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Review

Safety mechanisms in lithium-ion batteries

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Abstract

With increasing use of lithium-ion power packs, reports of occasional incidents of severely debilitating and sometimes fatal tragedies appear in the news. This review analyzes possible scenarios that trigger such hazards before proceeding to discuss safety mechanisms such as pressure release valves, one-shot fuses, reversible and irreversible positive temperature coefficient elements, shutdown separators, chemical shuttles, non-flammable electrolytes and coatings.
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Keywords: Lithium-ion batteries; Safety; Battery hazard; Non-flammable electrolytes; Thermal runaway

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1. Introduction

Perhaps the word lithium itself has questions of safety tagged to it. In fact, safety is a recurring theme even with lithium-ion cells where metallic lithium is replaced with lithium-insertion active materials. Ridden with a poor understanding of the fledgling lithium-ion battery technologies, what manufacturers and consumers fear are accidents during use or inadvertent abuse. For example, in an incident that occurred at Apple in 1995, lithium-ion batteries got overcharged during an in-house testing of a newly manufactured PowerBook 5300 portable computer [1]. Apple then removed all lithium-ion power packs from their product lines [2]. Hereabouts, Ericsson announced that its mobile phones and other portable electronic applications would wean away from lithium-ion batteries [3]. In fact, several other OEM manufacturers have also been proactive in recalling their products. In 2000, in cooperation with the U.S. Consumer Product Safety Commission, Dell voluntarily recalled 27,000 lithium-ion batteries, manufactured by Sanyo Electric Co. Ltd., and sold in notebook computers. Compaq also recalled 55,000 notebook lithium-ion batteries manufactured by Sony Corporation because of a defect in the circuit board that controls the recharge and discharge processes. One of the recent lithium-ion battery recalls with the USPSC was in 2002 when, upon receiving five reports of batteries overheating (in three of the instances they caught fire), EV Global Motors Company announced the recall of 2000 batteries in their electric bicycles.

Withdrawal of products, loss of market and even a ban on lithium-ion batteries were part of a backlash prompted by these incidents. Thus arose the need for safety in commercial lithium-ion battery applications. Today, lithium-ion batteries are the state-of-the-art power sources for a variety of portable electronic devices. They combine high energy density and excellent cycle life, and have no memory effect. That no lithium battery-related accident has been reported in the recent past is testimony to improved safety characteristics of present-day lithium battery products. The excellent safety record has been brought about by regulations governing the safety of the cells [4]. Continual improvements in safety are being made especially with large battery packs as for electric traction and load leveling [5]. The gravity of the situation becomes evident considering the market share for lithium batteries. Of the US$ 37 billion battery market in 2000, about US$ 2.9 billion was shared by lithium batteries, the share for primary and secondary lithium batteries being US$ 1.1 and 1.8 billion, respectively [6]. According to a prediction rechargeable lithium battery market should grow to more than US$ 2.1 billion by 2009 [7].

Lithium-ion batteries combine highly energetic materials in contact with a flammable electrolyte based on organic solvents. They can suffer premature failure if subjected to conditions for which they are never designed. Any abuse, including disposing in fire, overcharging, external short circuiting or crushing, can trigger spontaneous heat-evolving reactions, which can lead to fire and explosion. Lithium-ion batteries must pass a number of safety tests before they can be certified for use by a consumer. The tests include electrical tests such as external short circuit, mechanical tests such as nail penetration, crushing, dropping to the ground, and environmental tests such as heating in a microwave oven, throwing into a hot liquid, and leak tests in a vacuum. Several techniques have been devised to improve safety. They include use of safety vents, positive temperature coefficient (PTC) elements, shutdown separators, more oxidation-tolerant or less flammable electrolyte constituents and redox shuttle mechanisms. In this paper we review safety mechanisms adopted in commercial lithium-ion batteries.

2. Lithium-ion battery hazards

Apart from the fact that lithium batteries have highly oxidizing and reducing materials, their safety is compounded by the fact that the design of these non-aqueous cells has an inherent drawback of poor heat dissipation. Compared to lithium metal-anode batteries, lithium-ion cells are considered to be safer. The redox potentials of metallic lithium and lithiated carbons (Li_xC_6), for example, are similar. The reactive surface area of the carbonaceous anode with a typical particle size of about 10 μm is large. Although the specific surface area of the lithiated carbon electrode has been demonstrated to increase by a factor of five upon cycling [8], the reactivity of anode is kinetically limited by the slow transport of lithium from the galleries to the surface of the graphitic electrode [9–11]. Another important factor that contributes to enhanced safety of lithium-ion batteries vis-à-vis lithium metal anode batteries is the much higher melting point of Li_xC_6 as compared to that of lithium metal. The low melting point of lithium (180 °C) poses an additional risk of fire hazard from molten lithium generated by inadvertent overheating. However, exothermic reactions between Li_xC_6 and the electrolyte can be triggered by the application of heat [12,13].

The potential ranges experienced in common 4-V lithium-ion cells are beyond the thermodynamic stability windows of the electrolytes. Electrolytes, therefore, decompose upon contact with the charged active materials, both anodes [14–19] and cathodes [20–24]. The interface between the cathode and the electrolyte is further complicated by partial dissolution of the positive active materials [25–27]. This is particularly a problem at the end of charging and at elevated temperatures, conditions under which electrolyte oxidation can proceed at accelerated rates [28–34].

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The temperature of a cell is determined by the heat balance between the amount of heat generated and that dissipated by the cell. When a cell gets heated above a certain temperature (usually above 130–150 °C), exothermic chemical reactions between the electrodes and electrolyte set in, raising its internal temperature. If the cell can dissipate this heat, its temperature will not rise abnormally. However, if the heat generated is more than what can be dissipated, the exothermic processes would proceed under adiabatic-like conditions and the cell's temperature will increase rapidly. The rise in temperature will further accelerate the chemical reactions, rather than the desired galvanic reactions, causing even more heat to be produced, eventually resulting in thermal runaway [9,35,36], whose onset temperature determines the safety limit of the device. Any pressure generated in these processes can cause mechanical failures within cells, triggering short circuits, premature death of the cell by irreversible interruptions in the current path, distortion, swelling and rupture of cell casing.

It is clear that the thermal stability of batteries depends on its ability to dissipate the heat. The ability of an object to absorb heat is defined by its thermal capacity. Obviously, for a given amount of heat, bigger and heavier objects would suffer less temperature rise than would a similar object that is smaller and lighter. Thus, for lithium-ion batteries, which are designed for applications where size and weight are a premium, a decrease in the thermal capacity is an unavoidable penalty. Thus, heat dissipation in lithium-ion batteries turns out to be a major engineering challenge, especially for those designed for high power applications. Designs for effective heat dissipation must be adopted both at the cell and battery pack levels. Heat dissipation can occur by convection and radiation at the surface of the cell. Heat dissipation by convection depends, among other things, on the external surface area and geometry of the cell. However, heat dissipated by radiation depends on the nature of the surface of the cell and makes up nearly 50% of the dissipation [37]. Radiation dissipation can be improved by use of cell cases that have high thermal conductivity and labels that have high emissivity. Thermal performance is rarely a cause for cell failure in low-power cells that have simple designs. However, thermal design of high-power cells is not that simple. Poor designs can result in localized hotspots within the cell, which can lead to cell failure.

Possible exothermic reactions that trigger thermal runaway include [36,38]: (i) thermal decomposition of the electrolyte; (ii) reduction of the electrolyte by the anode; (iii) oxidation of the electrolyte by the cathode; (iv) thermal decomposition of the anode and cathode; and (v) melting of the separator and the consequent internal short. Moreover, high-voltage metal cathodes are known to release oxygen at elevated temperatures [39,40]. Thermal runaway is often caused under abuse conditions, which can be thermal (overheating), electrical (overcharge, high pulse power) or mechanical (crushing, internal or external short circuit) [36,41].

It must be noted that the release of materials from batteries can be benign, mild or violent. Battery hazards are classified according to the damage they cause [35]. Physical hazards involve a simple rupture of battery case; chemical hazards result from leakage or venting of corrosive or toxic materials in the battery; both chemical and physical hazards can cause equipment damage due to breakage or corrosion of electrical/electronic components; environmental hazards arise from the reactive and flammable nature of lithium and/or leakage of toxic materials from batteries that are improperly disposed.

An area that has often been overlooked is the possible embrittlement of container metal with lithium (similar to hydrogen embrittlement). This can happen if the metal in question is capable of alloying with lithium. In such a case, a spontaneous transfer of lithium to the alloying metal casing can occur [42]. This can lead to a structural destruction of the container material, resulting in leakage paths. Lithium embrittlement at highly stressed regions of battery containers can accelerate crack propagation. Although lithium battery leakages have been observed, no conclusive evidence is available to merit extensive research in this direction.

3. Conventional safety devices

A predominant mechanism by which lithium batteries are rendered safe involves limiting the current passing through them. Current-limiting devices such as positive thermal coefficient devices are designed to respond to high temperatures. Several factors play a role in the operation of these devices: the ambient temperature, thermal insulating properties of the container, heat generated in the equipment, cumulative heat in the battery pack, and rate and duration of discharge. Thus, it becomes necessary to consult the manufacturer or conduct tests in order to determine the suitability of a battery pack for a particular application.

Apart from preventing flow of excessive currents that can potentially damage cells, current-limiting protection devices must withstand continuous flow of the load's design current and tolerate normal surges and transients. Furthermore, safety devices must also fit into very small spaces and must be relatively cheap. For acceptance in commerce, the current-limiting device must be fail-proof, which also means that it should not be prone to false tripping, factors that can decide customer dissatisfaction. It must be pointed out that batteries regulated with external electronic devices such as PTC elements and integrated circuits would not only have higher manufacturing costs but also lower energy density.

3.1. Safety vents

Conventional safety mechanisms include such devices as vents and current-limiting devices like fuses and circuit breakers. Safety vents open in response to a sudden increase in cell pressure, allowing gases to escape. If the pressure inside a cell builds up, a plastic laminate membrane is punctured by a spike incorporated in the vent in the cell top. A safe release of internal pressure precludes dangerous rupture of the cell casing. Safety vents can be designed to operate at pre-set internal cell temperatures. Today, vents are a back-up safety device. During instances of electrical abuse, other devices such as a positive temperature coefficient device (described below) override the vent. If batteries are subjected to severe mechanical abuse conditions, the

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safety vent provides a means of releasing internal pressure and prevents the cell from reaching excessively high temperatures.

Kato et al. [43] developed a safety mechanical link by which a concave aluminum disk welded to the cathode would break the circuit upon release of gas. In this design, lithium carbonate deliberately added to the $LiCoO_2$ cathode mix would decompose to yield CO_2 when the cell is overcharged to greater than 4.8 V. The built-up pressure would push the aluminum disk, disconnecting the cathode lead from the circuit. This simple mechanism prevents the cell from the thermal runaway caused by an excessive overcharge. Choi et al. [44] have shown that in addition to providing safety, the added lithium carbonate can suppress the initial irreversibility of the carbon anode.

Since the safety vent opens up the cell, spewing out a significant quantity of volatile organics, it is used as a back-up safety device. In fact, other safety devices such as PTC elements override the safety vent during abuse. Under severe mechanical and electrical abuse conditions, the vent provides a safe means of releasing internal pressure before the cell reaches excessively high temperatures.

3.2. Thermal fuses

The oldest and most common current limiter is the one-shot fuse, which is a wire of a fusible alloy with resistance and thermal characteristics that allow it to melt when a pre-set current flows through it. Some fuses require several seconds to trip, but they are inherently fast-acting. The advantages of the fuse as a safety device lie in its simple construction, low cost and availability in a wide range of currents and voltages ranges. Fuses act by destroying themselves, thereby positively and permanently opening the circuits they protect. Thus, they must be replaced once blown, which is another advantage (as it draws the attention of the user to take action for resuming service) although the mechanical action involves labor. However, fuses can prematurely blow under other conditions such as pulse discharges (or repeated pulse discharges that can degrade the alloy), which are normal operational modes of batteries. Moreover, there is the possibility of inadvertent replacement with fuses with higher or lower current ratings, which can result in improper use of equipment. Fuses are wired in series with the cell stack and will open when a pre-set cell temperature is reached. Thermal fuses are employed as protection against thermal runaway and are usually set to open at 30–50 °C above the maximum operating temperature of the battery. Fuses are cheap and are ideal for low-cost, throwaway products with limited warranties.

3.3. Other circuit breakers

Other circuit breakers such as magnetic switches, bimetallic thermostats and electronic protection circuit modules can be used to protect power packs and to monitor their temperature. They must also tolerate continuous design current as that of the load as well as occasional current surges, without tripping. However, their size and cost often rule out the application of the first two in many onboard circuits, especially where space is at a premium.

Thermistors sense the internal temperature of the battery, and provide information to an external control through a calibrated resistance. Thermistor controls may be located in a battery charger. The thermistor is attractive as the control can be set to meet specific conditions of charge and to regulate input current to the battery. This device can also be used to control the battery through $\Delta T/\Delta t$ control, where T and t are the temperature and time, respectively. PTC thermistors have a positive temperature coefficient, as will be described below. Similarly, thermistors whose resistances decrease with increasing temperature are called negative temperature coefficient (NTC) thermistors. Both are used for monitoring and protection of control circuits.

The thermostat or temperature cut-off (TCO) devices operate at a fixed temperature, and can be used to terminate charge (or discharge) when a pre-set internal battery temperature is reached. TCOs are usually resettable. They are connected in series with the cell stack.

Electronic safety circuits, commonly referred to as protection circuit module (PCM), are usually attached to battery packs as separate modules. In the event of a wrongful condition, such as short circuit, the PCM opens the battery circuit and prevents damage to the pack. Some groups believe that the cell chemistry in lithium-ion cells can be modified and safety levels raised, rendering PCMs redundant [45].

Unlike aqueous electrolyte cells, which have an inherent balance-adjusting mechanism such as gas recombination, lithium-ion cells require an external overcharge/overdischarge protection system, particularly those for use in specialized applications as in electric traction and spacecraft. This can be provided through an electronic control circuit. However, the cost component of the circuits is kept small as compared to the cost of the batteries themselves. The basic circuitry consists of a bypass circuit controlled by a microchip based on MOSFET. The bypass circuit gets activated when a cell in a pack reaches a given state-of-charge/discharge earlier than other cells. Thus, the charge/discharge process is terminated until balance is regained. Open-circuit voltage of lithium-ion cells can be used as indicators of their state-of-charge, electronic controllers can be designed to sense voltages and, thereby, switch on or off the charging/discharging circuit. This ensures charge balance among cells in a pack and damage by overcharge/overdischarge of individual cells. In specialized applications, battery packs come with protection circuits that monitor cell temperature and activate cooling gadgets such as fans.

4. Self-resetting devices

Factors such as inconvenience of replacement and premature failure of fuses (which call for time-consuming technical services), unsuitability of integrating devices such as magnetic/thermal switches onboard, size restrictions and cost led to a search for a self-resetting, fuse-like device. Thus, emerged safety devices called positive temperature coefficient devices based on materials whose resistance increases dramatically with a rise in temperature. For example, if a large current flows across the PTC element, as during external short circuiting, its temperature rises up abruptly up due to Joule heat evolution within the

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PTC element. A concomitant and abnormally high resistance of the PTC element prevents current flow. Thus, upon activation, the resistance of the PTC element shoots up, leading to a precipitous fall in the current, which limits heat generation in the cell. Once the cause for alarm is removed, the cell and PTC element cool and the resistance of the latter drops, allowing resumption of charge/discharge. PTC elements are generally installed inside cells. The temperature above which the resistance of the PTC element jumps to an infinite value is called the "trip temperature," whose value is generally set at about 100 °C.

Although the primary purpose of PTC devices is to protect batteries against external short circuits, they also provide protection under certain other electrical abuse conditions. This is accomplished by limiting current flow when the cell temperature reaches the designed activating temperature of the PTC device. For extended equipment life, the PTC must work reversibly. Although PTC devices can operate in this way several times, it will not reset indefinitely. Fortunately, when they cease to reset, they remain in their high-resistance condition, rendering the cell unusable. PTC devices usually come as surface-mountable units and are compatible with pick-and-place equipment. Thus, they carry little assembly-costs. But because they are costlier than fuses, they become economically attractive only when used in equipment that are costly or demand long-term warranties.

4.1. Ceramic PTC materials

Ceramic materials with fuse-like action were the materials of choice for early PTC elements. Ceramic PTC devices can operate under high voltages and can return to their normal resistance mode with great accuracy. Thus, they are attractive for application in several high-voltage circuits although their relatively large sizes preclude their use in miniature high-component density gadgets. It must be noted that their applicability in low-voltage circuits is undermined by their high inherent resistance, the high voltage drop across which can cause problems with the operation of the gadget. Another intrinsic disadvantage with ceramic PTC materials is their high thermal mass, which renders their reaction time to moderate over-currents longer than those of the components in the gadget. The sluggish response can damage costly equipment.

4.2. Conductive-polymer PTC devices

Conductive-polymer PTC devices are non-linear PTC thermistors based on a composite of polymers and conductive particles. It is known that above their glass transition temperatures (T_g) polymers transform into an amorphous state and return to their crystalline state upon cooling to temperatures below their T_g. At normal operating temperatures, the conductive particles embedded in a crystalline polymer matrix provide a low resistance path for current flow. At elevated temperatures (typically ~125 °C), the polymer's structure changes to an amorphous state. The accompanying expansion of the matrix breaks the conductive pathway between the embedded particles, rapidly increasing the device's resistance by several orders (Fig. 1). This reduces the current to a relatively low and safe level. An advantage of PTC devices is that this trickle current maintains the internal temperature of the cell high, prevents the conductive chains from returning to their original state. In other words, the trickle current "latches" the PTC device in its tripped state. Upon opening the circuit the device cools, allowing the polymer matrix to return to its normal state and returns the resistance of the device to its normal low value. Fig. 2 shows the variation of the resistance of a PTC device as a function of temperature.

Conductive-polymer PTC devices are made from a blend of plastics and conductive materials. The temperature of the conducting-polymer PTC device is determined by the ambient temperature and heat generated by internal I^2R losses. Under normal operating conditions, the I^2R losses are too low to generate enough heat to transform the polymer into its amorphous state. However, under abuse conditions when large currents flow through the device, the I^2R losses become sufficiently high, increasing the temperature and hence the resistance of the PTC element. The reduction in the current in turn reduces the I^2R losses. Upon regaining thermal equilibrium, the PTC device

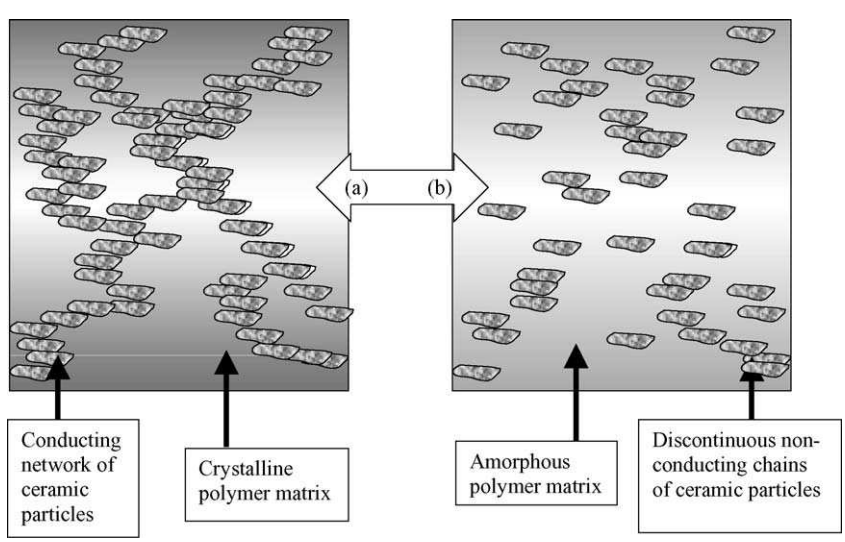

Fig. 1. Principle of a conductive-polymer PTC device. Distribution of ceramic particles at: (a) normal operating temperature and (b) trip temperature.

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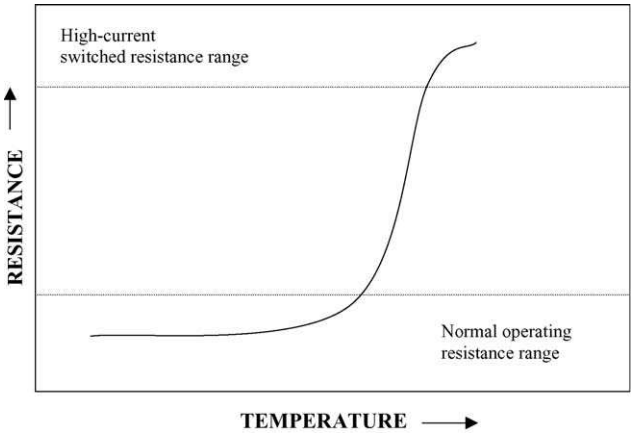

Fig. 2. Representation of the variation in the resistance of a PTC device as a function of temperature.

allows a circuit current insufficient to cause damage but enough to maintain the device's trip temperature. The safety device thus gets latched in its tripped state. It must be pointed out that conductive-polymer PTC devices allow a small residual leakage current through the circuit after its tripped state. The resulting voltage drop across the device can be a concern in certain gadgets, especially those that demand precise power requirements.

Conductive-polymer PTC current-limiters still have some inherent problems. Although they can trip in a few milliseconds' time, their response times are still inferior to those of fuses. However, they are suitable for applications where a slow-blow fuse-like characteristic is tolerated. They are also costlier than common fuses. Moreover, the maximum current and voltage they can tolerate are also limited. However, as compared to their ceramic counterparts, conductive-polymer PTC current limiters have low normal resistances, which means that they do not influence the normal operation of the battery. Moreover, because of their low thermal mass, polymeric PTC devices react quickly to over-current conditions. Additionally, small surface-mount polymeric PTC devices can be constructed.

As noted above, an important concern with external safety mechanisms such as PTC devices is their ability to respond when hazardous reactions occur at high rates [46]. In order to obviate this problem, Feng et al. [47] developed an internal self-actuating thermal cut-off mechanism. Here, the electrodes themselves would have a PTC effect, an effect that is achieved by coating the current collector with a suitable PTC material. According to Feng et al. [47], this would be much more responsive to internal heat changes than external PTC devices, providing cut-off at a pre-set activation temperature. Moreover, these internal PTC devices are reversible, which ensures reusability of the batteries once the reason for heat build-up is removed.

5. Shutdown separators

Separators for lithium-ion batteries are polyolefin microporous films and are generally uniaxially drawn polyethylene (PE) and polypropylene (PP), biaxially drawn PE or multiaxially drawn PP/PE/PP [48,49]. In addition to conventional characteristics such as good mechanical strength, electrolyte permeability, these microporous separators display a protective property during cell abuse. For example, if the cell temperature rises abnormally because of an excessive overcharge, for example, the heat generated softens PE and closes the micropores in the film. This is called separator "shutdown" [50,51]. Once shutdown occurs, ionic transport between the electrodes is effectively stopped and current ceases to flow [51]. If the separator can retain mechanical integrity above its shutdown temperature, it can provide a margin of safety to the device; otherwise, the electrodes can come into direct contact, react chemically, leading to thermal runaway. However, it is possible that due to thermal inertia the temperature can continue to rise even after shutdown. Under such conditions the separator would melt and short the electrodes, leading to violent reactions and heat generation. This phenomenon is called "meltdown" or "breakdown" of the separator [48]. Therefore, in order to ensure safety of the cell, the difference between the "shutdown" and "meltdown" temperatures should be as large as possible.

Separators made entirely of high-density polyethylene melt at 135 °C and lose mechanical integrity above this temperature. However, separators made by laminating layers of polypropylene and polyethylene maintain mechanical integrity at least up to 165 °C, the melting point of polypropylene. It is interesting to note that although ultrahigh molecular weight polyethylene melts at 135 °C, separators made from this material retain their mechanical integrity up to at least 180 °C as the viscosity of the material is such that it maintains physical integrity. Shutdown separators are reliable and lithium-ion battery manufacturers are increasingly opting for their incorporation in their products. The most common shutdown separators have high molecular weight polypropylene blended with super-high molecular weight polyethylene [45]. Here, the unique shutdown property of polyethylene is combined favorably with the high mechanical integrity of polypropylene at elevated temperatures. Because the shutdown is irreversible, once actuated, these separators leave the cells permanently damaged.

6. Electrolytes

The key to a safe high-performance lithium-ion cell lies in the identification of a suitable electrolyte. Lithium is intrinsically unstable with any commonly known electrolyte. Moreover, lithium battery electrolytes based on alkyl carbonate solvents are known to react vigorously at elevated temperatures with lithiated graphite and delithiated cathodes (e.g., Li_xCoO_2 ($x<0.5$)) [19,52–54]. At elevated temperatures, the SEI on the graphite anode gets destroyed, allowing rapid and direct reaction with the lithiated graphite underneath the passivating layer. In their delithiated forms, cathodes are highly oxidizing and enter into exothermic reactions with alkyl carbonates, especially at elevated temperatures. Careful calorimetric studies have thus become mandatory to determine the safety of electrode–electrolyte combinations. According to Aurbach et al. [55], commonly used electrolytes such as $LiPF_6$ in EC–DEC–DMC are only a compromise. They are flammable and their electrochemical windows are limited to about 4.5 V. Alternatives to such alkyl carbonate solvents are

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not on the horizon although alternative salts such as lithium bis(oxalato)borate, $LiBC_4O_8$ (LiBOB) [56], and lithium fluoroalkylphosphates (e.g., $Li[PF_3(C_2F_5)_3]$) [57–59] are being considered in place of $LiPF_6$. Aurbach et al. [55] suggest that under the circumstances, it is only prudent that additives that can protect electrode-active materials even at high temperatures by forming highly protective films on the electrodes be investigated. In fact, new formulations of solvents and salts are unveiled continually with an eye on safety and performance. A number of additives are also being investigated to make up for problems due to protective films at the positive and negative electrodes. Additives have also been sought to lower electrolyte flammability under cell venting. Redox couples that shuttle back and forth as additives to limit overcharge and additives that produce gas for activating current interrupter devices have also attracted interest.

6.1. Non-flammable electrolytes

Solvents used in lithium-ion batteries are typically low-boiling and have flash points around 30 °C. Thus, a major danger from a cell that vents or explodes arises from the flammability of the hot electrolyte vapors that are spewed out. Although identification of a solvent–salt combination that not only possesses desirable properties for use in batteries but also has the ability to resist combustion under heat or in the presence of an external flame may only be a dream, it is possible to develop electrolytes that are not easily flammable [60–67]. Thus, the aim is to look for "low flammability" or "flame retarding" electrolytes that do not support continued combustion when the source of heat, spark or flame is withdrawn. An important consideration here is that the heat of reaction of the electrolyte with the charged electrode materials should also be low so that a self-sustaining combustion reaction does not occur under accidental heating. Present-day electrolyte formulations are a trade-off between the electrolyte's flammability and performance in the cell. The reduced battery performance is due either to electrochemical instability (which leads to capacity fading) or increased viscosity of the additive (which affects capacity utilization and power). Since performance cannot be sacrificed, studies mostly focus on flame-retardants as the additives or co-solvents in known electrolytes [60–64]. Fluorinated compounds [61] and organophosphorus compounds [61,62,68] are among the most investigated as co-solvents to decrease flammability. For example, trimethyl phosphate, a popular flame retardant, has been studied for its electrochemical stability on the positive and negative electrodes of lithium-ion cells [60–63]. However, it is important to note that since electrolytes react with the active materials in lithium-ion batteries, the surface chemistry at the anode and cathode is a key factor that decides cell performance. Therefore, the design of new electrolytes must also consider the properties of the SEI formed with the electrolyte.

6.2. Redox shuttles

Redox shuttles are among the most promising mechanisms for overcharge protection [69]. The working of redox shuttles, added to electrolytes, involves electrochemical oxidation at the positive electrode at potentials slightly higher than the typical charging plateau. The oxidized forms of these molecules diffuse to the negative electrode, where they get reduced without side-reactions back to the starting neutral molecules, which then shuttle back to the positive electrode (Fig. 3). Thus, redox shuttles shunt the excess charge injected into the cell during overcharge. In this way, redox shuttles can indefinitely 'lock' the cathode potential at the oxidation potential of neutral molecules until termination of the charge. In principle, all the Faradaic current goes for the reversible reactions, which means that the redox couple acts as a controlled internal short. A necessary condition is that both the oxidized and reduced forms of the molecules be mobile in the electrolyte.

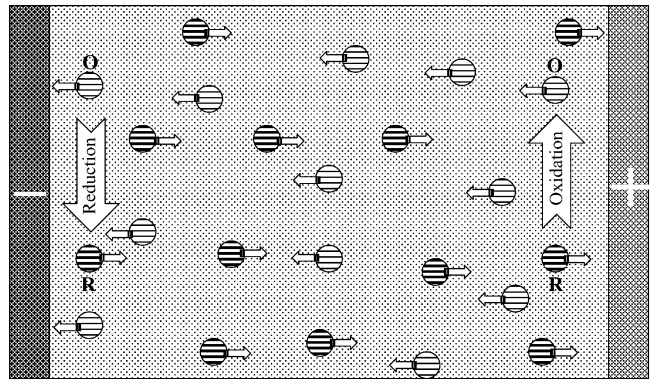

Fig. 3. A schematic showing the working of a redox shuttle. Compound R gets oxidized at the positive electrode to O, which diffuses to the negative electrode and gets reduced to the original molecule.

It is possible to visualize scenarios under which the overcharge current becomes too high for the redox couple to carry, letting the excess current to delithiate the cathode and causing irreversible decompositions. To avoid consequent safety hazards arising under this condition, the current limit that can be shunted should be maximized by employing large concentrations of the shuttling molecules [70]. The identification of such a redox species is fraught with several conditionalities: (i) both the oxidized and reduced forms of the redox molecule must not only be inert towards cell constituents, but also have sufficient thermal stability; (ii) the solubility and diffusion coefficient of the shuttling molecules in the non-aqueous battery electrolyte should be high; (iii) the oxidation potential of the redox couple must be lower than the decomposition potential of the electrolyte solvents but slightly higher than the overcharge cut-off voltage; (iv) the shuttle must be electrochemically reversible and must not enter into side-reactions; and (v) the reversibility of the couple should last for the entire lifetime of the cell. A number of soluble redox couples have been suggested as shuttles for overcharge protection, but they work only at high charging voltages, which means they actually do not respond to heat generation in batteries.

6.2.1. Halide shuttles

The earliest shuttles, employed for 3-V lithium metal batteries, were based on halides [71,72]. For example, the iodine/iodide couple can be oxidized at the cathode at 3.20 V

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and reduced at the lithium anode. Halide shuttles were, however, abandoned as the volatility and reactivity of the oxidized forms (free halogens) rendered such cells impracticable.

6.2.2. Metallocene shuttles

Metallocenes, which form redox pairs, MC/MC^+, are among the earliest chemical shuttles investigated, and were tested in 3-V lithium cells [73–76]. The redox potentials of these couples can be tuned by varying the substituent groups at the cyclopentadienyl rings [77]. In fact, the potential can be tailored by as much as 450 mV by varying the number and electron-donating or electron-withdrawing nature of the substituents. Ferrocene shuttles have withstood over a hundred "turnovers" in lithium cells. However, ferrocenes can block ionic paths on the surface of the cathode, which can reduce the power capabilities of the cell. Moreover, their adsorption on the cathode can result in capacity loss [74]. The situation is more complex in the case of lithium-ion cells, for application in which the potential of the redox couple must be higher than the end-of-charge electrode potential (say, 4.3 V versus Li^+/Li). Additionally, the SEI-covered graphite electrode in lithium-ion cells does not support the reduction of MC^+, rendering the soluble redox couple inoperable.

6.2.3. Aromatic redox shuttles

Redox shuttles based on aromatic compounds have also been investigated. They include 3-V cell shuttles such as tetracyanoethylene and tetramethylphenylenediamine [78]. The selection of 4-V cell shuttles for lithium-ion cells based on $LiMn_2O_4$, $LiCoO_2$ and $LiNiO_2$, however, presents more challenges as only a handful of substances are amenable to reversible turnover at potentials around 4.0 V versus Li^+/Li. These include complexes of cerium, iridium, iron or ruthenium with phenanthroline or bipyridine. Again, their redox potentials can be tuned by varying the number, nature and position of the substituents on the aromatic rings [79]. However, their shunting currents are low due partly to their limited solubilities in non-aqueous electrolytes and partly to the low diffusion coefficients resulting from their large sizes and molecular weights.

According to Adachi et al. [79] anisole-based compounds, which have high solubility in lithium battery electrolytes, should make for a better class of redox shuttles. Anisole compounds with two methoxy groups at 1,2-(*ortho*-) and 1,4-(*para*-) positions display reversibility at the 4-V region [79]. The authors suggest an empirical structure–property relationship for anisole-type shuttles, which can help in the design and selection of more efficient redox shuttles [80]. Adachi et al. [79] conclude that 4-bromo-1,2-dimethoxybenzene provides the best shunting performance among 4-V shuttles. Furthermore, anisole-type shuttles are stable against reduction at carbonaceous anodes. Other 4-V shuttles reported in the literature include bipyridyl and biphenyl carbonates as well as difluoroanisoles [81,82].

6.3. Shutdown additives

Some less known additives, also intended for overcharge protection, terminate cell operation permanently. For this reason they are called "shutdown additives" in the battery industry [81,83]. There are two classes of shutdown additives: one releases gases, which in turn activate a current interrupter device, while the other undergoes polymerization, thereby blocking ion transport in the electrolyte. Gas-releasing shutdown additives include biphenyl [81,84], cyclohexylbenzene [81], pyrocarbonates [81] and phenyl-*tert*-butyl carbonate [85]. Biphenyl and other substituted aromatic compounds constitute the polymerizable class of shutdown additives [86–88]. It can be deduced that both the gassing and polymerizable additives are sure-shots against overcharging. Thus, an approach to a reliable line of defense against catastrophic failure due to overcharging would be to incorporate a redox shuttle and a shutdown additive in the cell such that the activation potential of the latter is higher. Nevertheless, given the paramount importance of safety, especially in consumer gadgets and children's toys, redox chemical shuttles, which can only provide limited overcharge protection [79,89] and cannot prevent catastrophic failure as obtained during severe overcharging, shutdown protection mechanisms such as polymerizable additives must be incorporated even at the cost of termination of useful life of the battery. Some studies have extended the polymerization reaction into the separator, immobilizing the electrolyte [90].

6.4. Ionic liquids

Several room temperature ionic liquids (molten salts) present themselves as possible electrolytes in lithium-ion batteries [91–95]. Not only are they not prone to forming SEI on the electrodes, they have inherent safety characteristics by virtue of their thermal stability, non-flammability, non-volatililty and low heat of reaction with active materials. The non-flammability is effective in preventing batteries from catching fire, while non-volatility prevents batteries from bursting. Furthermore, they have favorable electrochemical stability windows for application in lithium-ion cells. One of the central issues is identification of ionic liquids with sufficient lithium-ions to allow high flux of lithium-ion through the electrolyte [96].

Ionic liquids based on the (1-ethyl-3-methylimidazolium) cation are particularly interesting because of their low viscosities [97–99], but are not sufficiently stabile towards reduction in the lithium-ion cell environment [95]. An otherwise potential electrolyte, the imidazolium salt, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMI\text{-}BF_4$), has a reduction potential of about 1 V versus Li^+/Li, which is too high for lithium battery electrolytes [93,99–102]. However, with the hope that the reduction potential of the EMI^+ cation can be tailored by incorporation of organic functional groups [100], Hayashi et al. [103] developed alkylated $EMI\text{-}BF_4$ molten salts, 1-ethyl-2,3,4,5-tetramethylimidazolium tetrafluoroborate and 1,2-diethyl-3,4(5)-dimethylimidazolium tetrafluoroborate. Both salts exhibited very little decomposition at 0 V versus Li^+/Li and a wide electrochemical window (up to 5 V versus Li^+/Li). Additionally, the latter electrolyte had a relatively low melting point of about 20 °C and a good specific conductivity of 1.44 mS cm^{-1} at 20 °C. Quaternary ammonium

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cations are another class of compounds that can withstand reduction at the anode. Sakaebe and Matsumoto [104] have shown higher coulombic efficiency and larger utilization of the positive electrode as well as improved safety with a *N*-methyl-*N*-propylpiperidinium–bis(trifuoromethanesulfonyl)imide electrolyte. It is hoped that with sustained research an ionic liquid electrolyte with desirable safety and electrochemical characteristics will emerge.

6.5. Electrolyte salts

State-of-the-art lithium-ion cells use $LiPF_6$ as electrolyte salt. However, $LiPF_6$ is thermally unstable and decomposes to LiF and PF_5 [105,106], a reaction that gets accelerated in the presence of organic solvents. PF_5 hydrolyzes to form HF and PF_3O, which react with both the anode and cathode, deteriorating cell performance [107]. However, $LiPF_6$ possesses some properties desirable for lithium-ion battery environment that replacing the salt will entail certain trade-offs. But today it is the best compromise, for alternatives to $LiPF_6$ pose too many problems [55]: $LiClO_4$ is potentially explosive in contact with organics, $LiBF_4$ interferes with the SEI at the anode (but it has better thermal stability and lower sensitivity towards moisture [108,109]), $LiAsF_6$ is toxic, solutions of $LiSO_3CF_3$ have too low conductivities, and $LiN(SO_2CF_3)_2$ and $LiC(SO_2CF_3)_3$ do not effectively passivate the aluminum current collector at the positive electrode, leading to its corrosion [110]. Salts such as $LiBF_4$, $LiPF_6$, $LiAsF_6$, etc., form a layer of LiF on the graphite anode surface [111,112]. Larger the amount of LiF in the SEI, the lower is the onset temperature for thermally activated reactions in the SEI [113–115]. Below we discuss new salts being considered for lithium battery use: $LiPF_3(C_2F_5)_3$ (LiFAP) [57,59], $LiN(SO_2CF_3)_2$ (LiTFSI) [55,116] and $LiBC_4O_8$ (LiBOB) [56,117–119].

6.5.1. $LiPF_3(C_2F_5)_3$

In order to overcome the easy hydrolyzability of $LiPF_6$, a new class of compounds known as lithium fluoroalkylphosphates was introduced [57–59]. The premise for their development was that the substitution of one or more fluorine atoms in $LiPF_6$ with electron-withdrawing perfluorinated alkyl groups should stabilize the P–F bond, rendering it stable against hydrolysis. In fact, lithium fluoroalkylphosphates exhibit good resistance against hydrolysis. The hydrophobic perfluorinated alkyl groups sterically shield the phosphorus against hydrolysis. The new compounds also have conductivity comparable to that of $LiPF_6$ [57]. The stabilization of the P–F bond results in an improved thermal stability of the salt [57,58]. Oesten et al. [58] showed that $LiPF_3(C_2F_5)_3$ (LiFAP) exhibits a far superior stability towards hydrolysis and that electrolytes containing LiFAP exhibited reduced flammability. The authors suggest that LiFAP has a combination of flame-retardant moieties, fluorinated derivatives and phosphoric acid esters [58]. Gnanaraj et al. [120], who investigated the thermal stability of solutions of $LiPF_6$ and LiFAP in EC–DEC–DMC mixtures using accelerating rate calorimetry (ARC), showed that the onset temperature for thermal reactions of LiFAP solutions were higher than 200 °C ($LiPF_6$ solutions: <200 °C) although their self-heating rate was very high.

6.5.2. $LiN(SO_2CF_3)_2$

Commonly known as LiTFSI, lithium bis(trifluoromethylsulfonyl)imide [121] has an electronic structure that delocalizes its negative charge, thereby reducing ion pairing [122]. LiTFSI also has good thermal and hydrolytic stability. Although good cycling efficiencies with lithium have been reported [123] with LiTFSI, it tends to corrode the aluminum current collector in cells with $LiCoO_2$ electrodes [124] for which the nominal rated voltage is 4.1 V. Wang et al. [125] demonstrated superior rate capability of $Li_4Ti_5O_{12}/LiCoO_2$ cells in which solutions of the salt in 3-methoxypropionitrile or 3-ethoxypropionitrile were used as the electrolyte.

6.5.3. $LiBC_4O_8$

Chelating boronate salts with six- and seven-membered rings [126] as well as those with five-membered rings [119,127] on the boron atoms are presently being considered. The unsubstituted five-member ring salt, lithium bis(oxalato)borate, commonly called LiBOB, has been found to have good high-temperature stability [57]. LiBOB has many unique properties [56,112,128]: has a thermal stability up to 300 °C (much above the 80 °C for $LiPF_6$) [57]; stabilizes aluminum (the current collector in the cathode) up to >5.0 V versus Li^+/Li [116] in a manner similar to $LiPF_6$; forms a stable solid electrolyte interface graphite anode even in propylene carbonate-containing electrolytes [57,128,129]; forms solutions of high conductivity; has low cost; and its disposal in water does not release toxic materials. Most importantly, it has superior safety characteristics [130,131]. LiBOB-based electrolytes have also been shown to be stable for electrochemical cycling up to 4.3 V with $LiNiO_2$ [132] and up to 4.5 V with $LiCoO_2$ [133]. One attraction with LiBOB is that it does not form LiF on graphite during cell cycling [112].

Despite its projection as a potential electrolyte salt, it must be noted that several properties of LiBOB remain unknown. Additionally, several other things need to be factored into before LiBOB can be accepted as an electrolyte salt. This includes its low solubility in solvents with low dielectric constant, lower conductivity of their solutions in typical carbonate mixtures as compared to $LiPF_6$, easy hydrolyzability (although the monohydrate of LiBOB is stable [57]) and difficulty in large-scale synthesis of high-purity LiBOB [134,135]. Safety features of LiBOB-bearing cells are being evaluated [132,133,136,137]. Although enhanced safety can be realized with fully lithiated graphite, safety concerns remain in the case of cathodes where a higher self-heating rate is observed, which suggest reactions between LiBOB and oxide cathodes.

7. Active materials

Commercial lithium-ion batteries are thermally stable up to ∼60 °C [138], above which their performance declines. Anode/electrolyte reactions occur first [139], while cathode/electrolyte reactions dominate the heat-evolution processes at elevated temperatures [19]. The latter if allowed to progress can be hazardous. Violent reactions are known to occur in the charged state of lithium-ion batteries. In fact, although lithiated

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carbon anodes are considered safer than metallic lithium anodes [9], at large values of x in Li_xC_6 ($x \sim 1$ for graphite) they can react with the electrolyte under abusive conditions, releasing heat. Similarly, at small values of x in Li_xCoO_2, Li_xNiO_2 and $Li_xMn_2O_4$, the cathodes can adversely influence their thermal stability [31,140]. Therefore, thermal studies on negative electrodes are performed in their lithiated state and positive electrodes in the delithiated state. Because cell temperatures during abuse reactions can melt the aluminum current collector but not the copper current collector, Biensan et al. [141] conclude that cell temperatures should reach between 659 °C (mp of Al) and 1083 °C (mp of Cu).

7.1. Carbon anode

The composition of the SEI on graphite depends on the electrolyte composition and strongly affects the onset temperature for thermal reactions at the graphite anode [142–144]. While the composition of the SEI is dictated more by the salt in the case of electrolytes with $LiBF_4$ and $LiPF_6$, the solvent takes a prominent role with electrolytes containing salts such as $LiCF_3SO_3$ and $LiN(SO_2CF_3)_2$ [114]. Thermal reactions at salt-based SEIs proceed via surface salt decomposition, yielding mainly LiF [113]. On the other hand, thermal reactions in predominantly solvent-based SEIs proceed via decomposition of lithium-alkyl carbonates to Li_2CO_3 [114]. For this reason, the latter type of SEIs is thermally more stable. Thermal stability of salt-based SEIs can be improved by controlling reactions involving salts complexing their anions with anion acceptors [145–148]. Besides, anion acceptors increase lithium-ion diffusion and transport number by suppressing ion-pair formation. In fact, Herstedt et al. [115] showed that the addition of tris(pentafluorophenyl)borane (TPFPB) to $LiBF_4$–EC–DEC improves the cyclability and raises the thermal stability of graphite anodes by as much as 60 °C.

DSC and ARC studies have shown that carbon anodes cycled in carbonate-based electrolytes undergo exothermic reactions between 60 and 200 °C [19,149–151]. Components of the SEI on MCMB cycled in $LiPF_6$–EC–DMC have been shown to be the source of an exothermic reaction below 100 °C [149], while above 100 °C intercalated lithium is believed to participate in the thermal reactions. According to Menachem et al. [151] a chemically bonded SEI formed by mild oxidation of graphite suppresses exothermic reactions and has a lesser tendency to 'peel off' from the anode during heating. In an exciting discovery, Jiang and Dahn [130] found that the addition of LiBOB to EC–DEC significantly improved the thermal stability of LiC_6. LiBOB is believed to form a robust SEI on lithiated carbon surface, preventing any exothermic process until 170 °C as compared to an onset temperature of 80 °C with $LiPF_6$–EC–DEC [130].

7.2. $LiCoO_2$

Li_xCoO_2 is thermally unstable and can decompose, releasing oxygen at elevated temperature [152–155] according to the reaction [31]

$$Li_{0.5}CoO_2 \rightarrow 0.5LiCoO_2 + \tfrac{1}{6}Co_3O_4 + \tfrac{1}{6}O_2.$$

The released oxygen can then react with organic solvents to generate heat. By ARC, Jiang and Dahn [156] showed that organic solvents can reduce $Li_{0.5}CoO_2$ (the normally fully charged composition) to Co_3O_4 and CoO, eventually even to Co metal and that the reactivity of Li_xCoO_2 in electrolyte can be affected by particle size, surface area, electrolyte composition, etc. [156,157]. MacNeil et al. [158] reported that the first thermal processes between Li_xCoO_2 and electrolyte can be described by an auto-catalytic reaction. In fact, the reaction of $Li_{0.5}CoO_2$ with EC–DEC begins at 130 °C, which is much lower than the decomposition temperature of $Li_{0.5}CoO_2$ itself [152]. Baba et al. [154], who evaluated the thermal stability of chemically delithiated $LiCoO_2$ ($Li_{0.49}CoO_2$) by DSC, the active cathode decomposed the electrolyte at 190 °C, the mechanism of which may be written as follows for EC [152]:

$$Li_{0.5}CoO_2 + 0.1C_3H_4O_3\ (EC) \rightarrow 0.5LiCoO_2 + 0.5CoO + 0.3CO_2 + 0.2H_2O.$$

A DSC peak at 230 °C is ascribed to the oxidation of the electrolyte caused by oxygen released from $Li_{0.49}CoO_2$ [154]. Jiang and Dahn [156] showed that the reactivity of $Li_{0.5}CoO_2$ was higher in LiBOB–EC–DEC than in $LiPF_6$–EC–DEC. The lower stability of the LiBOB-based electrolyte must be seen in the backdrop of the fact that the LiBOB can effectively stabilize the SEI of LiC_6. This means that graphite/$LiCoO_2$ cells cannot be rendered safer by replacing $LiPF_6$ with LiBOB in the electrolyte.

7.3. $LiNiO_2$

In its delithiated state, $LiNiO_2$ has a poor thermal stability due to the presence of the unstable Ni^{4+} ion [159]. Li_xNiO_2 ($x = 0.3$) releases oxygen at a lower temperature than Li_xCoO_2 ($x = 0.4$). The lower stability of Li_xNiO_2 is attributed to easier reduction of Ni^{3+} as compared to Co^{3+} [160]. Hence, a cell with $LiNiO_2$ may be less tolerant under abusive conditions [31]. Ohzuku et al. [161] have reported that $Li_{0.15}NiO_2$ undergoes an exothermic reaction at about 200 °C. Arai et al. [160] suggest that at 200 °C, Li_xNiO_2 transforms into a rocksalt structure due to cation mixing. The decomposition of $LiNiO_2$ in the absence of air may be described by [162]

$$2LiNiO_2 \rightarrow Li_2O + 2NiO + \tfrac{1}{2}O_2.$$

At x values less than 0.25, Li_xNiO_2 undergoes highly exothermic reactions with common electrolytes with an onset temperature around 200 °C.

7.4. $LiMn_2O_4$

The better thermal tolerance of $LiMn_2O_4$ as compared to $LiCoO_2$ was demonstrated by studies on $LiMn_2O_4$ electrodes [140] and 18650-type cells with $LiMn_2O_4$ [163]. ARC studies showed that cells with $LiCoO_2$ exhibited thermal runaway beyond 155 °C, while those with $LiMn_2O_4$ were stable up to

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180 °C [164]. MacNeil et al. [164] demonstrated that the reaction heat generated by $LiMn_2O_4$ in $LiPF_6$–EC–DEC increased with increasing amount of electrolyte. Improved cycling performance of $LiMn_2O_4$ at 55 °C with the addition of TPFPB in an EC–DMC-based electrolyte has been reported [147]. In fact, the additive improves the thermal stability of $LiPF_6$–EC–DMC electrolytes [148].

7.5. $LiFePO_4$

Probably the most exciting alternative to $LiCoO_2$ for large-size lithium-ion cells is $LiFePO_4$. It is thermally stable for its reactivity with electrolytes is very low [131,139,165] and no heat evolution is observed below 200 °C. Edstrom et al. [166], who characterized the SEI formed on carbon-coated $LiFePO_4$ in $LiPF_6$–EC–DEC by photoelectron spectroscopy with synchrotron radiation, detected no solvent reaction or decomposition products on the cathode surface, which suggests that the phosphate group does not react with the solvents.

8. Coatings

Thermal stability of the electrolyte in contact with active materials is of great concern in lithium-ion batteries [167]. In order to mitigate this problem, electrolyte additives that prevent direct reaction of the electrolyte with the active material have been tested. For example, additives such as γ-butyrolactone have been shown to reduce direct reaction of nickel-based cathodes in their charged states with electrolytes. The additive was reported to decompose, encapsulating the cathode with decomposition products [168]. Although lithium-ion cells with this additive did not explode during nail penetration tests at 4.35 V and overcharge tests up to 12 V, concerns about its compatibility with the anode and cathode remain.

Improvement of thermal stability by encapsulation of active material particles has been applied to anode active materials also. Kuribayashi et al. [169] synthesized the first prototype of core-shell-structured carbon composites. Yoshio et al. [170] showed that coating carbon on graphite can effectively suppress the decomposition of propylene carbonate on the anode as well as subsequent exfoliation of graphite. They also showed that the coating arrested the decomposition of ethylene carbonate-based solvents and thus the formation of solid electrolyte interface on the anode. Moreover, the coating improved the coulombic efficiency and decreased the irreversible capacity. Similarly, Yu et al. [171] showed that microencapsulation of graphite with nanosized nickel-composite particles blocked some of the edge surfaces exposed to the electrolyte, diminishing solvent co-intercalation and subsequent exfoliation in propylene carbonate-based electrolytes. It also led to decreased gas evolution during charging. The encapsulation led not only to improvements in charge–discharge performance, but to improvement in the safety of the negative electrode as well. The coating will also have sufficient capacity to absorb lithium generated on overcharging [172]. This prevents potentially hazardous lithium plating on the anode during charging.

Recently, several studies have concentrated on enhancing the cyclability of cathodes by coating cathode particles with oxides, glasses, etc. [173–182]. An attendant benefit is an increase in the thermal stability of the coated materials in contact with the electrolyte. Cho et al. [183] demonstrated that $LiCoO_2$ coated with nanoparticle-$AlPO_4$ blocked the thermal runaway of lithium-ion cells in addition to significantly reducing electrolyte oxidation and cobalt dissolution into the electrolyte. Cho et al. [184] also demonstrated the 12 V overcharge behavior of the $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ in terms of their exothermic behavior. Cho [185] showed that a thickness of 20 nm for the $AlPO_4$ coating was optimal. Although increased thickness of the coating drastically reduced the exothermic reaction between Li_xCoO_2 and increased the onset temperature of oxygen evolution, the reduced lithium-ion diffusivity was detrimental to cycling performance.

Fey et al. [186] showed that $LiCoO_2$ coated with cobalt oxides displayed increased resistance to decomposition reactions with the electrolyte. Not only was the temperature of the reaction raised by 11 °C, but the coating also reduced the exothermicity of the reaction. With the objective of improving the elevated-temperature performance of $LiMn_2O_4$, Vidu and Stroeve [187] investigated the electrochemical characteristics of $LiMn_2O_4$ coated with poly(diallyldimethylammonium chloride) (PDDA). By in situ electrochemical atomic force microscopic analysis under potential and temperature control, Vidu and Stroeve [187] showed that the PDDA layer blocks surface reactions that cause degradation of the cathode and led to improved thermal stability in an organic electrolyte under charge and discharge.

9. Conclusions

If abused by the user or not carefully designed by the manufacturer, batteries can be potentially dangerous. Conscious of the consequences, battery manufacturers incorporate a variety of safety measures in the design of their cells. While the manufacturer does what is best to render their products foolproof, an equal responsibility lies with the user, who must adhere to *Instructions For Use* that the manufacturer supplies with the power pack in order to avoid mishaps in their handling. Consumer education is also important. Consumers must specifically refrain from abuses such as short circuiting or drawing more current than the battery is designed for, use of undersized batteries, operation or storage at too high or too low temperatures, use of chargers designed for other battery chemistries, overcharging (both at too high a voltage and for too long a period), overdischarging, use in environments with excessive vibration and improper disposal.

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