is similar to the redox shuttle. When overcharge, the polymer monomer will be oxidized on the positive electrode surface at a specific potential and then produce a solid polymer layer on the surface leading to shutdown[96] or slowly micro-short-circuit the cells.[95]

3.2. Flame-Retardant (FR) Additive

The safety problems of lithium-ion batteries have strong relationship with the using high flammable solvents as electrolytes. Hence, reducing the flammability of the organic liquid electrolyte with flame-retardant (FR) electrolyte additive is the most important one of the effective methods to solve the above-mentioned safety problems. Generally, flame-retardant additives are investigated mainly based on the typical electrolytes used in the lithium-ion batteries, in terms of the solubility, compatibility and negative effects of the additives to performance of the lithium-ion batteries. Therefore, a number of researches have been performed to develop efficient flame-retardant (FR) additive.[97–103]

Currently, the flame-retardant molecules as flame-retardant additives are mainly focused on phosphate class compounds, which can efficiently block the chain reactions of hydroxyl radicals during the combustion of the organic electrolytes solution. The performance of trimethyl phosphate (TMP(a)) and trimethyl phosphite (TMP(i)) as FR additives were systematic investigated by Yao,[100] whose results showed that both of TMP(a) and TMP(i) significantly increased the thermal stability of the electrolyte, 1 M $LiPF_6$/EC:DEC (1:1 by wt.), and the exothermic heat generation of the electrolyte around 120 °C were totally suppressed. In addition, the TMP(i) additive largely increased the impedance stability of the batteries with $LiNi_{0.8}Co_{0.2}O_2$ as cathode material. In the further efforts,[101,102] dimethyl methylphosphonate (DMMP) was used as a flame retardant additive to 1 M $LiPF_6$ /EC:DEC (1:1 by wt.) system. The addition of DMMP to electrolytes provided a significant suppression in the flammability of the electrolyte concluded from the measurements of self-extinguish time and limited oxygen index. The totally non-flammable electrolytes could be achieved with only 10 wt% DMMP addition. The other phosphate compounds, including triphenylphosphate (TPP) and tributylphosphate (TBP),[98] and triethyl phosphate (TEP),[97] have also been reported as the effective FR additive to the electrolytes of lithium-ion batteries.

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The alkyl phosphates additives have excellent FR ability by reducing self-heating rate because of the high content of phosphorus.[97–103] However, this kind of additives are electrochemically unstable and undergo reductive decomposition under the low potentials on the graphite anode surface, which will result in severe capacity fading during the long-cycles process of the batteries. In addition, high viscosity of the additives will reduce the ionic conductivity and thus influence the capacity and power utilization.[97] Several methods have been proved to be effective to the improved stability of phosphates, including increasing the number of carbons in the alkyl groups,[98] partially replacing alkyl groups with the aryl (phenyl) group,[98,99] forming cyclic structural phosphate (e.g., ethylene ethyl phosphate (EEP))[103] and so on, as reviewed by zhang.[56] For example, Wang et al.[99] developed a modified flame-retardant agent, 4-isopropyl phenyl diphenyl phosphate (IPPP), which displayed good anti-flammability, improved thermal stability and good compatibility with $LiPF_6$/EC-DEC (1:1 by wt.).

In addition to above mentioned phosphate class compounds, the fluorinated propylene carbonates have been considered to be an attempt to associate high FR ability and electrochemical compatibility with currently used carbonate-based electrolytes. The detailed information about their FR ability and stability in commercial batteries have been investigated and reviewed recently.[56] Although a series of additives have been detailed investigated, it is not easy to find a practical additive into electrolytes with

high FR ability and no any expense of the other performance. There is a long way to go for the studies on the FR additives.

3.3. Positive Temperature Coefficient (PTC) Device

Thermal runaway is mainly caused by the accumulation of over heat-generation when Li-ion batteries were variously abused. To overcome thermal runaway, the positive temperature coefficient (PTC) devices are commonly equipped as components of commercial batteries. These PTC devices are composed of a thin conductive polymer layer, the resistance of which is positively sensitive to the temperature. When the temperature of LIBs is high enough to a critical point, the PTC devices are activated by overheat and then increase its own resistance (PTC effect) to restrict current flow across the batteries. Once the PTC device cools down, it can reversibly remain conductive.

However, this PTC devices are not reliable in the high capacity batteries.[104] The outer PTC devices are hard to sense the internal temperature in real time, because of the delay of heat conduction from inside to outside. Therefore, an internal self-activating thermal shut-down mechanism has been developed.[105–109]

Kise et al. proposed a carbon black/polyethylene composite as a PTC material.[106–108] Feng and Ai proposed a PTC electrode by coating a thin PTC layer of epoxy–carbon composites in-between the cathode-active $LiCoO_2$ layer and cathode current collector.[105] However, above improved methods still can not efficiently shut down the thermal runaway reactions in time. In their continued efforts, Ai and

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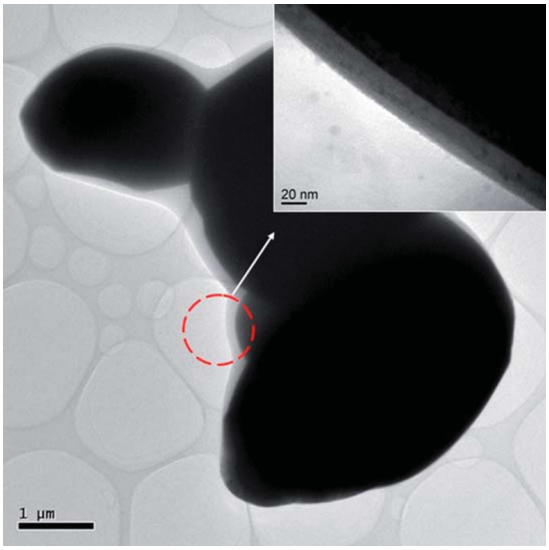

Fig. 7. TEM image of $LiCoO_2$@P3DT particles. Upper right: HRTEM image of a part of $LiCoO_2$@P3DT particle showing the thickness of the polymer layer. Reprinted with permission from [109], L. Xia et al.; Temperature-sensitive cathode materials for safer lithium-ion batteries; *Energy Environ. Sci.* 4, 2845 (**2011**). © 2011, Royal Society of Chemistry.

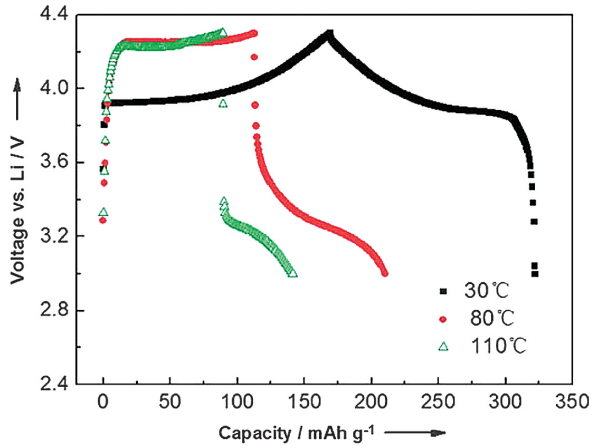

Fig. 8. Voltage profile of the $LiCoO_2$@P3DT material at different temperatures. Reprinted with permission from [109], L. Xia et al.; Temperature-sensitive cathode materials for safer lithium-ion batteries; *Energy Environ. Sci.* 4, 2845 (**2011**). © 2011, Royal Society of Chemistry.

his group innovatively developed a temperature-sensitive cathode material by coating a thin layer of conducting polymer with the required PTC effect on the surface of the cathode-active particles, poly(3-decylthiophene)-coated $LiCoO_2$ particles ($LiCoO_2$@P3DT).[109] From the TEM image (Fig. 7), $LiCoO_2$ coated by a dense layer was successfully synthesized. The battery with $LiCoO_2$@P3DT composites material showed the obvious DC conductivity drop as temperatures varied from 20 to 120 °C. The charge and discharge voltage difference of the batteries obviously increased as the temperature was elevated from 30 to 110 °C (Fig. 8), which showed efficient self-activated thermal protection for the batteries.

4. CONCLUSION AND OUTLOOK

In this paper, we have reviewed the recent progress in the development of safety issues for lithium-ion batteries based on the materials chemistry. Several key facts and corresponding mechanisms of the safety issues of LIBs have been taken a highlighting demonstration. A few of important methods to improve the safety issues of LIBs have been introduced. Among these safety issues, overcharge is one of the most common and dangerous problems associated with commercial lithium-ion batteries now. Overcharge abuse often results in thermal runaway, gas generation and short circuits, corresponding to high temperature (HT), high pressure (HP) and high current (HC) respectively, which actually originate from high voltage (HV) due to overcharge. Hence, developing the methods of efficient controlling voltage plays more important role in the solutions of safety issues of LIBs.

The more reliable solution to voltage abuse is electrolyte redox shuttle additive, which requires appropriate

potential, high solubility and diffusion coefficient to tolerate large current overcharge, chemical and electrochemical stability to endure longtime overcharge. However, it is not easy to find a practical redox additive combining above requirements. Moreover, it should be the trend to develop higher-potential redox additive (>4.5 or 4.8 V or higher) because of the practical applying more high-voltage cathode materials.

In addition, the nonflammable electrolyte by FR additive is the most essential one of the solutions to thermal abuse (high temperature (HT)). The FR additive is required to have high anti-flammability, improved thermal stability and good compatibility with the electrode materials or electrolytes. It should be noted that important also is the SEI film-forming additive to electrolytes, which can promote rapid formation of stable SEI film to avoid lithium dendrite growth (high current (HC)) under overcharge or large current charge of lithium-ion batteries.

The above-mentioned aspects are partly confined to existing lithium-ion battery system and techniques. To provide more secure lithium-ion battery, developing novel lithium-ion battery system or system components is very important. Based on this consideration, several key issues of fundamental science as following should be increasingly focused on in the future:

(1) Safety problems associated with the electrode material: For cathode materials, two important targets, high specific energy density and high safety, usually contradict each other. A cathode material with high energy density (possessing high voltage or high specific capacity) will become more active at charged state and hence might decompose at elevated temperature. Inherent structure-stability of the electrode materials also plays an important role in the safety of long-life battery. The more stabilities of the material itself, such as the wide electrochemical windows and hosts for Li reversible insertion/extraction, have more positive influences on the improvement on the safety. For example, the structure instability is reflected by the O_2 release of some cathode materials containing O anions (e.g., $LiCoO_2$) at high voltage due to the charge compensation, stimulating combustion of the organic electrolyte. Therefore, exploiting new electrode materials is very important for designing safe lithium-ion batteries.

(2) Electrolyte/electrode interface: Many of the side reactions causing safety problems of Li-ion battery occur at the interface between the electrolyte and the electrode material. The surface of electrode particles may be directly involved in the reaction with electrolyte, or act as catalyst in the electrolyte decomposition. Therefore, in-depth study on the interface aiming to alleviate the harmful reaction is crucial to a safe Li-ion battery.

(3) Developing intrinsically safe electrolyte: Currently the widespread adopted electrolytes contain liquid organic solution, which is intrinsically prone to combustion. The development of flame-retardant additive mentioned above, however, can not fundamentally solve this problem. The polymer electrolyte of lower flammability and excellent Li-ion conductivity and electronic insulation should be paid more attention. In addition, another more effective method to solve the safety problem is that it can anchor the hope on all-sold-state battery (solid state electrolyte), which is intrinsically safe against flaming and becoming a hotspot of Li-ion battery research.

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