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[ijrset@gmail.com](mailto:ijrset@gmail.com)

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# Overview of Thermal Runaway in Lithium-ion Batteries Used in Electric Vehicle Applications and Methods to Prevent It

Krishna Arvind<sup>1</sup>

Class XI Student, Sishya School, Chennai, India<sup>1</sup>

**ABSTRACT:** Lithium-ion batteries (LIBs) show great promise as efficient energy storage solutions for Electric Vehicles (EVs) and renewable energy systems because of their impressive energy densities and long cycle lives. However, heat issues such as thermal runaways continue to remain a deterrent to their widespread use in EVs. The severity of thermal incidents in LIBs is influenced by various factors, including material selection, design, manufacturing process, electrochemical reactivity, and thermal management options provided. Additionally, application conditions such as operating temperature, overcharging, over-discharging, charge and discharge rates, and vibrations have a significant impact on the occurrence of thermal incidents. In countries with tropical climates such as India, the elevated operating temperatures present a significant challenge for preventing thermal runaway in batteries, especially in two- and three-wheel EVs. The absence of effective thermal management and control mechanisms in the battery pack amplifies the risk of thermal incidents. For instance, two-wheel applications in India often face limitations in implementing active cooling due to size and cost constraints. This paper examines different aspects of Li-ion batteries, including their components, an overview of thermal runaway occurrences, and potential preventive strategies involving advanced chemistry, design, and thermal management at both the cell and pack levels. The specific focus is on addressing these issues within the context of India.

**KEYWORDS:** Thermal runaway, Lithium-ion cell, Electric Vehicle, thermal Management, India

## I. INTRODUCTION

The use of renewable energy in the transportation and power sectors is key to addressing climate change. Sustainable energy advancements create an opportunity to transform lives and economies while safeguarding the planet and laying the foundation for low-emission economies and societies around the world [1]. Efficient energy storage systems play a vital role in achieving the target of net zero carbon emission by 2070. Therefore, various governments around the world are focusing on utilizing the potential of available renewable energy resources. Batteries play a crucial role in energy storage systems, and several prominent battery chemistries such as Nickel metal hydride, lead-acid, Lithium-Ion Battery (LIB), and alkaline batteries serve various applications including Electric Vehicles (EV), Telecom, Solar, Inverters, Grid, and more.[2]

Lithium-ion batteries, initially developed by Exxon, a U.S. company, in the 1970s, was commercially introduced by Sony, a Japanese company, in 1991, and is now used in a variety of application. These batteries are favored for use in electric vehicle (EV) applications due to several key advantages, including high energy density, long cycle life, and fast recharge times [Figure 1]. Despite promise, there continue to be economic, technological, social, and environmental challenges associated with the use of LIBs that must be addressed [3].

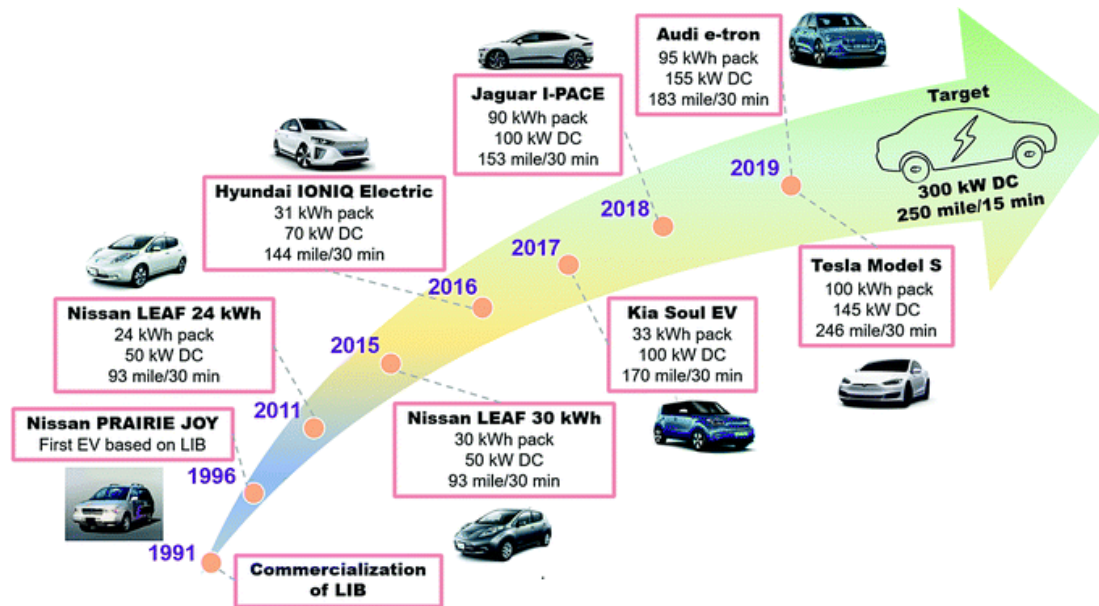


Figure 1: The history of LIB in EV. Image reproduced without modification from [4]

The safety of electric vehicle (EV) batteries has garnered considerable attention, especially following incidents such as the battery fires that occurred after EVs were submerged in salt water during Hurricane Ian in Florida [5]. In 2020, there was significant emphasis on EV fires, resulting in the recall of nearly 100,000 vehicles by manufacturers like Hyundai and GM [6]. While EV fires are typically less common than fires in traditional combustion vehicles, they are often more severe and receive heightened media attention due to the relatively novel nature of EV technology.

EV Battery fires are typically caused by thermal runaways. Thermal runaway is one of the most important technological challenges in EVs even though several safety measures are being taken in the battery pack. Thermal runaway is characterized by an exponential increase of cell temperature in which, the rate of heat generation is higher than the rate of heat removal. This leads to an increase of cell internal pressure causing the vent valve to open or the cell housing to burst, resulting in the escape of flammable gases that initiate the flame. This flame generated from a cell can propagate to neighboring cells and eventually lead to the whole battery fire [7]. The main reasons for LIB fires include poor design, insufficient thermal management (TM) inadequate Battery management system (BMS), and poor quality of material at both cell and pack level.

There has been a considerable increase in the electrification of the vehicular sector in India, particularly in the two- and three-wheeler segments. According to EV Reporter, EV sales in India surpassed one million for the first time in 2022, with two-wheelers accounting for 63% of the local EV market and three-wheelers claiming a substantial 32% share [8]. With the increasing use of EVs on Indian roads, and the likelihood of Indian vehicles being exposed to higher temperatures, it becomes important to address the fire and thermal runaway issues associated with lithium-ion batteries used in them [9].

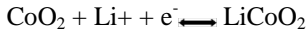
This paper presents an overview of the topic and presents existing knowledge in the area of thermal runaway of LIB.

## II. RELATED WORK

A lithium-ion battery is a type of rechargeable battery in which positively charged lithium ions move from the negative electrode (anode) to the positive electrode (cathode) during discharge and in the reverse direction when charging. Li-ion batteries use an intercalated lithium compound as electrode material rather than metallic lithium as is used in non-rechargeable lithium batteries. The electrolyte acts as a medium for ionic movement between the two electrodes. Electrical energy flows out from or into the battery when electrons flow through an external circuit during discharge or charge, respectively. Both electrodes allow lithium ions to move in and out of their structures by a process called insertion (intercalation) or extraction (deintercalation), respectively. During discharge, the (positive) lithium ions move from the negative electrode (usually graphite = "C<sub>6</sub>" as below) to the positive electrode (forming a lithium compound)

through the electrolyte while the electrons flow through the external circuit in the same direction. When the cell is charging, the reverse occurs with the lithium ions and electrons move back into the negative electrode in a net higher energy state. The following equations exemplify the chemistry of the LIB.

**The positive (cathode) electrode half-reaction:**



**The negative (anode) electrode half-reaction:**



**The full reaction being:**



There are three types of cell formats available in the market for EV applications, namely Cylindrical, Prismatic, and Pouch. Any chemistry can be accommodated in the above cell formats. The main components of a cell are anode active material, cathode active material, binder, separator, and electrolyte. Thermal management materials & BMS are critical components at the battery pack level.

**Anode:**The anode in lithium-ion batteries is the negatively charged electrode where oxidation occurs, and graphite is the most dominant anode material used due to its mechanical stability, electrical conductivity, and lithium-ion transport. However, to improve energy density, silicon, and lithium metal are being investigated as anode materials. Lithium titanium oxide (LTO) is another potential anode material with low energy density but good cycle life and low-temperature performance. Additionally, alloying elements such as silicon, tin, antimony, aluminum, and germanium can also be used as anode materials, which undergo alloying reactions rather than intercalation processes. The anode material should have good lithium intercalation/de-intercalation ability, long cycle life, and be thermally and chemically stable with the electrolyte [10].

**Cathode:**The cathode is the positively charged electrode where reduction occurs in a lithium-ion battery. The most common cathode materials are LiCoO<sub>2</sub>, NCA, LMO, LiFePO<sub>4</sub>, and Li-NMC. Cathode materials can be categorized based on their crystalline structure, such as Layered, Spinel, and Olivine. The top three cathode materials in the market are LFP – Lithium Iron Phosphate (LiFePO<sub>4</sub>/C), NMC– Lithium Nickel Cobalt Manganese Oxide (LiNiCoMnO<sub>2</sub>), and LCO – Lithium Cobalt Oxide (LiCoO<sub>2</sub>). NMC811 and NMC955, with higher nickel content, are gaining popularity in EV applications, but higher nickel content poses a challenge to thermal stability. LFP is known for its stability, low cost, and long cycle life, while LCO is known for its high energy density and long cycle life. NCA has a higher percentage of nickel than NMC, which makes it popular in EV applications. LMO gives high voltage but has low thermal stability. Some other cathode active materials are LMO (Lithium Manganese Oxide (LiMn<sub>2</sub>O<sub>4</sub>) and NCA (Lithium Nickel Cobalt Aluminium Oxide (LiNiCoAlO<sub>2</sub>)) [11] [Table 1].

Table 1. Various Cathode active materials and their cell performance. Data from [12].

	LFP	LCO	LMO	NMC	NCA
Chemical formula	LiFePO <sub>4</sub>	LiCO <sub>2</sub>	LiMn <sub>2</sub> O <sub>4</sub>	LiNiMnCO <sub>2</sub>	LiNiCoAlO <sub>2</sub>
Structure	Olivine	Layered	Spinel	Layered	Layered
Nominal voltage (V)	3.2	3.6	3.8	3.7	3.65
Operating voltage (V)	2.6 - 3.6	3.0 - 4.2	3.0 - 4.2	2.5 - 4.2	3.0 - 4.2
Energy density (Wh/Kg)	90 - 170	150 - 200	100 - 150	150 - 220	200 - 300
Cycle life	2000-6000	500-1000	500-1000	800-2000	1000-3000
Thermal stability	Good	Excellent	Average	Good	Good

	LFP	LCO	LMO	NMC	NCA
Applications	Smart phone, Watches, E-vehicle	Digital cameras, Laptop, Computers	Medical devices & Power tools	Hybrid vehicles	Electric automobiles

**Electrolyte:** The electrolyte is an ionic conducting medium, and it is available in both aqueous and non-aqueous forms. Organic electrolytes contain Lithium Hexa fluorophosphate (LiPF<sub>6</sub>) or Lithium bis (oxalate) borate (LiBOB) dissolved in a mixture of ionic conductive organic solvents with specific additives. Organic solvents are mainly carbonate based such as ethylene carbonate (EC), Propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), Di-butyl Ether (DBE), Vinylene Carbonate (VC), Acetonitrile and Adiponitrile. Each solvent has unique properties to achieve certain parameters such as higher ionic conduction, low & high temperature withstanding capability, etc. [13] Ethylene carbonate has high viscosity & low melting point, which means it requires thinning agents such as DMC, EMC & DEC to improve the power performance.

As LiPF<sub>6</sub> is highly hygroscopic, it tends to absorb water when exposed to the environment and reacts with water to release HF gas. HF has a detrimental effect on cell life and performance.



The thermal stability of different salts used in Lithium-ion batteries in the increasing order is LiDBOB > LiBOB > LiBF<sub>4</sub> > LiPF<sub>6</sub> and the corresponding ionic conductivity of these salts are LiPF<sub>6</sub> > LiBF<sub>4</sub> > LiBOB > LiDBOB [14].

**Aqueous Electrolytes** are of three types namely: Alkaline, Neutral, and Strongly acidic, which are used in different battery chemistries. While Ni-MH and Ni-Cd chemistry batteries are designed with alkaline-based electrolytes, neutral electrolytes are used in carbon-Zinc, and acidic electrolytes are used in Lead acid batteries. However, Lithium-ion batteries do not use aqueous electrolytes because of the extreme reactivity of water with lithium and lithium-containing negative electrodes [15].

**Separator:** The separator is a crucial component in lithium-ion cells as it prevents direct contact between the cathode and anode, allowing only ions to pass through. Porous polyolefin membranes, such as polyethylene (PE), polypropylene (PP), and their blends (PE-PP), are widely used due to their low cost, flexibility, mechanical strength, and thermal properties. Commercial separators have a thickness of 15 to 40 μm and a porosity of 40 to 50%. Coating separators with ceramic materials like alumina, silica, and magnesia has been a recent advancement to enhance high-temperature durability. Additionally, multilayers with PP/PE/PP configuration are gaining popularity to improve thermal stability. Other materials like non-woven liquid crystalline polyester, aromatic polyamide, and cellulose are being researched as alternative separator options [16].

**Binder:** Binders hold the active materials to the current collector, and they aid in cohesion between the active material particles and help in the formation of a stable active material network during cycling. The most frequently used binder materials for both anode and cathode are Polyvinylidene fluoride (PVDF) and CMC. The characteristics of the binders are they must be flexible, inert, soluble in organic solvents, and stable under a wide range of temperatures and voltage ranges.

**Thermal management:** The thermal management of Lithium-ion batteries is divided mainly into active cooling, passive cooling, and composite cooling. While active cooling involves the flow of either air or water, passive cooling involves techniques such as the use of Phase change materials (PCM) [17] and heat pipe cooling [18]. For batteries working under high temperature conditions, the current cooling strategies are mainly based on air cooling [19], liquid cooling [17], and phase change material (PCM) cooling [17].

Active cooling systems are challenging to incorporate in batteries used in vehicles, especially 2- and 3- wheeled vehicles due to space constraints and cost factors. Hence, it is necessary to ensure effective thermal management using advanced thermal management materials inside the battery pack. Paraffin wax is the most used PCM material which stores thermal heat in the form of sensible and latent heat. PCM changes state from solid to liquid or liquid to gas or

vice versa at its phase change temperature. As PCM suffers from lower thermal conductivity, efforts are being taken to use composite materials using PCM and graphite [20]. The placement of thermally conductive materials such as thermal pads or tapes between and around the battery cells is also an effective solution for efficient heat removal from the batteries [21]. As each one of these cooling methods has advantages and limitations, research work is in progress to use a combination of these solutions.

**Battery Management System (BMS):** The BMS is a crucial component that ensures the safety and optimal performance of battery packs. It monitors parameters such as temperature, voltage, and current, and acts as a safety switch in case of issues like thermal runaway. The BMS also balances cell voltages to maximize capacity utilization and estimates the State of Charge (SoC) and State of Health (SoH) of the battery pack. SoC indicates the available energy and remaining range, while SoH assesses the battery's condition and suitability for its intended application.

### Thermal Runaway

Thermal runaway is a chain reaction within a battery cell that can be very difficult to stop once it has started. When thermal runaway occurs in a single cell, the materials inside the cell such as cathode & anode active material and electrolyte react with each other, resulting in strong exothermic reactions, which contribute to a rapid increase of the internal temperature. A problem in a single cell of the battery pack can create a thermal situation in the battery. If the cell is damaged either by heating, crushing, penetration or overcharging, then other unwanted chemical reactions replace the normal electrochemical reactions and produce heat and flammable and toxic gases. Eventually, the gases escape and create a cloud of inflammable gases. When this vapor cloud mixes with oxygen it can be very dangerous and explode without warning. Cell heating will continue, and this starts affecting nearby cells. The mechanism of Thermal runaway can be interpreted by the chain reactions as illustrated in Figure 2. A range of chemical reactions occurs one after another, forming chain reactions once the temperature rises abnormally under abuse conditions. The abnormal heat generation rises the temperature of the cell, and initiates the side reactions, e.g., the Solid Electrolyte Interface (SEI) decomposition. Side reactions release more heat, forming the High Temperature Reaction (HTR) loop. The HTR loop cycles at extremely high temperatures until the cell undergoes thermal runaway.

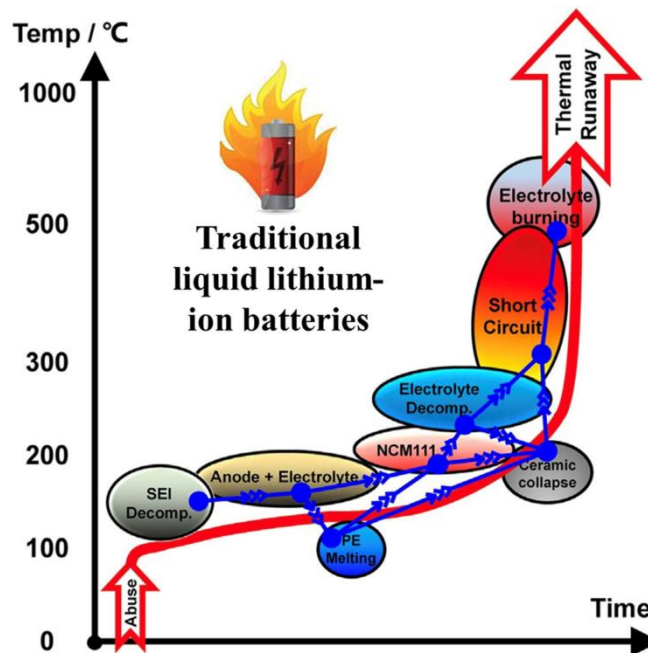


Figure 2. Thermal stability of cell components at different temperature. Image reproduced without modification from [22].

During the process of temperature rise, the solid electrolyte interface breaks down and there is a reaction between the anode and the electrolyte, the separator material melts, and the decomposition of the cathode and the electrolyte is

initiated sequentially. Once the ceramic coating of the separator collapses, massive internal short circuit releases the electric energy of the cell instantaneously, leading to Thermal Runaway with possible burning of the electrolyte.

Some studies have determined the composition and volume of the partially flammable gases produced during the thermal runaway of commercial battery cell types, e.g., NMC, LCO, LFP, LMO. These studies found concentrations of 5–30% of H<sub>2</sub>, 5–30% of CO, 20–90% of CO<sub>2</sub> and 0–9% of various hydrocarbons (ethane, methane, ethene, propene, butene, propane, butane), whereas variation of concentrations is related to different state of charge (SOC) of the investigated cells. As reported by Sandia national laboratory, the rate of temperature increase depends on the type of cathode active material, with LFP being most safe cell followed by NMC111, NCA and LCO [23]. This difference in thermal runaway profile is related to oxygen release and combustion at different cathodes.

#### Causes of thermal Runaway

Thermal runaway is a significant safety concern in lithium-ion batteries, and several factors can contribute to this phenomenon. Overcharging is one such factor that can cause thermal runaway by increasing the cell temperature beyond safe limits. This can happen when the battery is charged beyond its recommended voltage or current limits. Internal short circuits are another potential cause, which can occur when the separator between the positive and negative electrodes breaks down, allowing the electrodes to come into contact with each other. This can result in a rapid increase in temperature and a release of gases, leading to an explosion.

Thermal runaway can also be triggered by external short circuits. Such incidents happen when a conducting material, like metal, comes into contact with both the positive and negative terminals simultaneously or when it is inserted into the cell, resulting in an electrical connection with the electrodes. Physical battery damage, such as punctures or crushing, can harm the electrodes or separator, leading to a short circuit.

High ambient temperatures can also cause a battery to heat up, which can lead to thermal runaway. Certain types of electrolytes used in lithium-ion batteries are flammable and can ignite if exposed to high temperatures. Moreover, the presence of metallic impurities in the battery components can also increase the risk of thermal runaway. Therefore, it is essential to carefully monitor and control the battery's operating conditions to prevent thermal runaway and ensure safe battery operation.

### **III. THERMAL RUNAWAY CHALLENGES UNIQUE TO INDIA**

Electric vehicles are crucial for India to meet the UN goals as they contribute to reducing greenhouse gas emissions and improving air quality, helping combat the country's significant air pollution challenges. Additionally, widespread adoption of electric vehicles in India promotes energy diversification and reduces dependence on fossil fuels, supporting sustainable development and climate change mitigation efforts.

With so much of India's future depending on the successful adoption of lithium-ion cells, it is easy to understand why preventing thermal runaways is crucial, especially in countries like India. India has additional complications that increase the possibility of thermal runaway and hence it is even more important to investigate additional mechanisms to prevent thermal runaway. Some of the India-specific concerns that increase the probability of thermal runaway are listed below.

**High ambient temperatures:** Indian vehicles face some of the harshest climate conditions with temperatures ranging from -20°C in the mountains to +50°C in the deserts. This degrades battery materials more rapidly and cooling remains a major challenge.

**Lack of proper cooling:** Most applications of EVs at this point of time are in two-wheelers. Due to cost and space reasons, there is insufficient place for liquid cooling systems to be adopted and air cooling is required. This has limitations due to the temperature conditions.

**Potential battery swapping:** To enable faster adoption of EVs, the government is encouraging battery swapping where batteries can be taken out of the vehicle and exchanged with the central pool. If the quality of batteries is not maintained this can become a huge danger.

Requirement of rapid charging: there are chemistry limitations to the speed at which batteries can get charged. Even in the mobile phone market, we have seen faulty chargers cause battery explosions resulting sometimes in death.

Smaller batteries, such as those found in mobile phones, necessitated a global recall due to manufacturing defects. If a similar issue were to occur in electric vehicles (EVs), the consequences would be disastrous. Ola, Okinawa Electric, and Pure EV have already initiated recalls of their vehicles following incidents of EV fires [24]. As the usage of EVs continues to rise across various modes of transportation, there is a possibility that lithium-ion batteries may power buses used for public transportation in the near future.

The widespread adoption of EVs would require the installation of charging stations in communities and even residential areas. However, in a vast and diverse country like India, enforcing quality standards has always been a challenge, which would also affect the quality of these chargers. As chargers become more prevalent, faulty ones could cause damage to the battery cells. Moreover, the Indian power grid's unreliability can further contribute to defects during the charging process.

Another factor that would affect the safety of EVs in India is that most repair work on vehicles is handled by small roadside mechanics. An untrained mechanic can unknowingly damage the lithium-ion batteries leading to significant damage and potentially even loss of life.

While it is true that IC vehicles face a higher risk of fire than EVs, since the technology has been around for longer, and an entire ecosystem of trained people is available, there is better handling of the risks. There will be invariably new things we learn as there is more widespread adoption of EVs. Given that thermal runaway can lead to loss of life and significant damage it is important that we focus all our efforts to prevent these issues. The occurrence of several EV fires in Indian four-wheelers and two-wheelers caused significant panic and compelled the government to intervene and ensure that manufacturers comply with proper safety standards [25][26].

#### IV. STRATEGIES TO MITIGATE THERMAL RUNAWAY

While several battery chemistries are being developed, Lithium Ion remains the most energy-efficient mechanism for the future. It is also one of the most challenging systems to manage, especially from a thermal perspective. Traditional battery management systems were based on older chemistries that were not at as much risk for thermal runaways. Today's systems are evolving as we learn more about the performance of Lithium-Ion cells. BMS strategies today primarily focus on monitoring the state of health of each of the cells and shutting down in case of any cell exceeding certain safety parameters. These strategies are useful for preventing over-charging and over-discharging [27].

One of the key strategies to mitigate thermal runaway is to ensure the thermal stability at the cell level by incorporating advanced materials to reduce the likelihood of short circuits, shut down the cell at elevated temperatures, and prevent the release of volatile gases through flame retardant materials, electrolyte additives & improved separator materials. **Flame-Retardant Materials:** Incorporating flame-retardant materials into the cell design can prevent the thermal event from escalating into a full thermal runaway. This could include flame-retardant additives in the electrolyte, or flame-retardant coatings on the separator or other cell components. For example, a conductive electrolyte with flame retardant additives such as lithium bis (fluoro sulfonyl) imide (LiFSI)/trimethyl phosphate (TMP).

**Improved Separator Materials:** The separator is a critical component of lithium-ion batteries that keeps the anode and cathode apart to prevent short circuits. Advanced materials, such as ceramic-coated separators, can offer better thermal stability, reducing the risk of separator failure that could lead to thermal runaway. For example, a layer of Polyethylene and Polypropylene (PP) and Polyethylene (PE): PP/PE/PP can be coated with a layer of graphene.

**Electrolyte Additives:** Fluorinated gases, such as hexafluoroethylenecarbonate (HFEC) and fluoroethylene carbonate (FEC), are commonly used as electrolyte additives in lithium-ion batteries. They improve battery performance by forming a stable interface between the electrolyte and the electrode (the SEI or the solid-electrolyte interface), which enhances the battery's capacity, cycle life, and safety.

Considering the Indian high ambient temperature, LFP would be the most suitable chemistry, but in the case of other low thermal stability chemistries such as NMC, NCA, etc need a higher level of thermal management at the pack level. For Indian Two- and Three-wheel applications, irrespective of the thermal management or external cooling system, it is



essential to improve the thermal stability at the Cell level. It is evident that in many fire incidents, the origin of the thermal runaway is from the cell. Therefore, the following strategies are proposed to improve the thermal stability to address at the cell level

- Use of Non-flammable electrolyte-containing additives like lithium bis (fluoro sulfonyl) imide (LiFSI) / trimethyl phosphate (TMP).
- Fluorinated gas like (Novac.3M) or Argon can be filled after Electrolyte filling followed by sealing, however, the effect of these gases with the electrolyte is to be studied
- Coating of Non-conductive Graphene ( Graphene oxide) over Separator to increase thermal stability
- Boron Nitride Graphene coat on a trilayered polyethylene and polypropylene separator.

## V. CONCLUSION

The Lithium-ion battery is one of the most exciting developments in today's world. They can rapidly de-carbonize the world's economy by allowing vehicles to move from IC engines to EVs and also help in the storage of renewable energy. However, Thermal runaway is one of the major risks associated with LIBs that needs to be addressed for faster adoption. There is no single solution to prevent thermal runaways and most manufacturers use a combination of strategies such as effective battery management systems, thermal management, the use of high-performance materials, improved cell design, the use of solid-state electrolytes etc. In a country like India where two-wheeler and three-wheeler adoption of EVs is on the rise, the size limitations of the vehicles and the high temperatures of the subcontinent also pose additional challenges to the implementation of effective cooling systems. Therefore, there should be an improvement at the cell design level which includes the use of high-performance materials, apart from effective thermal management systems

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