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A Roadmap For Future Lithium-ion Batteries: Thermal runaway, it's Cause and Remedy

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ABSTRACT: Lithium-ion batteries (LIBs) are currently the most preferred secondary sources of energy due to its intrinsic properties such as high energy density, longer life cycle as compared to the other available batteries. However, it faces a significant challenge related to thermal safety concerns such as thermal runaway when utilized over an extended period, prolonged charging, and the use of incompatible electrolytes or separators with low stability. Addressing the safety concerns of Lithium-ion Batteries (LIB) is clearly not a matter of an immediate solution, given the multitude of external and internal factors involved. Therefore, a comprehensive approach is required, spanning from the manufacturing process to end-use, to effectively tackle this highly critical challenge associated with LIB. The mechanism of thermal runaway commences from the time of its first cycling process, which involves transfer of ions from anode to cathode via electrolyte medium and vice-versa and separator in-between acting as a barrier to their free movement. As time passes, the electrolyte degrades and is resistant to absorb heat, resulting in breaking the SEI (solid electrolyte interface) and dendrite structure is formed gradually leading to short-circuit. The abnormal rise in the temperature of cell beyond a threshold point and thermal runaway result in explosion of cell. In this paper, the authors have reviewed some of the recent works done by the researchers on this critical issue starting from its initiation, gradual development to intensification, and final stage of blasting. Here, the roles played by various elements of cell have been studied in detail on the research data available. Then, an analysis has been made on this study and few recommendations have been proposed at the end, which, the authors think, will help to a great extent to mitigate the issue of TR(thermal runaway) in LIB and clear the roadway for a safe and sustainable design in future.

Keywords: Storage cell, polymer Electrolyte,Dendrite, Thermal runaway

INTRODUCTION:

It will not be an overstatement to say that in today's world, 'energy' is the most essential amongst all the resources available to the human civilization by the nature.

The whole world will come to an abrupt halt if energy supply is stopped even for a second. It has been estimated that US will be losing a sum of $ 5 billion roughly in manufacturing sector only, if there will be a shortage of supply of energy for even an hour as reported by the department of US Energy. As per the reports of US energy information administration (EIA) -2023, per capita energy demand of developing countries varies within 10,000KWh, against 10,000 -5,00,000KWh for developed nations. As per recent report released by EIA World energy outlook, 2022, out of total energy demand of energy worldwide, about 66-70% are met from fossil fuels, a primary and non-renewable source of energy. (i.e., from oil, gas, coal and nuclear). The rest of the demand is obtained from other renewable energy sources like hydro, wind, solar, geo-thermal and biomass. This corresponds to the fact that the primary sources are under high depletion, whereas, renewable sources are quite meagre indicating a very high potential to tap solar (1.9%),hydro(2.3%),geo-thermal(0.2%)and wind(3.8%) as per EIA report, April 2022.

It is further reported by EIA that along with consumption of energy, there is huge release of greenhouse gases by these sectors as given below: -

Sector	Consumption (% of total energy)	Emission of CO2
Industry	29	27
Transport	33	25
Residential	27	20
Commercial	8	23

Emission of the GHG (green house gases) has severe bad effects on environment like atmospheric pollution which can result in depletion of ozone layer. This could lead to an increase in atmospheric temperature resulting in Global warming. Global warming could result in natural calamities across the whole world, which was a great concern for global leaders at the recent G20 meet held in India.

This can be resolved by taking following measures:

a. Shifting focus to tap from non-renewable sources to renewable sources.
b. Devising a sustainable storage system of energy to meet balance demand thereby limiting continuous production of energy and reducing huge depletion of these natural resources.

Hence, the concept of energy storage is meant to safeguard for future need.

1. Energy storage:

1.1 Storage of energy, secondary energy system.

In the realm of the energy sector, the evolution of storage systems dates to as early as 1800 with the creation of the first battery cell, known as the Volta cell. Researchers progressively refined this system, leading to the development of the first secondary cell in the form of a Lead-acid rechargeable battery in 1859. The Lithium-ion battery, widely used today, was introduced in 1983. The significance of energy storage systems gained further recognition when pioneers in the field, namely Prof. John B. Goodenough, Prof. M. Stanley Whittingham, and Prof. Akira Yoshino, were awarded the Nobel Prize in Chemistry in 2019 for their groundbreaking invention of the Lithium-ion battery.

1.2 Working of Li-ion cell:

This device is based on a principle of conservation of energy, i.e Conversion of electrochemical energy to electrical energy and stores energy for a considerable period for future use. The cell consists of an electrode called anode, which is normally a carbon based(graphite) material and other one is cathode, normally made of oxides of Lithium in a LIB. During the process of charging, the Li-ions are released from cathode and moves towards anode and deposited there. During discharging, Li-ions, which were earlier deposited at the interface of anode and electrolyte, loses electron that moves towards cathode through external circuit and balance Li-ions move back to cathode through the electrolyte medium and this process continues till the end of battery life or next charging, which ever is earlier. For an ideal cell, the electrodes and electrolytes should be compatible to each other which is determined by the functioning of interface between electrode and electrolyte.

However, Lithium-ion batteries (LIBs) encounter significant challenges, particularly in terms of thermal safety. Issues such as thermal runaway, short-circuiting, and explosions pose critical concerns. Thermal runaway, a complex problem influenced by factors like prolonged charging and operation periods, the use of flammable electrolytes, incompatible electrodes and electrolytes, and manufacturing defects, is a primary issue. This phenomenon is often triggered by the accumulation of charging-discharging cycles, leading to the formation of dendrites that decompose the Solid Electrolyte Interface (SEI) near the anode. This process raises the electrolyte temperature, resulting in ignition and ultimately explosion.

Recent incidents, such as the explosion of an electric cycle battery in a bedroom that claimed three lives in February 2022 and the 2018 incident in Utah, Jordan, where a Tesla car battery exploded causing loss of human life, underscore the severity of these thermal safety concerns. While current LIBs have already been enhanced to deliver six times the energy density of a lead-acid battery (0.5 mega joules/second), further improvements can be achieved by replacing carbon materials with silicon, potentially reaching 3 mega-joules/kg. For those seeking even higher energy density, Zinc-air batteries present a promising option, offering a theoretical energy density of 5.3 mega-joules/kg. Hence, the immediate task for the researchers and scientists is to find out the safest way of designing a storage cell (LIB), which will be safe enough for use. Besides, the time has come to bring out international standards and guidelines, to be followed during manufacturing, use and subsequent period of maintenance.

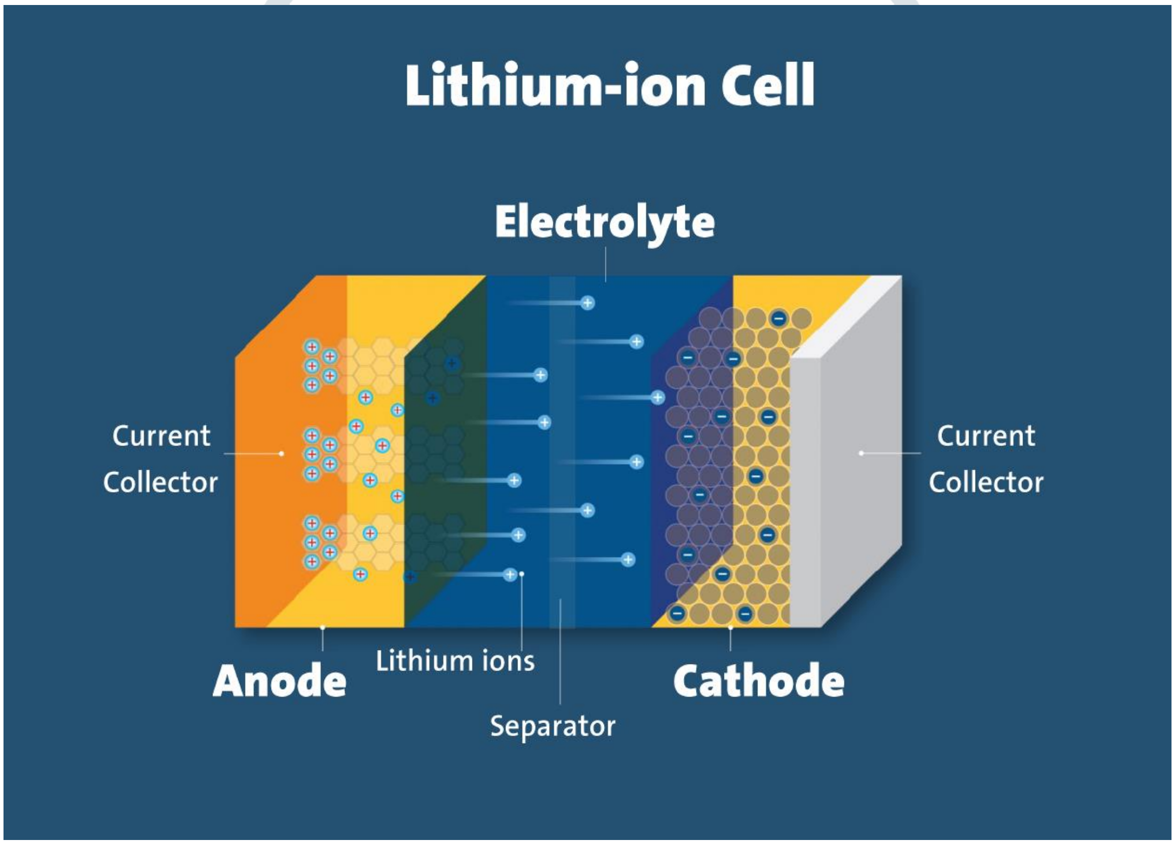

Figure 1:Lithium Ion Cell(51)

2.0 LITERATURE REVIEW:

Lithium-ion battery has a non-aqueous electrolyte medium, which helps it to maintain cell voltage nearly 3 times higher than its aqueous counterparts like Ni-mH, Ni-Cd battery and hence, it is now preferred to. Though, it has higher specific energy, higher energy density as compared to others now in battery market, it suffers from some limitations like safety, cost and life which need to be resolved.

The researchers here (1) have reported that at present, there is no standard testing method to measure the degradation rates of LIB in its life period and have suggested an establishment of a suitable testing standard for it. Besides, they also have recommended the idea of modifying the presently used cathode material Lithium using transition metal hydrides through coating, dopants etc. to extend battery life. In regard to modification of anode material, they have suggested gradual transition to silicon or blends of carbon and silicon instead of using pure carbon material along with compatible electrolyte. The safety aspect, which is the most important of all present challenges, can be assured by use of layered safety protection measures for all parameters like electrodes & thermo-static electrolytes. But, in future, they have recommended for implementation of a sensor-based security system to monitor various parameters like temperature, voltage, current, pressure, quantum of dendrite formation etc. complying to EUCAR, USABC, NEDO guidelines to minimize safety and security threats.

In this paper (2), the authors have made a comprehensive review of various challenges faced by Li-ion battery and their innovative solutions making it the future battery. They have examined various issues such as limitations of energy density of existing cells and ways to enhance it, thermal runaway issues and their prevention, adoption of proactive recycling measures and use of alternate materials for electrolytes like solid state electrolytes and electrodes.

In this article (3), the author has reported that supremacy may continue till nearly two decades more unless any improvised form of Li-ion is commercialized. The researchers around the world are thinking of tagging Li-ion battery to renewable sources like wind and solar, which can supply power at night. Author here has recommended use of solid electrolytes in a Li-metal battery, which has higher energy density, to minimize the fire hazard and add protective circuit to avoid thermal runaway. He has further recommended use of microporous polymer membranes and inorganic membranes as separator in battery for minimizing short-circuiting. For anode, Si-Sn and for cathode, Mn- and Fe- based composites will best fit along with low-cost. He has reported about green battery with low carbon foot-print having organic/in-organic electrodes, solid polymer electrolytes and microporous membrane as separator for future market.

In this paper (4), the author had highlighted the importance of performing some standard tests on evaluation of various functioning of Li-ion battery prior to its use in prototype. For parameter like (a) In a Li-ion battery, the new anode is to be evaluated at a range of 0-0.8 Volt and for cathode evaluation at range of 0-3.0 volt. High-rate performance of battery can be achieved by using thin electrode layer and thin particles. The rate performance and coulombic efficiency are evaluated at 80% capacity retention. The theoretical energy density is to be calculated by using Nernst equation. Then, the highest ratio of real energy density of cell to that of theoretical energy density of electro-chemical cell , which is normally at 58%, is used in calculation of possible energy density of battery .

Due to problems like immature dysfunction, improper handling, extra loads, huge amount of waste are being dumped and eventually causing environmental pollution. This urgently needs devising a best recycling process. Present scenario reflects that roughly only 3-5%of global waste reaches for Recycling (6). As per CAS study in 2019, recycling of 5 lakh batteries has yield of about 15,000 tons of aluminum,35,000 tons of phosphorus, 45,000 tons of copper, 60,000 tons of cobalt, 75,000 tons of lithium and 90,000 tons of iron after re- cycling. This will reduce mining of fast depleting raw materials reserves for LIB production and reduce greenhouse gas generation. Out of various technologies evolved for recycling of waste, Hydrometallurgical methods are preferred to normally used Pyrometallurgical method and direct recycling .

Safety problem of LIB such a thermal runaway occurs when flammable electrolyte medium gets easily oxidized due to excess heat development and causing high rise in cell temperature, finally leading to blasting. The author here (7) has reviewed the dynamism of thermal runaway, its causes and various measures like using flame-retardant additives, stable lithium salts, design of safe electrolytes for LIB such as solid-state electrolyte, ionic liquid electrolyte, thermosensitive electrolytes etc .

Here, the authors (8) have recommended use of phase change materials , which can absorb a major portion of heat and safeguard the battery system against thermal eventuality. Here, the authors have produced the results of experiments on use of CPCM(composite phase change materials) at different charging- discharging rates . Their finding was that this composite filler CPCM (silica and graphene at ratio 1:1)material could help not only in increasing thermal conductivity of electrolyte to highest i.e. 1.307 W/(m.K) , but also reducing the cell temperature as high as by 13.7^{o}C and 19^{o}C under 2C and 3C conditions , thereby have a significant cooling effect on the system.

Here (9), the authors have experimental study on thermal runaway (TR) and thermal runaway propagation (TRP) by using various unconventional testing process i.e. by nail penetration, side heating and over-charging. The extended volume accelerating rate calorimetry (EV-ARC) test was performed on the cell with an internal planting of thermocouple to measure the heating effect caused by above 3 abused methods. The results obtained showed that maximum temperature of inside cell rose to 994.8ºC, 964.3ºC and 1020ºC through nail penetration, side- heating and over-charging tests respectively. It was observed that the thermo-couple placed inside cell was damaged inferring severe effect of over-charging of cell and confirmed that TRP through over-charging was most hazardous of all.

Here (10), the authors have used a novel methodology to test the efficacy of ASSBs (all –solid-state batteries) on mitigation of thermal runaway. The authors have used a specialized designed closed calorimeter with highspeed synchrotron X-ray radiography to measure the thermal effects on ASSBs. In the process, the electrodes were first removed from LIBs after charging LIBs to 100% and reassembled with an LLZO(lithium lanthanum zirconium niobium oxide) electrolyte. The result was that there was 11% decrease of heat release in LIB as compared to that during thermal runaway.

As the charging time increases, the problem of thermal runaway process begins with rise of temperature of cell. In the process, solid electrolyte interface between anode and electrolyte starts decomposing ,when the temperature of cell rises above a threshold level(130ºC) along with breaking of separator, leading to short-circuiting and break-out of fire in electrolyte. The authors here (11) have recommended use of flame retardant phosphorus based additives in the electrolyte like Ethyl phosphate-polyethylene glycol based copolymer(EPCP),alkyl based phosphate ester like trimethyl phosphate(TMP), triethyl phosphate (TEP), phenyl phosphate based ester such as TPP(triphenyl phosphates), diphenyl methyl phosphate(CDP) etc. These additives will be helpful in formation of a dense and stable SEI layer thereby protecting anode surface and preventing formation of short-circuiting and breakout of fire. Other additives like composite flame retardants with phosphorus and fluorine based, ILS (types of organic molten salts) which not only helps in prevention of formation of excess heat, but enhances ionic conductivity of electrolyte.

Battery safety problem increases non-linearly with increase of capacity . In high capacity cells, tremendous heat is released from the reaction between flammable electrolyte and cathode under mechanical, thermal and electrical excesses . The authors (12) have studied the quantum of heat released by fully charged cathode and various solvents in electrolytes and selected fluorinated bis(2,2,2-trifluoroethyl) carbonate to prepare a non-flammable, low-exothermic electrolyte. Their study showed significant drop in cell temperature by one-third and decrease in maximum heating rate from 206.0ºC/S to 82.6ºC during thermal runaway process.

The authors (13) have viewed that addition of the flame-retardants though reduces the fire hazards of LIBs , may have adverse effects on electro-chemical performance of cell. They have reported that use of phosphate ester flame retardants decomposes on the surface of negative electrode. The research carried out by the authors found that by addition of polypropylene film (PP film) package as flame retardant prevents the thermal runaway process to develop, when a heat-triggered mechanism is instantly activated by subjecting battery to any abuse circumstances.

In this article (14), the authors conducted experiments to find out the intensity of heat generated in a LIB through a thermal runaway process. As it is known, all solid-state –batteries are designed to yield high energy density by replacing the lithiated graphite negative electrode by lithium metal foil and to increase safety, organic compounds are removed. The thermal effect of all-solid-state battery was studied using X-ray radiography and a high speed camera. It was observed that the entire process of thermal runaway was very fast and lasted for 5 minutes. In contrast, the thermal runaway of a LIB lasted for 500ms and there was development of a huge pressure to the tune of 188-mbar as measured through a piezoelectric sensor. This amount of huge pressure developed in a LIB through the process of thermal runaway was found to be equivalent to 2.7 g of TNT.

High energy density alkali-ion batteries such as Li^+, Na^+ and K^+ have a great unresolved problem of TR. The researchers all around the globe are experimenting to find the ways for a full-proof LIBs by trying on fire-safe materials, improving thermal management system. Here (15), the authors have recommended for a holistic approach design of battery starting from choice of proper materials with efficient thermal management property , control of use and building-in an early warning devices in the battery , which will go a long way in minimizing this critical issue.

The main player behind this safety hazard issue like thermal runaway is the organic liquid electrolyte, which is flammable and easily catches fire with a little abuse. The authors (16) have reviewed the mechanism of use of flame retardant and updated progress of research on a no of flame-retardant additives such as phosphorus -based, nitrogen-based and halogen-based flame-retardant additives and their design strategies and their impact on LIB batteries.

As per data available, among all types of failure modes of a LIB, failure due to development of internal short-circuiting (ISC) leading to thermal runaway is the most critical. In spite of a large no of researches are being carried out to find out the mechanism behind this ISC, no confirmatory report is yet available . In this study (17), it has been demonstrated that mechanical indentation techniques can address and regulate the development of Internal Short Circuit (ISC). This is achieved by classifying the electrochemical safety behavior of Lithium-ion Batteries (LIB) based on factors such as state of charge (SOC), ISC resistance, and electrode area. Then the authors have examined the safety boundaries and developed an electro-chemical behavior map for LIB after occurrence of ISC. Thus, they are hopeful by adopting above technique, one will be able to minimize the post-occurrence effects of ISC on LIB.

The authors (18) have reviewed the earlier works in the field of thermal management of LIBs and recommended for installation of system for accurate heat generation measurements in the LIBs and improved modeling for early detection of magnitude of heat generated and other thermal effects during charging and discharging of EVs.

The authors (19) have reviewed the fundamentals of origin of thermal issues in LIB and reported about current progress in this area and highlighted the most effective design process to improve safety aspect in a LIB .The authors have recommended use of flame retardant additives in electrolyte, emphasis on use of non-flammable liquid electrolytes, use of newly developed polymers with high melting points, use of solid electrolytes to reduce possibility of internal shorting, composites of inorganic and polymer electrolytes etc along with building-in an early warning system, robust operation manual for ensuring accurate check at different stages of use .

The authors here(20) has used (FMMEA) failure mode method effects analysis instead of normally used (FMEA) failure mode effects analysis as the earlier one helps in a deeper analysis focusing on dynamics of failure at component level. As reported, the mitigation strategies to mitigate safety failure in a LIB can be dealt at (1) intrinsic level, i.e. by modifying the materials used at cathode, anode and electrolytes with additives, (2) using protection devices like pressure vents, circuit breakers, fuses etc., and (3) battery management system like maintaining cell temperature below a threshold level by using air, liquid and phase change materials – based cooling. Thus, identifying fire at preliminary stage and using suppressive additives is very critical for fire management of a cell. The anode materials need to have lower potential than cathode material along with higher reducing power and better mechanical strength to safeguard any kind of abuse. Lithium metal, which has high specific capacity(>3860mAh/g) and lowest potential (-3.040V), is an ideal choice for anode. Similarly, for cathode, layered cathode in form of $LiCoO2$ (LCO), LMO (Lithium manganese oxide), Lithium iron phosphate ($LiFePO4$) i.e. LFO are potential materials as found till date.

Fixing the optimal threshold for temperature in a LIB battery is of paramount importance for assuring safety during its operation. Adequate heat is generated during charging and discharging process and needs to be examined in detail for its source of generation, reasons etc. The authors here (21) have reported about 2 types of heat generation such as Joule heat and reaction heat, which depend on factors like SOC (state of charge), current intensity, and temperature of cell after validating their intensity through experiments.

The authors (22) have reported about the thermal analysis database prepared on the results of works conducted by Tsinghua University and its collaborators. This database mainly contains comparable data for different types of cells, cell chemistry using accelerating rate calorimetry and differential scanning calorimetry. The data are compiled for 3 nos of characteristics temperatures, which have been used to interpret thermal runaway mechanism and found to be common causes of Thermal runaway (TR). It is reported that cause of major heat is the redox reaction between cathode and anode at high temperature, where as, the contribution of short- circuiting is very little of total heat generated. The only exception is that this short-circuiting helps in triggering the redox reaction after breaking down of separator. This will provide a new insight into the understanding of thermal runaway.

The authors here (23) have reviewed the progress in research works in characteristics of TR propagation and its prevention strategies to avoid any TR-related accidents. The reasons of initiation and triggering of TR in most cases happened till date was from short-circuiting, high exothermic chemical reaction, overheating, overcharging, mechanical abuse, manufacturing defects, materials used in electrodes, fire-prone electrolytes etc. Hence, the authors feel that choice of suitable thermal stable electrode materials, separators flame retardants and cooling additives for electrolytes, installing external safety devices like sensors and a well designed BMS (Battery management system) to intelligently monitor operating temperature, heat generation, issue early warning etc., will help in mitigating this hazard to a great extent.

To test improvement in performance in a Li-ion cell, separator's surface was coated with ceramic materials. Here (24), the separator was prepared by coating the polyethylene membrane with nano-sized Al203 powder and hydrophilic poly(lithium4-styrenesulfonate) binder. When tested, this separator showed improved performance on thermal stability at high temperatures without any thermal shrinkage. With use of this coating, the wettability of separator in non-aqueous liquid electrolyte increased and when tested for their cyclic performance, the cells showed better capacity retention than the cells prepared with only polyethylene membrane.

In order to testify the LIB's resistance to stand against ignition and TR, the authors here (25) added some flame retardants of organic phosphate compounds like triphenyl phosphate(TPP) and tributyl phosphate(TBP) and tested at fully-charged state and showed superior improved performance, when Horizontal burning test was also conducted in a flame test chamber .Similarly, thermal stability test on electrodes were also performed using accelerating rate calorimetry(ARC).It was observed that anode with electrolytes containing flame retardant additives showed less heat generation and higher decomposition temperatures. Similar observation (28) was found that the LIB showed better thermal resistance with less heat generation, when flame retardants were added to electrolytes.

It is a fact that thermal runaway is initiated in a storage cell due to intercalation of ions in the electrolyte and subsequent formation of dendrites due to excess oxidation at anode face (decomposition of SEI) during cycling. Here (27), the authors have used a new method of designing a SMART battery that will monitor the internal battery health in-situ. By using this technique, the authors have achieved early detection of dendrite formation inside the battery through installation of a a bi-functional separator, that acts as a third sensing terminal in addition to existing ones. This third sensing terminal provides unique signals in form of a pronounced voltage change, thereby, indicating sudden penetration of dendrites through the separator. This was found to highly effective to act as an early warning system for short-circuiting and can act for improved safety of many batteries including LIBs.

Here, (29), the authors have reported about a concentration-gradient cathode material made up a layered lithium nickel cobalt manganese oxide. In this case, each particle has a central bulk rich in Ni and outer layer rich with Mn ,with decreasing Ni concentration and increasing Mn and Co concentration towards top surface. This sorts of concentrated gradient cathode material provided high capacity as high as 209mAh/g and retained 96% of this capacity after 50 cycles at a temperature of 50ºC indicating good thermal stability.

Here (30), the authors have reported about a novel temperature-sensitive cathode material namely LiCoO2 at P3DT developed with a conductive polymer "skin", which will provide improved cycle at ambient temperature along with shutting down the working of cell at elevated temperature of 110ºC, thereby acting as a self-activating thermal protection to contain TR for LIBs.

For a LIB, higher the energy density requirements, higher is its propensity to thermal runaway.The authors (32) have reported 3 characteristics temperatures , which are common features of thermal runaway process of all LIBs . These temperatures are named as T1,T2 and T3 corresponding to 3 states of Thermal runaway process in a battery system. T1 is temperature of cell at the onset of heat generated due to decomposition of SEI and determined by the intercalation process between electrodes , T2 is the triggering temperature ,which is very important element for promoting TR and is determined by collapse of the separator .At this stage, if due care is taken to prevent its triggering effect, TR will not advance further. T3 is the maximum temperature that the cell can reach during TR process. These 3 temperatures actually determine the safety design of the LIB.

The authors (33) have reported about a multi-functional additive diethyl phosphonate (DETSP), a phosphate-silicon-integrated electrolyte additive , which has been tested to suppress the spread of fire in the electrolyte along with increasing cycling period of NCM811 cathode with a capacity retention of 89.9% after 400 cycles at 1C against 61.3% of normal electrolyte .Besides. this additive is compatible with graphite anode without any adverse electro-chemical performance and may be a suitable material for LIBs in providing adequate safety and stability of high voltage cathodes.

In a LIB, there are multiple electro-chemical cells function together .Hence, it is very complex to exactly determine the cause of malfunctioning at any time. Here (34), the authors have investigated the impact of change in electrode thickness on the overall electro-chemical and thermal functioning of the battery. It is observed that thickness of electrodes play a significant role in various attributes like energy density, temperature response, heat generation, capacity retention rate etc.

Two major challenges before LIBs are lack of high safety and electro-chemical performance during TR process. It has been observed that though adding flame-retardant additives to electrolyte provides some relief to TR, but it adds up other negative effects on performance due to chemical and physical incompatibility with electrolyte & electrodes. In order to circumvent this problem, the authors here(35) designed an intelligent , self-adaptable gel polymer electrolyte(GPE) using a copolymer with functional pendent groups, which assisted in increasing lithium- ion mobility, provided redox stability, helps in improving cyclization reaction alongwith reducing combustion .

It is now felt that SPEs (solid state polymer electrolytes) with good healing capability will be the materials for future batteries. In the present case(42), the authors have prepared a SPEs with combination of a poly-network(HFBM-co-SBMA),imidazole-based ionic liquid(EMI-TFSi) and LiTFSi, which have properties of very high stretchability(>4000%),stress>130kpa, non-flammable and notch-insensitive intrinsic self-healing capacity. The use of imidazole cation and fluorine atom helped in formation of super molecular bonds inside the electrolyte, thus empowering the SPEs with adequate healing capacity (i.e. recovery time<60 min,25ºC.The electro-chemical window of SHSPE(self- healing solid-state polymer electrolyte) achieved a higher voltage Level of 4.9V,adequate to meet the requirements of lithium batteries. Besides, the SHPSE was capable of having excellent interfacial compatibility with lithium electrode and better adhesion (load>200g).The assembled battery(Li/SHSPE3/LiFPO4) was observed to deliver a high discharge capacity of 144.8mAh/g at 0.2C with its capacity retention of 82% after 100 cycles with coulombic efficiency of 97%.This novel electrolyte could fully recover to function after repeated damage.

In this article (36), the authors have presented about the all- solid- state batteries (ASSBs) ,which will be able to overcome the safety hazards along with meeting energy requirements and providing excellent electrochemical – mechanical stability. This ASSBs contains solid-state electrolytes (SSE) as its nomenclature indicates. This SSEs are of types SIE (solid inorganic electrolyte), SPE(solid polymer electrolyte), SHE(solid hybrid electrolyte).

The authors (37) have proposed for use of polymers both in electrolyte and electrodes to minimize these problems and provide trouble free safe and enhanced cycle and capacity. Composite separators made of ceramic and polymers provided higher tolerance of abuses. The modified surfaces of cathode by polymers (PI) polyimides) could help in enhancing electro-chemical performance, especially LiNixCoyMnzO2. Again, by coating of cathode surfaces with reactive oligomer/polymer had good effect on reducing short-circuiting and reducing the probability of TR. Then , trials were made by coating anode surfaces with polymers such as PI(polyimide),Polyurea and Poly cyanoacrylate and showed there is ample suppression of dendrite formation.

In current times, Si-based anodes are found to be better alternatives in LIB as regards attributes like electro-chemical performances, thermal stability etc go. Here (38), the authors have used (DSC) differential scanning calorimetry to compare thermal behavior of Si and Sio (silicon monoxide) electrodes with reference to different SOC (state of charge) and electrolyte type. It is observed that there is reduction in heat generation due to reduction in amount of lithiation and incorporation of oxygen matrix. Besides, the existence of F- containing species on electrodes with addition of fluoroethylene carbonate (FEC) into electrolyte reduces reaction between electrolyte and active material , thereby lowering heat generation.

Future generation Lithium-metal battery demands for high specific energy in the order of >400Wh/kg, but it suffers from poor electrolyte-electrode compatibility and a compound of safety concerns. Here (39), the authors have used a modified form of conventional electrolyte, a hybrid electrolyte, prepared by simply formulating the composition of conventional electrolyte, which was helpful to ensure high chemical and thermal stability with Li-metal anode and high-nickel layered oxide cathodes. By use of this hybrid electrolyte, LiNi0.6Co0.2Mn0.2 cells showed improved cycling and rate performance.

It is known that highly concentrated electrolytes normally show better electro-chemical performance and thermal stability due to their low flammability property. Here (40), the authors have used $LiN(SO_2F_2)$ based concentrated electrolytes to demonstrate the mechanism of TR(thermal runaway).They have reported about generation of huge quantity of heat in LIB due to reaction between the lithiated graphite and $LiN(SO_2F_2)$ that triggers thermal runaway(TR) of LIB, in spite of the flammability/ non-flammability characteristics of the electrolyte. The mechanism of TR in a battery is initiated, when the electrolyte starts oxidized with more oxygen released at anode and this helps in triggering effect of heat in the electrolyte.

3.0 SUMMARY OF RESULTS OF REVIEW:

AUTHOR/YEAR	INTERVENTION TYPE	PURPOSE	DETAILS OF INTERVENTION
Sun, Y.K. et al. (2009)	internal	Design of high capacity and high rate of retention LIB	By using layered lithium-cobalt-manganese - oxide with varying degree of concentration of material along body
Wu, H. et al. (2014)	internal	Improving battery safety by early detection of dendrite formation in LIB	By Using a bi-functional separator
De, Dang. (2015)	internal	1.Prevention of fire hazard(TR) issue in LIB	By using protective circuit and solid electrolyte
		2.To improve separator function and minimize short-circuit in LIB	Microporous polymer and inorganic membrane
	external	Anode modification	Si-Sn based composites
		Cathode modification	Mn^- and Fe^- based composites
J, Helen. et al. (2016)	external	Recovery of materials of defunct LIB through Recycling	Hydro-metallurgical process
Liu , K . et al.(2018)	internal	Control and prevention of TR In LIB	1.Early warning system and robust operation manual 2.use of polymer with high melting point, solid electrolyte to prevent ISC and inorganic and polymer composite electrolyte
Liu, Binghe. et al.(2018)	internal	Safety issue concerning internal short-circuiting in LIB	Preparation of electro-chemical behavioural map for parameters like SOC, ISC and electrode area
Xuning , F. et al.(2019)	internal	Scientific evaluation and control of TR (Thermal runaway) in LIB	Identification of 3 characteristics temperatures(T_1,T_2 and T_3) at different stages in TR process
Hong, Li . et al.(2019)	external	1.High rate of performance in LIB	Use thin electrodes
		2.Evaluation of cell potential, temperature	Use of Nernst equation

Xiaolu, Tian.et al.(2020)	internal	Prevention of TR In LIB	Use of flame-retardant additives, stable lithium salts, ionic liquid electrolyte, thermos-sensitive and solid state electrolyte
Alvaro Masis. .et al.(2021)	external	Measurement of degradation of electrodes in LIB	Establishment of suitable testing process
	internal	1.Extension of battery life in LIB	Using dopants of lithium-hydrides cathode
			For anode, replacement with silicon/ blends of carbon and silicon
		2.minimise threat of TR in LIB	Fixing of sensor based security system to monitor parameters like temperature, heat ,voltage, current etc.
Quoc-Thai, P. et al.(2022)	internal	Enhancing battery safety, cycle life and electro-chemical performance of LIB	By coating cathode surface with Polyimides such as $LiNixCoyMnzO_2$
Dan, Wei. et al.(2022)	internal	Study of TR behaviour of LIB	Out of abuse methods such as nail penetration, side heating and over-charging, Over-charging is most severe of all.
Juliette, C. et al (2022)	external	Safety evaluation of all solid state batteries	By use of in-situ synchrotron X-ray radiography
Weijie, Ji. et al.(2023)	internal	To reduce development of TR mechanism in LIB	By use of poly-propylene film package as flame retardant
Shi Chao, Zhang. et al. (2023)	internal	Reduction in temperature of electrolyte of LIB	Use of non-flammable, low-exothermic electrolyte such as fluorinated bis carbonate
Xiawei, Mu. et al.(2023)	internal	Safety of LIB and prevention of TR	Use of phosphorous based flame retardant additives EPCP,TMP,TEP,TPP,CDP
Kai, Zhang. et al. (2023)	internal	Prevention of TR risk and bring cooling effect in LIB	Use of phase change material CPCM (silica and graphene ratio 1:1)

As seen from above table, internal interventions are more intense than external interventions in a LIB for safeguarding against Thermal runaway and over all safety and sustainability. The list of internal and external interventions are quite long because of involvement of a no of factors in functioning of a LIB. Hence, it is quite cumbersome to pick-up a single strategy for a LIB cell , rather it requires judicious combinations of appropriate internal and external interventions depending on size, capacity, purpose and place of use, for overall safety, sustainability keeping cost economy in priority list among others.

4.0 Conclusion:

The most critical issue for a LIB is generation of thermal runaway

Process. As the research finds, some other reasons for its occurance are increased weight of battery to accommodate higher capacity,

Continuous operation for a longer period, use of incompatible electrolyte materials etc. It has been reported that this process is initiated right from the time of 1st operation of battery, when the ions released from cathode move towards anode. While moving in the conducting electrolyte, it is subjected to frictional force due to viscous property of electrolyte and in turn raising the temperature of electrolyte. Then it's bombardment against separator wall further assists in heat generation . Hence, this initial rise of temperature (T1) is very crucial. Unless proper measures are taken to contain this initial set-back, further problems add up with decomposition of electrolyte, breaking of separator wall,formation of dendrite leading to short-circuit at temperature(T2) and final blasting, when temperature(T3) exceeds some threshold point. Hence, taking proper types of measures at these 3 levels will help in mitigating this catastrophy and safety issue will be resolved.

It is revealed from research works currently on safety of LIB; some thousands of research papers are being published globally on annual basis. Despite these activities, no single strategy has been found to completely solve this issue, as it involves a no of factors. This state of

In-sufficiency are clearly seen from summary of results of review presented here. It needs a holistic approach considering the contributions of all components of a LIB cell, which can be both externally as well as internally. Following are some important external interventions selected from above table, which may be mandatory for a LIB before use. Besides, selective use of following internal interventions either singly or in groups may be undertaken depending on LIB type to mitigate the thermal runaway process along with maintaining its overall safety ,capacity and cyclability.

External interventions: (Recommended for mandatory use)

i. Strong outer pack to stand against any external load, thrust in dropping.
ii. Installation of sensors to monitor temperature of cell and pressure measuring instruments to give early warning.
iii. Regular testing of various parameters like temperature, heat generated, pressure rise.
iv. Devising a good BMS (battery management system) considering all attributes.
v. Robust Operation manual and international standards
vi. Avoid over-charging of batteries.

Internal Interventions: (Recommended for selective use)

i. Use of suitable flame retardants, exo-thermic and thermo-static electrolyte.
ii. Use of all-solid electrolytes, ceramic electrolyte
iii. Use of polymer based inorganic electrolyte.
iv. Reduction in thickness of electrodes
v. Use of composite separators made of ceramic and polymers to contain temperature and excess heat generation.
vi. Coating surfaces of cathode with polymers (polyimides) ($LiNixCoyMnzO_2$) and anode surfaces with polymers (polyurea) .
vii. Change over to graphene battery (graphene-sodium/ graphene-aluminium battery for larger storage, quick recharge, higher electrical conductivity and high temperature range.

CONFLICT OF INTEREST:

The authors declare no conflict of interest as regards the materials produced here.

Ethical Approval: Authors declare that there is no need of ethical approval for this work.

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1st author: She has full contribution towards writing total content of papers.

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