Lithium-Ion Battery, Thermal Runaway and Its Fire Suppression

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Abstract: Lithium-ion batteries (LIBs) have been proved a technology for energy storage systems. It is a battery of choice in most portable gadgets like mobiles, electronics, power tools, aerospace, automotive and maritime applications. LIBs have attracted interest from academics to industry due to their high power and energy densities compared to other battery technologies. Despite the extensive usage of LIBs, there is a substantial fire risk associated with their use especially when utilized in electric vehicles, airplanes, and submarines. This review covers some relevant information regarding the material constitution and configuration of the cell assemblies, and phenomenological evolution of the thermal runaway reactions, which in turn can potentially lead to flaming combustion of cells and battery assemblies. This is followed by short descriptions of prevention and suppression runaway within LIBs.

Index terms: fire suppression, lithium-ion battery, prevention, thermal runaway

I.INTRODUCTION

An Energy storage system provides a means to store energy for later use to local grid. Batteries have historically been of limited use in large scale electric power systems due to their relatively small capacity and high cost. However, newer battery technologies have been developed that can provide significant utility scale capabilities[1]. The Lithium-ion battery (LIB) is an important technology for the present and future use of energy storage. Its high specific energy, high power, long cycle life and decreasing manufacturing costs make LIBs a key for sustainable mobility and renewable energy supply. Lithium ion is the electrochemical technology of choice for an increasing number of industries, ranging from small cells in consumer electronics to large scale in electric vehicles, airplanes, and submarines[2]. Recent studies by the National Fire Protection Association (NFPA), Fire Protection Research Foundation (FPRF)[3–6] highlight the potential hazards of LIB cells and large format packs during the life cycle of storage, distribution, and use in products. Although LIBs had reported hazards, the advancement in safety features and development over time has decreased the risk factors to certain extent.

The first LIB was proposed by Yoshino in 1985, based on earlier research by Whittingham[7]. LiBs became commercially available in 1991[8]. The chemistry of LIBs different from previously popular rechargeable batteries (e.g., nickel metal hydride, nickel cadmium, and lead acid) in a number of ways. Because of high energy density and adaptability for cyclic applications, Li-ion technology found to be effective. From a safety and fire protection point of view, a high energy density coupled with a flammable organic, non aqueous electrolyte has created new challenges with regard to the design and fire suppression of LIBs.

This paper reviews the processes associated with LIB, thermal runaway, its prevention and fire suppression.

II.COMPONENTS OF LIB

A typical lithium-ion cell comprises a positive pole which is also called the anode, a negative pole called the cathode, a diaphragm known as separator, electrolyte, and shell. In a Lithium-ion cell, alternative layers of anodes and cathodes are divided by a porous film (separator). When compared with previous rechargeable batteries such as lead-acid batteries, Li-ion batteries have a higher specific capacity, energy density, and power density. These advantages allow Li-ion batteries to support long-term operation and high-current usage, on aluminum and copper foil the cathode and anode foils are deposited. The solution allows the movement of Li-ions between the electrodes, whereas the separator fits between the anode and cathode preventing shorting between the two electrodes however allowing particle transfer. Separator and electrolyte solution present in the cell has less forbearance to temperature than the electrodes and current collectors, that area unit is made from the metal oxide/graphite or metal[9]. A LIB uses a chemical compound separator and an inflammable solution, that area unit each forced to sure temperature limits for safe performance.

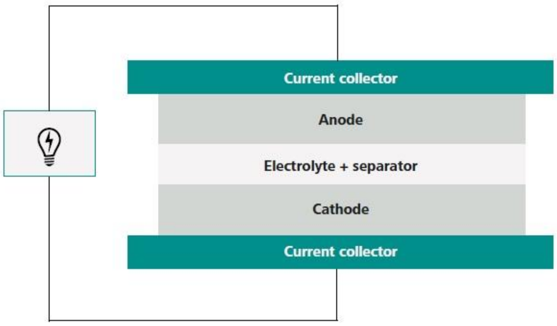

Fig-1: Components of LIB

III.LITHIUM ION BATTERY SYSTEMS

Commercially LIBs are available in cylindrical, pouch, button and prismatic designs. For desired power supply the cells are connected in parallel to each other. Multiple battery modules containing number of cells arranged in parallel or series configuration in a battery system[10].

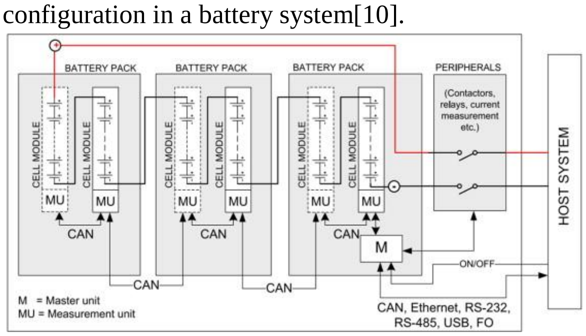

Fig-2: Lithium ion battery system

IV. THERMAL RUNAWAY IN LIBs

It is a chain of reactions within a battery cell that can be very difficult to stop once it has started. Thermal runaway is one of the safety concerns of lithium-ion batteries. The rapid increase in temperatures can result in catastrophic and often explosive failures of battery systems.

Mainly there are three usual types of lithium batteries: lithium-metal, lithium-ion, and lithium-ion-polymer. Once the lithium metal cells are discharged they are of no use and must be disposed of. Lithium-ion cells are rechargeable and are typically found in laptop computers or electronic devices. Finally, rechargeable lithium-ion-polymer battery/cells are typically found in electronic devices like computers, tablets, smart phones and differ from the lithium-ion cell only in terms of outer structure and external material. The temperature of the battery increases, this will further encourage the reaction. However, in the case of short circuit, high temperature, collision, and other abuse, the battery inside easy to cause thermal runaway When a Li-ion batteries temperature increases to approximately 266-302°F, the high-power materials and the biotic constituents are not stable and are susceptible to generating more heat. If the heat which is generated during the process is not tackled, this may result in rising battery temperature and accelerate the heat dissolution process. Very warm flashes can also be activated when the battery attributes a flaw that will result in a slowdown in rotation, overheating, and puncturing. Generally, the passivating film (solid electrolyte interphase, SEI) on the electrode decomposes roughly 69℃[11]. After the retrogression of the solid electrolyte interphase layer, the electrolyte solution reacts with the electrode and expels out combustible hydrocarbon gases[12]. At high temperatures, an electrode decomposes and releases oxygen. If the heat which is generated through the process is not tackled, the battery temperature will additionally increase and reverse the heat-releasing procedure to cause thermal runaway. When the lithium-ion battery starts burning, the cathode substance cracks and discharges O_2, also the battery explosion will eject CO and other volatile gases. These factors also make lithium-ion batteries burn even in confined environments the immediate escape of energy results in electrolyte combustion and the temperature of the battery increases rapidly. As other constituents of the LIB are all ignitable material, like graphite anode, diaphragm, cathode, which causes the battery materials to burn and even explode. If the shell of the battery ruptures, a large amount of oxidation air accompanied by Li causes the ignition in the battery in some cases it may also result in an explosion. Once ignited, it is very hard to suppress. In the majority of cases, it is lithium-ion and lithium-ion polymer which catches fire and needs to be suppressed as early as possible[13].

IV. THE CAUSES OF THERMAL RUNAWAY IN LIBs[14]

Electrical abuse (over-charging/discharging) [15, 16, 17]:
Over-charging or discharging to voltages beyond the manufacturers specified charge window can cause lithium plating, or dendrite formation, on the anode. Over time, this may pierce the separator causing a short circuit between electrodes and lead to thermal runaway.
Thermal abuse (over-temperature) [18,19,20]: Internal temperature in the 90–120℃ range will cause the SEI layer within a LiB to decompose exothermically. At temperatures above 200℃, the hydrocarbon electrolyte can decompose and release heat.

Mechanical abuse (penetration, pinch, and bend) [21,22]:
Mechanical abuse, usually caused by external mishap to the LiB such as car crash or during installation, can result in electrical shorting between the electrodes, via the electrolyte, producing localised heating.

Internal short circuit (ISC)[23]:
An ISC occurs due to the failure of the separator, allowing contact between the cathode and anode via the electrolyte. This can happen due to any of the above abuse conditions, or as a result of a manufacturing fault. The electrochemical reaction of $LiCoO_2$ lithium ion battery during charging and discharging[24,25]

Manufacturing defects: Presence of impurities or other imperfections originated during manufacturing process.

Cathode:

$$LiCoO_2 \underset{discharge}{\overset{Charge}{\rightleftharpoons}} Li + Li_{1-x}CoO_2 + e^- \quad (1)$$

Anode:

$$x\,Li + e^- + 6C \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_xC_6 \quad (2)$$

The overall reaction is

$$LiCoO_2 + 6C \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_{1-x}CoO_2 + Li_xC_6 \quad (3)$$

Functioning of battery involves certain chemical reactions. Some of which are exothermic reaction. Heat generated during such reactions gets dispersed surrounding. The heat liberated by battery and external heat applied to the battery leads to increase in temperature, which accelerate some exothermic reactions leading to thermal runaway.
When temperature of battery exceeds 120^0C, it experiences solid interphase decomposition. The separator breaks at about 130^0C which results in internal short circuit[26] and generates heat. When temperature reaches above the critical temperature, the charged $LiCoO_2$ undergo disproportionation reaction as

$$Li_{1-x}CoO_2 \longrightarrow (1\text{-}X)\,LiCoO_2 + X/3Co_3O_4 + X/3\,O_2 \quad (4)$$

Where X is determined by the stage of charge as in equation 3
At high temperature Co_3O_4 decomposes further to release more oxygen to bring about oxidation of electrolyte to generate heat. Again a chain of exothermic reaction takes place inside the battery generating heat causing thermal runaway.

$$Co_3O_4 \longrightarrow 3CoO + 1/2\,O_2 \quad (5)$$

$$CoO \longrightarrow Co + 1/2\,O_2 \quad (6)$$

$$2LiCoO_2 + CO_2 \longrightarrow Li_2Co_3 + 2CO + 3/2O_2 \quad (7)$$

$$O_2 \xrightarrow{electrolyte} CO_2 + H_2O + Heat \quad (8)$$

$$2CO + O_2 \longrightarrow 2CO_2 + Heat \quad (9)$$

As oxidation reaction takes place continuously, CO_2 and heat generated continuously

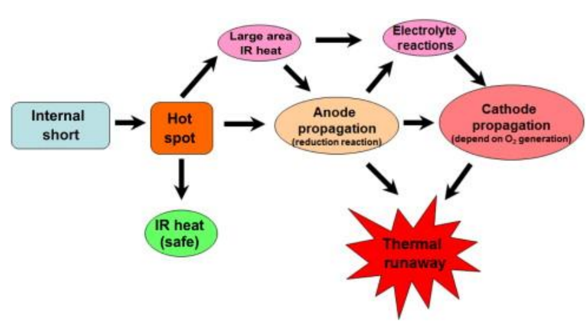

Fig -3: Thermal runaway cycle

V. PREVENSION OF THERMAL RUNAWAY IN LITHIUM ION BATTERIES

At present there are several preventive methods for thermal runaway which includes adding retardants to battery electrodes. Electrolyte and separator[27]. Also building a protective external system to a battery and use of suitable polymer.

Within a cell polymers can be used in two different ways to reduce thermal runaway. One in the form of separator which keeps electrodes apart to prevent internal short circuit and another way a thin layer of polymer is applied on electrodes. Liquid electrolyte which releases inflammable gases can be replaced by solid or gel polymer electrolytes. Use of suitable binder also helps to prevent thermal runaway. If the polymer has large enough expansion, increase in temperature causes binders to expand to prevent electron pathway from the reaction site.

Polymer separator: Literature studies shows that Celgard has developed a polypropylene/ polyethylene/polypropylene trilayer material which has melting temperature 130℃ and collapse temperature of 107℃. The collapse temperature can be enhanced using ceramic coating of $SiO_2$and Al_2O_3[28]. Other alternative polymers are polyimide/polyvinyldinelfluoride/polyimide tri layer [29]. In recent years progress has been made on polyacrylonitrile membranes[30] whose melting temperature reported around 322℃[31] and prevents leaking issues.

Solid or gel polymer electrolytes: To overcome the issues of releasing flammable gases by liquid electrolytes, solid or gel polymer electrolyte can be used. Gel polymers are prepared from a solid that has bee n wetted with standard liquid electrolyte, while solid electrolyte has no liquid at all. The drawback related with use of solid or gel electrolyte is inferior power densities and low ionic conductivities. For example, gel electrolyte, polymeric lithium tartaric acid borate and plyvinylidinefluoride-co-hexafluoropropane is stable upto 80℃ ℃ with ionic conductivities of 1.408×10^{-4} Scm^{-1} at20℃ and $7.836{\times}10^{-4}$ Scm^{-1} at 80℃. Examples of solid polymer electrolyte formed by casting lithium bis(oxalate)boratesuccinonitrile-polyethylene oxide polymer solution into porous polyimide nano fibrous film which has been shown to operate at temperature of 170 ℃ with ionic conductivity of 1.46×10^{-3} S cm^{-1}

Binders: Binders are the composite matrix of polymers with certain additives for mitigating thermal runaway. Binders should have high thermal expansion. While functioning as temperature rises, the polymer expands separating conductive pathway. For example more complex cabon black particles in ethylenebutylacrylate copolymer matrix have been studied, showing large increase in resistance at around 40℃[33].

VI. LITHIUM ION BATTERY FIRE SUPPRESSION

Many researchers have studied LIB fire in order to find an effective suppressant. Literature survey mentions the effectiveness of heptafluoropropane and Novec[34]. Many systems extinguishes fires but water based systems had better cooling ability. Tests performed by Federal Aviation administration[35] concluded that water based extinguishers like Hartindo AF-31, AqueousA-B-D(classA,Band D) are found to be effective suppressant and coolant medium as compared to non aqueous extinguishers. An alternative water extinguishing system is water mist[36]. Testing conducted by the National Fire Protestion Research Foundation, US, mentions that water mist can effectively suppress a fire invilcing an electric vehicle battery[37]. The extinguishing property of water mist can be improved by adding 5% F500 solution and 5% anionic surfactant to pure water[38]. In gas phased cooling process, the heat in the combustion zone is absorbed by the vaporization of water droplets which leads to decrease in temperature of the flames. The flemes will be extinguished if temperature falls below the critical temperature required for combustion. The coling processalso diminishes the flame radiation to the fuel surface, decreasing the rate of pyrolysis of fuel.

VI. CONCLUSION

Even though LIBs have been proved a technology for energy storage system and it’s a battery of choice, the hazards and safety concern associated with it are of great importance as fire incidence do still occur. There should be more emphasis on use of water as cooling material with improvement in the selection of material of battery component. Water mist with proper surfactants and additives can provide most promising green method of fire extinguishing.

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