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Lithium-ION Battery Chemistries & Battery Cooling Systems: A Review

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Abstract - *Lithium-ion battery pack technology is the current trend in the automotive industry. For this study, we compared the different materials and systems available, according to the working conditions of automobiles in India, where aspects like operating temperatures, fuel efficiency, cost-effectiveness, charging capabilities and ease of maintenance were the prime factors taken into consideration. The study has been divided into two parts i.e. battery chemistries, thermal management systems. The principle commitment of this work lies in the similar investigation of these frameworks, to choose a particular setup for the utilization of small commercial vehicles like farm haulers, pickup trucks and ATV's. This study shall help anyone interested in using Lithium-ion technology for their projects and wants to understand different chemistries and ways to manage their temperature which affect the selection procedure depending upon the application of the user.*

***Key Words*: Lithium-ion battery pack, Battery cooling, Battery chemistry, Thermal management system, EV technology**

1. INTRODUCTION

In the past decades, battery-pack technology in an automobile continues to maintain their place in the literature, due to their wide range of uses in different segment4s of automobiles. Batteries are usually created by combining various elements in the form of cathodes, anodes and electrolyte. Each combination of the batteries has various properties; some are better with storage capacity or storage density while some are good at reducing heat generation. Lithium-ion batteries are probably the best battery created in the previous few decades. As a technology, they have had exponential growth in the usage in various sectors in the different markets, especially in the automotive sector. This is because currently, they have the most energy-dense, efficient, long-lasting and lightweight properties. Which when contrasted with different batteries like Lead-acid and Nickel-Cadmium is better. Therefore, the use of lithium-ion batteries is in many different fields such as Laptops, Smartphones, Automobiles, Power-banks, Cordless Power-tools, etc. The only downside to lithium-ion batteries is that they have to be continuously monitored and maintained between a certain temperature range for efficient working. For this, lithium-ion battery-packs are incorporated with Battery Management System (BMS) and Thermal Management System (TMS). TMS keep tabs over the temperature of the battery pack and prevents heat generation. It keeps the cells in a specific temperature range and prevents thermal runaway. This study tries to focus on various possible ways to assemble a lithium-ion battery pack majorly focusing on aspects like battery chemistry and thermal management systems.

2. BATTERY CHEMISTRY

Usually, electricity is produced by using conventional sources (fossil fuel, nuclear energy etc.) But as we all know the conventional sources are limited and harmful for the environment. So renewable sources are a very good option to produce electrical energy. It can be stockpiled, used in automobiles and the best way to do it is electrochemical batteries. Batteries are made up of electrodes and electrolytes. Electrolyte acts as the medium through which ions pass and produce electricity [9]. Depending upon the characteristics, functions, requirements different varieties of batteries are available. Lithium-ion cells are generally categorized into three distinct forms as shown in Fig. 1. Among all the batteries Lithium-Ion batteries dominate the market [4]. Li-ion batteries have higher power density and higher specific energy compared to any other battery technology [4]. Used in portable electronics, power tools and mild hybrids or fully electric vehicles [5]. The cost and short life span are the major drawbacks of the lithium-ion battery. The manufacturing cost and raw cost of cobalt are also major factors [5].

Table1. Comparisons of different cell form factors [9]

	Cylindrical cell	Prismatic cell	Pouch cell
Strength	Very high	High	Low
Specific energy	Very high	High	Medium
Energy capacity	Medium	Very high	High
Heat dissipation	Low	High	Very high
Expense	Very low	Medium	Medium

2.1. Cathode

The cathode is where reduction occurs and ions enter. It is used for storing and removing guest ions (Li-ion) [9] energy, power versus cycle lifetime, safety and cost depends on the material used as a cathode.

1) Lithium Nickel Oxide ($LiNiO_2$)

Due to the use of nickel, "these batteries are lower in cost and has a higher theoretical capacity of 250 Ah/kg" [9]. But it forms "the self-passivation layers at the surfaces which causes difficulties with its use" [3].

2) Lithium Manganese Oxide ($LiMn_2O_4$).

It has a higher nominal voltage [4]. Its structure improves the ion flow rate and low internal resistance which prompts quick charging and high current discharge. It provides higher thermal stability but lower capacity and short life span than $LiCoO_2$, which is not suitable for EVs [4]. Sometimes cobalt is also used in these batteries (NMC) to increase the energy storage and life cycles. These batteries are used by many EV manufacturers [9].

3) Lithium Iron Phosphate ($LiFePO_4$)

High Capacity, low cost, low environmental impact, Good performance, low resistance, high current rating, works in wide temperature range, long cycle life and low cost are the benefits of this battery [4]. Selective recovery of Phosphate reduces overcharging and delivers higher resistance to heat [7]. "Suitable for being used in stationary, automotive and back-up power applications" [4].

4) Lithium Nickel Manganese Cobalt Oxide ($Li(Ni_xMn_yCo_{1-x-y})O_2$)

Most used "NMC cathode composition contains an equal amount of all 3 metals" [4]. "The secret of NMC lies in combining nickel and manganese; nickel is known for its high specific energy but poor stability; manganese has the benefit of forming a spinel structure to achieve low internal resistance but offers low specific energy" [10]. "Provides high specific energy with high density. Researchers are using nickel-rich electrodes to increase energy density, while the reduction in cobalt is also helpful since it lowers costs" [9].

5) Lithium Nickel Cobalt Aluminum Oxide ($Li(Ni_xCo_yAl_{1-x-y})O_2$)

Like NMC batteries, NCA batteries offer high specific energy and specific power and a long life expectancy [7]. These batteries are less safe than the other batteries & also costly to manufacture even though it is used by tesla in Tesla model 3 2012 [9].

2.2. Anode

The anode is where oxidation occurs and ions leave the cell. Most often used negative electrodes are lithium titanate and carbon-based electrodes. Lithium metal, lithium-metal alloys, lithium silicon alloy and conversion electrodes are in development [9]. "Anode materials are necessary for Li-ion batteries because Li-metal forms dendrites which can cause short-circuiting or start a thermal run-away reaction on the cathode and cause the battery to catch fire" [9].

1) Carbon Based Electrodes

"Carbon and synthetic graphite electrode have a relatively high specific capacity of 370 Ah/kg, low average voltage (150 mV) and a relatively flat voltage rendering a high overall cell voltage and high roundtrip energy efficiency" [8]. Also, "it is a very abundant, low cost and non-toxic material" [9].

2) Lithium Titanate ($Li_4Ti_5O_{12}$)

Graphite is replaced by LTO in negative electrodes and forms a spinal structure. Due to this spinel LTO electrode, zero volume change takes place which results in a long life of electrode and improved safety. "Titanate batteries are used in certain Japanese EV's" [9].

3) Lithium Metal

It has a "very large capacity (3860 Ah/kg) and the lowest negative electrochemical potential" [9]. But in secondary batteries, it produces metallic dendrites, these might create short circuits which results in thermal runaway or risk of explosion/fire [9].

4) Alloy Based Electrodes

Alloy based electrodes lead to the "creation of Li-ion batteries with higher specific capacity than that offered by conventional graphite electrodes" [6]. "The mechanical strain generated during the alloying/dealloying processes leads to cracking and crumbling of the metal electrode and a marked loss of capacity to store charge in the course of a few cycles" [9].

5) Silicon-Based Electrodes

"The lithium-silicon alloy has a theoretical specific capacity of 4200 Ah/kg" [1]. The major issue here is "the volumetric change in the electrode material. The transition between Si and $Li_{15}Si_4$ causes a 280% volumetric change, generating high internal strain in the active materials. The additional downsides of Silicon are a low Li^+ diffusion coefficient and high electrical resistivity" [2].

2.3. Electrolyte

The electrolyte used depends on the electrode materials. A separating membrane is used in the electrolyte for preventing internal short circuit and passage of li-ions. Contingent upon material choices, voltage, energy density, life and security of a lithium-ion battery can change drastically.

1) Aqueous Electrolytes

"The cell potential is limited by the electrochemical window of the electrolyte" [9]. Conceptually it is safer and has a less potential impact on the environment but it has a low electrochemical window [9].

2) Organic Liquid Electrolytes

"Electrolytes are based on organic solvent loaded with lithium salt" to increase the electrochemical window [9].

3) Polymer Electrolytes

Organic liquids can harm the environment and also have flammable properties (unsafe). So, for more safe batteries polymer electrolytes are used [9].

4) Ceramic Electrolytes

Ongoing improvements in battery innovation include utilizing earthenware production as the electrolytes, specifically the utilization of 'LiSICONs' (Lithium Super Ion Conductors). Incorporating polished constituents with comparative structures, bring about higher conductivities generally because of greater conductivity at particle limits. "Work to improve the conductivity of clay electrolytes to yield materials with execution like that of fluid electrolytes proceeds, with some encouraging outcomes" [9].

3. THERMAL MANAGEMENT SYSTEM

"A lithium-ion battery pack is possibly more compact just as light contrasted with other battery packs. However, compactness of Li-ion battery packs gives rise to safety issues such as battery overheating. This may lead to thermal runaway of some cells and propagation of excessive temperature throughout a module or pack" [11]. "The Li-ion batteries used in EVs and HEVs can barely meet the expectation of 10-years of lifespan as suggested by the United States Advanced Battery Consortium (USABC)" [18]. "Battery pack manufacturers spend a large amount of time and resources designing battery packs and thermal management systems that try to maintain each cell in identical thermal and electrical boundary conditions" [13]. A thermal management system ensures that the pack works within an optimal temperature range and has an even temperature spread throughout the pack. It also detects critical points of battery failure and prevents them from causing a thermal runaway or suppresses a thermal runaway.

3.1. Thermal runaway

"Thermal runaway may happen when the batteries are manufactured defectively or handled improperly. Thermal runaway often occurs at high-temperature states, in which the high temperature triggers the exothermic reactions in the operating batteries. These reactions release more heat, and in turn, promote the increase of temperature within the batteries. When such uncontrolled heat generation exceeds the heat endurance of the batteries, fire and exploration would occur" [18].

3.2. Temperature variation

The efficiency of Li-ion batteries is swayed largely even with small temperature changes. State of Charge (SOC) of a Lithium-ion battery cell, "which is defined as the ratio of the present residual capacity to the overall available capacity, was found to decrease by 23% when the operating temperature decreases from 25 °C to −15 °C" [18]. The efficiency of Lithium-ion batteries will degrade at temperatures below 0 °C. "The charge-transfer resistance is significantly increased when the temperature is decreased. Charging a battery at low temperatures is significantly more difficult than discharging it. At low temperatures, the degradation of performance is mainly caused by the reduction of ionic conductivity and the increase of charge-transfer resistance. The temperature effect on the rate of capacity degradation of a Sony Prismatic Li-ion battery during ageing from 25 °C to 55 °C was investigated, elevating temperature in the tested range partially increased the capacity of the battery, but it also accelerated the rate of degradation of capacity during the cycling process. High-temperature conditions accelerate the thermal ageing and may shorten the lifetime of Li-ion batteries" [18]. Hence, "the battery thermal management system to keep the temperature at an optimal range of 15 °C to 35 °C is essential for lithium-ion battery packs in electrical vehicles" [12]. The temperature variety from module to a module inside a pack can likewise prompt the electrical unbalance, which influences battery pack operational performance. With higher specific energy and high-rates capacity, the battery would produce a lot of heat, which is simpler to trigger thermal runaway.

3.3. Types of TMS

Companies have several different options while selecting an appropriate TMS for the Battery Pack. The TMS can be categorized into four distinct types depending upon the medium being used i.e. Air cooling, Liquid cooling, Refrigerant Cooling and Phase change materials. The selection process takes into account factors like Operating temperatures, Efficiency, Cost-effectiveness, Complexity and most importantly Safety.

3.4. Air cooling

Air cooling channels the cooler air surrounding the vehicle to manage the temperature of the battery pack. "Air cooling can be categorized into natural (indirect) and forced (direct) convection. The natural convection can allow the inner or external air to pass through the channel to sweep the battery pack and the forced convection usually adopts a fan or cooperates with the evaporator or condenser from HVAC to blow the air into the battery enclosure" [16]. When using cylindrical cells, they can be arranged in distinct alignments to guide airflow. "Compared with the forced-air cooling method, the natural convection cooling usually behaves better in sealing and waterproof" [16]. Air cooling consumes the maximum amount of battery power. "Considering the structure and extra weight added to a battery, air cooling is the simplest and lightest method" [12]. Nissan Leaf, Toyota Prius Prime, Honda Insight, Hyundai Ioniq are some commercial vehicles using Air cooling [16].

3.5. Liquid cooling

"Compared with air medium, liquid has a higher thermal conductivity and a higher heat capacity, which behaves better in the temperature distribution of the battery pack" [16]. Battery thermal management with liquid circulation loop as "also has some inconvenience in its complex structure with some accessories (heat exchanger, pump, etc.) and it may lead to leakages. But it has become the prevalent cooling technology in the industrial application, because of its flexibility in integration and precise control for heating and preheating" [16]. "The weight added in indirect liquid cooling and direct cooling is moderate, and direct liquid cooling adds less extra weight than indirect liquid cooling" [12]. In indirect liquid cooling, the weight is added due to coolant pumps and cooling plates which can be in two different types. "Increasing the fluid flow rate is found to be effective at lowering the temperature and improving the temperature uniformity in the battery module" in both Air & Liquid cooling [14] [15]. Chevy Bolt, Tesla Models, Audi R8 e Tron and Toyota iQ are some commercial vehicles using Liquid cooling.

3.6. Refrigerant cooling

"The direct refrigerant cooling behaves better in heat transfer efficiency, uniform distribution of temperature, simplified structure, and system weight reduction. Refrigerant direct cooling can take advantage of refrigerant (R134a, R410, etc. from HVAC) evaporative latent to chill battery pack straightway. For its efficiency in thermal control and heat dissipated ability, and avoiding refrigerant leakage, it can improve the systems performance matching and has been a promising strategy for BTM design" [16]. BMW i3, BMW i8, Audi A6 PHEV are some commercial vehicles using Liquid cooling.

3.7. Phase change material

"Under normal operating conditions the graphite–PCM matrix keeps the temperatures of individual cells in a favourable range, is similarly achieved by air-cooling, with very good uniformity from cell to cell without compromising the compactness of the pack. PCM–graphite matrix absorbs and spreads the heat very quickly due to its high thermal conductivity. Contrary to complex cooling systems, the packs with PCM offer safety under stressed conditions. The conduction and absorption of heat by the PCM–graphite matrix prevents propagation of thermal runaway due to a defect in a single cell which has reached its runaway condition" [11].

3.8. Immersed cooling

Immersion cooling is usually used at data centers, high-performance computer & power grids. It is still an emerging technology in the battery market. In this method, the batteries are fully immersed into a fluid-like '3M Novec Engineering Fluid'. "Unlike indirect cooling applications, which use water/glycol mixtures, Novec Engineered Fluids are non-conductive, reducing the need for electrical isolation. Using Novec Engineered Fluids for direct contact cooling which can help in reducing the number of materials needed to achieve optimal temperature control" [20].

4. RESULTS AND DISCUSSION

In this review, the outline of lithium-ion battery pack technology utilized in EVs is given. Characteristics of different battery components like anode, cathode and electrolyte are described. Different types of battery chemistries that are currently present in the market are compared depending on different factors. We can say that the characteristics of present Li-ion batteries can vary between different chemistries. Some chemistries have better storage density but contain rarer elements, which makes them expensive, while some chemistries offer more safety. Chemistries like NMC, NCA and LFP are widely used in EVs. Depending on the requirements of the application. With the selection of battery comes the selection and integration of a cooling system. A battery cooling system is selected according to the working conditions and environment in which the battery pack is used. Some cooling systems are more efficient than others but aren't used on a large scale due to their complexity and expense. When selecting a suitable cooling system, one also has to pay attention to factors like contact surface area of the battery with the cooling medium, flow-rate of the medium, the types of heat exchangers and coolants used and whether the system will work cohesively with the battery working temperature range. The study shows that air, fluid and refrigerant cooling are the most utilized cooling techniques in EVs, with more exploration and experimentation needed for phase change materials and immersed cooling.

5. CONCLUSIONS

In this study, the review of lithium-ion battery pack technology has been noted. The battery pack was studied on four different aspects i.e. Cell Chemistry, Thermal management system, Battery management system and EV charging system. These aspects have been categorized and compared to give a basic idea about the options available for making a lithium-ion battery pack. The results obtained from the study are as follows;

Lithium-ion batteries are revolutionary in the field of energy storing and transfer and yet a lot of research is going on it to make it durable, energy-dense, low costing etc. As it is playing an important role in saving our environment. As the study discussed all the pros and cons of various battery chemistries we can say that there is no ideal battery type. The best possible way to select a perfect battery composition must be based according to its requirements.

Heat generation in batteries accelerates ageing of the cells, reduces their life-cycle and has the potential to trigger thermal runaways if not cooled properly. The ideal temperature range of lithium-ion batteries is between 15-35°C. Liquid cooling has a greater heat transfer coefficient compared to air cooling, hence is the better choice terms of efficiency. The PCM cooling and immersed cooling are very efficient ways of cooling and have a huge scope in the EV market in the coming decade.

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