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Existing Lithium-Ion Battery Technology and Nanotechnology-Based Improvements

Mr Pratham Agarwal
B.E Student
Department of Information Science Engineering
RV College of Engineering, Bengaluru, India

Mr Shankar Tejasvi
B.E Student
Department of Information Science Engineering
RV College of Engineering, Bengaluru, India

Prof. Shwetha S
Assistant Professor
Department of Information Science Engineering
RV College of Engineering, Bengaluru, India

Prof. Kavitha S N
Assistant Professor
Department of Information Science Engineering
RV College of Engineering, Bengaluru, India

Dr Praveen Kumar Gupta
Assistant Professor
Department of Biotechnology
RV College of Engineering, Bengaluru, India

Abstract

Lithium-ion batteries (LIBs) are among the most common consumer electronics that deliver electrical energy due to Li+ ion transfer between their electrodes. They find their application in nearly every power-driven device ranging from daily use electronic gadgets to sophisticated infrastructure including aircraft and satellite industries. This paper provides an insight into the various parts of a Lithium-ion battery, their functionality and various materials used for the construction of its components. Detailed reviews on nanotechnology-based improvisations in LIB technology have been provided. The various precautions and usage guidelines regarding the installation and use of LIBs have been inspected. It is exciting to note the bright future battery technology holds concerning its specific capacity, shelf life and performance brought about by nanotechnology.

Keywords: Lithium-Ion Battery, Electrodes, Electric Vehicles, Nanotechnology

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I. INTRODUCTION

A battery is an electrochemical device that consists of one or multiple electrochemical cells that can be charged using an electric current and discharged as required when connected to external loads. Optimal batteries should have high explicit energy, high power output, long cycle and shelf life, wear resistance, and minimal cost. Lithium-ion batteries (LIBs) are one of the most popular rechargeable batteries due to their high open circuit voltage, low self-discharge rate, and best energy-to-weight ratio.

The main components of LIB include the cathode, anode, electrolyte and separator, as shown in Fig.1. The efficiency of LIB depends on the materials used to manufacture the components. Research has identified a variety of suitable materials for the manufacture of LIB components. Carbonaceous and lithium alloy anodes coupled to the lithium metal oxide cathode in the LIB show excellent performance in a variety of applications.

Several variants of LIBs are obtained by different combinations of selective cathode and anode materials. These variants have different characteristics which can be a differentiator in determining the correct variant to use for different electronic implementations. For example, power batteries used in phones and laptops need different battery parameters than those used in electric vehicles. They differ in terms of specific capacity, discharge voltage, specific energy, cost, performance, and safety. LIBs are offered in different shapes and sizes to meet structural needs and can be hierarchically configured for specific purposes based on energy requirements. Existing LIB technology has revolutionised lifestyles, but its improvisation is beneficial to engineers working in related fields. Scientists suggest that a nanotechnology is a promising approach to significantly improve LIB performance. This overview focuses on installation techniques, safety measures and precautions, as well as expectations for future improvements.

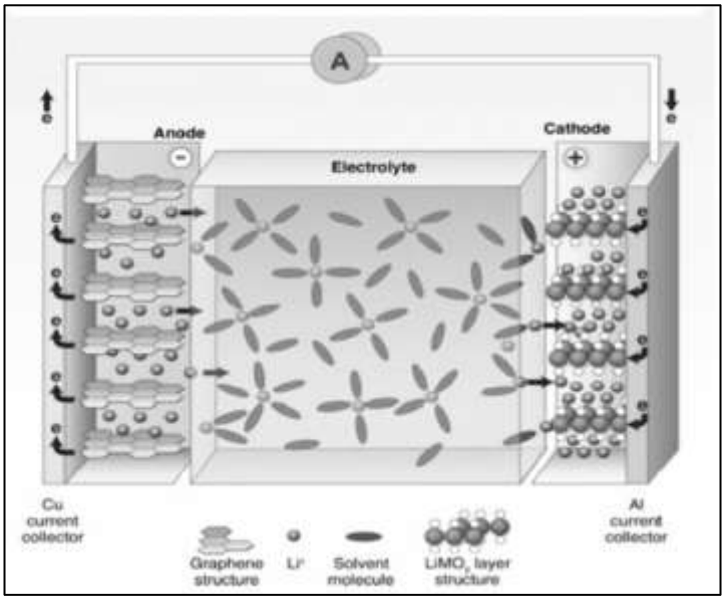

Fig. 1: General structure of LIB [22]

II. MATERIALS AND METHODOLOGY

Upon electrochemical reaction, the electrical energy delivered by the battery depends on the nature of the anode, cathode and electrolyte used in the battery material [2]. Some of the commonly used electrodes are $LiMO_2$ (where M is a transition element Co, Ni, Mn), graphite, olivine $LiFePO_4$ etc. which are illustrated in Fig. 2.

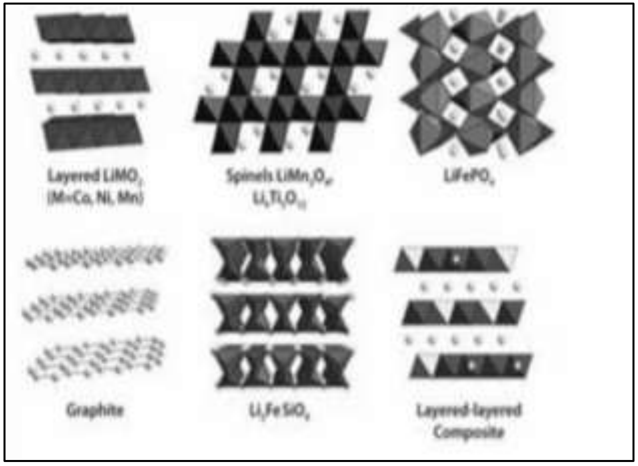

Fig. 2: Structures of common electrode material [21]

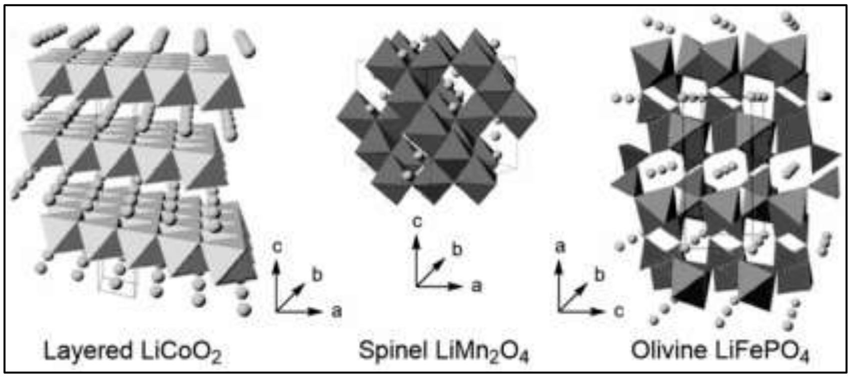

Fig. 3: Crystal structures of three families of insertion compound according to the dimensionality of Li+ ions diffusion [23]

A. Anode Materials

The most widely used anode materials include graphite and Li-alloyed metal. $Li_4Ti_5O_{12}$, whose structure is shown in Fig. 4 has found widespread application in anode preparation.

Graphite is also used extensively as an anode material due to its high conductivity, durability, compatibility of voltage with other cathode materials, lightweight and low cost.

1) Carbon-Based Anodes

The graphite electrodes consist of hexagonal and rhombohedral arrangements which are capable of rearrangement and staging on the insertion of Li ions. The graphite-made anodes are cost-effective but show poor Li interaction capacities. Crystalline carbon has been gaining attention due to its high Li acceptance, cycling abilities and temperature control flexibility.

Artificial development of graphite is the phenomenon of oxidation of graphite under high temperatures. They have shown higher discharge capacity and high efficiency. Moreover, disordered carbons paired with Li-Mn-oxide are found to be the perfect materials for anode building as they suffer from minimum solid electrolyte interface disruption [2].

2) Lithium alloy Anodes

Lithium-aluminium alloys with the introduction of substances like Dilithium phthalocyanine are preferred materials for anode preparation. However, volumetric changes are observed during the lithiation and delithiation process.

This problem is solved by making use of anodes in which degradation occurs at a slow rate and is limited to its surface layer (known as dimensionally stable anodes) [27]. These anodes are prepared by utilising a submicron particle alloy which is surrounded by a stabilising matrix and "intermetallic" host where one metal alloys with Li but the others do not. Al_3Ni, Fe-Sn, Sn-Sb and Sn-Cu have shown promising results as intermetallic elements [2]. The deposition of electrochemically active layers of RuO_2, IrO_2, and TiO_2 on the surface of the cathode can also serve this purpose [28]. Many other industries such as the Chlor-alkali industry, industries related to metal electrowinning etc. also benefited from the evaluation of these electrodes.

Lithium transition oxide is another offered alternative to Carbon-based anode. Although volume changes are not observed during insertion and de-insertion of Li, it requires a very high operating voltage. Thus, it should be nanostructured before it can be put to use [2].

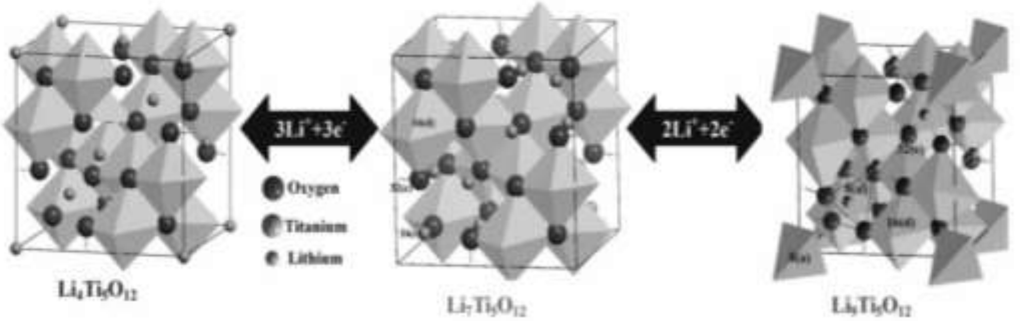

Fig. 4: Structure of $Li_4Ti_5O_{12}$, $Li_7Ti_5O_{12}$ and $Li_9Ti_5O_{12}$ [24]

B. Cathode Material

Cathode material, structurally the positive electrode, when coupled with a Li-ion battery acts as an active source of Li^+ ions. The selection of cathode materials depends on the selection of rechargeable Li-metal or LIBs. $LiCoO_2$, LiMnO, $LiFePO_4$ and other Li-layered metal oxides are generally used in the preparation of cathodes

1) Lithium-Manganese Oxide

LiMnO spinels are readily available, economically feasible, ideal for intercalation of Li ions and offer desirable electrochemical properties. Moreover, its high thermal threshold, good rate capability and minimum environmental impacts contribute to making it the most widely used cathode material. However, Mn^{3+} ions can show electrochemical instability and reduced capability of recycling. Improvements in the form of doping with Al, Co, Mg, Ni and by providing an acid-resistant coat of $LiMn_2O_4$ are practiced.

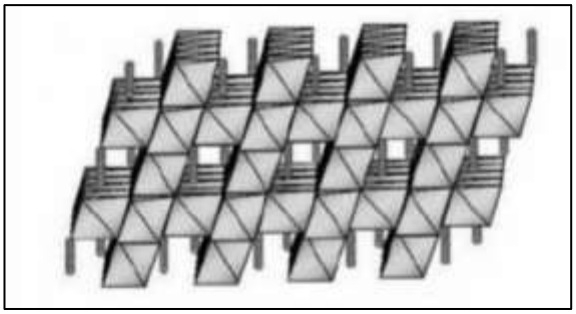

Fig. 5: Cubic spinel $LiMn_2O_4$ structures [2]

2) Lithium metal oxides

The Li metal oxide-made cathode functions well at high temperatures, offering high structural stability but is generally expensive and difficult to synthesise. To overcome these limitations, solid solutions of layered compounds are developed. It has been found that chemically combining transition metal ions in their lower oxidation state with low strain in the activated state produces cathodes capable of fast charging and discharging [2]. The structure of the layered Lithium metal oxides is shown in Fig. 6.

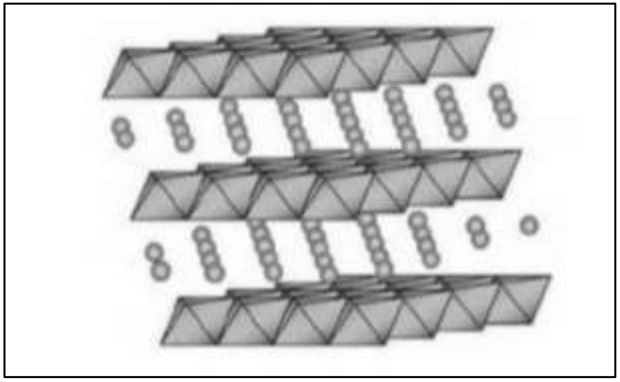

Fig. 6: Layered lithium metal oxide structure [2]

3) Electrolytes

There are three categories of electrolytes that are used in LIBs [26]. They are:

1) Polymer-based electrolyte
2) Liquid electrolyte
3) Hybrid electrolytes

The selection of electrolytes should be done delicately and accurately. It should offer high ionic conduction and electrochemical stability. Polymer-based electrolytes often pose challenges to the above-mentioned factors. Various other factors such as viscosity and dielectric constant should also be considered before electrolyte selection. Liquid electrolytes offer more variety than polymer-based electrolytes in terms of availability.

III. IMPORTANT VARIANTS OF LIB

The main types of LIB variants which are currently in use include

1) Lithium iron phosphate battery
2) lithium cobalt oxide battery
3) Lithium manganese oxide battery
4) Lithium nickel manganese cobalt oxide battery
5) Lithium nickel cobalt aluminium oxide battery
6) Lithium titanate battery

A. Lithium Iron Phosphate Batteries

Popularly known as lithium ferrous phosphate (LFP), these cells offer durability in terms of long cycle life, and ensure safety as a result of their chemical stability, heat resistant capacity, and consistent electrochemical performance [16]. They also exhibit other desirable characteristics like high current rating, excellent charge-discharge rates, superior low-temperature performance and stable voltage drop under rough conditions [17]. Thus, they find their applications in EVs [17]. However, they have a low specific capacity [15].

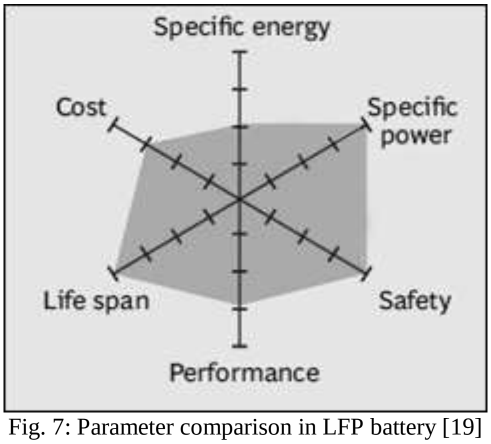

Fig. 7: Parameter comparison in LFP battery [19]

B. Lithium Cobalt Oxide Battery

The Li-Co-O batteries exhibit high specific energy [15]. They are used in the manufacturing of portable electronics like laptops, mobile phones and electronic cameras [15][16][17]. However, there are concerns over the efficient usage of this battery as its performance is moderate and shows other unfavourable attributes like low specific power, low safety and low lifespan [15]. Moreover, cobalt is expensive which makes the manufacturing process economically infeasible [16].

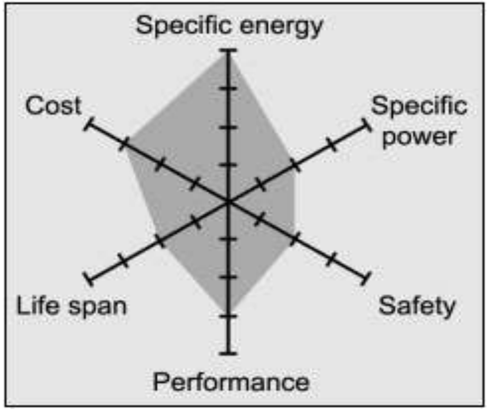

Fig. 8: Parameter comparison in Lithium Cobalt Oxide Battery [19]

C. Lithium Manganese oxide battery

Lithium manganese oxide batteries find their application in medical devices, power tools, and hybrid EVs [15][16][17]. They use Lithium manganese oxide as cathode materials which results in a 3D structure that improves ion flow, lowers internal resistance, increases current handling and improves thermal stability [16]. The downsides of this battery include low performance, low lifespan and moderate safety [15].

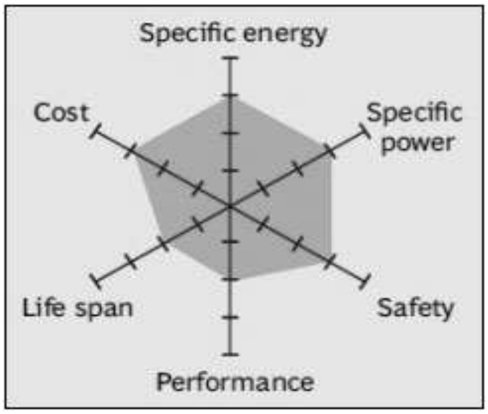

Fig. 9: Parameter comparison in Lithium Manganese oxide battery [19]

D. Lithium Nickel Manganese Cobalt oxide battery (NMC)

Durability in terms of long cycle life and high performance by the virtue of high energy density are the major benefits offered by this variant of LIB. [16]. Moreover, the combined advantages of low cost and high specific energy make their use desirable in electric vehicles [15]. They can be optimised to have a high specific density or high specific power [18]. However, it is moderate in terms of safety and performance [5].

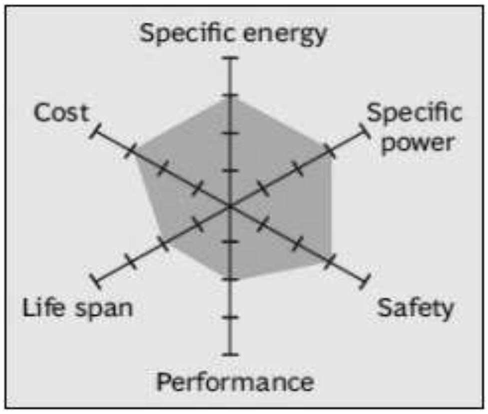

Fig. 10: Parameter comparison in NMC battery [19]

E. Lithium Nickel Cobalt Aluminium Oxide battery (NCA)

These batteries are capable of delivering high amounts of current for a long period as they possess high specific energy and good specific power [16][17]. However, these batteries show compromise in safety and maintenance [15][16]. Hence the need for suitable monitoring systems during their use crops up [18]. They are used to power electric power trains [15].

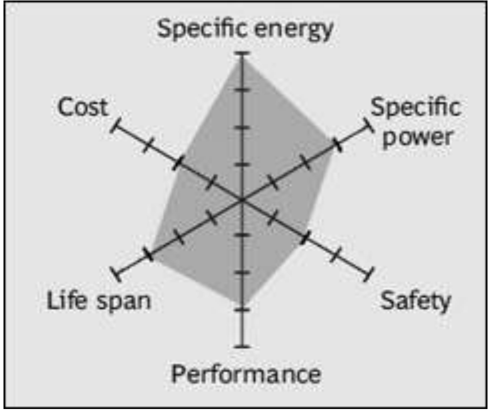

Fig. 11: Parameter comparison in NCA battery [19]

F. Lithium Titanate battery

These batteries cover various parameters such as high safety, high performance, high life span and extremely rapid recharge time [15][18]. Nanotechnological properties contribute to the enhancement of these parameters. Though these batteries are the safest, they have relatively low specific energy and are economically infeasible due to their high maintenance cost [15]. They are used for storing wind and solar energy, creating smart grids and also various aerospace applications [15][17].

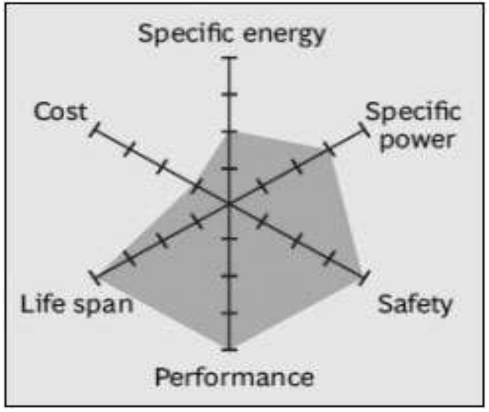

Fig. 12: Parameter comparison in Lithium Titanate battery [19]

IV. WORKING MECHANISM

The working of Li-ion batteries is based on a redox reaction which takes place inside the cell. The reaction involved mainly contributes to a charge-discharge cycle as shown in Fig.13 [1].

During discharge, the oxidation state of Li ions changes from 0 to +1 causing their oxidation in the anode. The oxidation half-reaction may be represented by-

$$LiC_6 \rightarrow Li^{+} + C_6 + e^{-}$$

These Li^{+} ions travel through the electrolyte to reach the cathode where they get reduced into Lithium Cobalt Oxide. The reduction in half-reaction may be represented as-

$$CoO_2 + Li^{+} + e^{-} \rightarrow LiCoO_2$$

Thus, the following cell reaction is obtained:

$$LiC_6 + CoO_2 \rightleftharpoons LiCoO_2 + C_6$$

The following diagram represents a full charge-discharge cycle

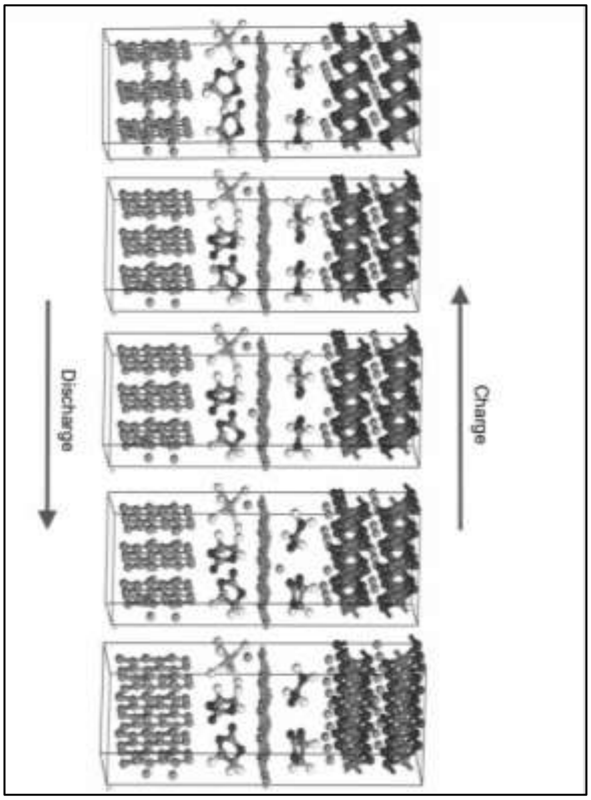

Fig. 13: Charge-Discharge Cycle

V. LIB APPLICATION AND THE NEED FOR THEIR REPLACEMENT

A. *Application of LIB in Electric Vehicles (EVs)*

With rising concern regarding environmental pollution and issues of energy storage, the development of EVs is indeed observed as one of the most effective solutions due to the growing demand for both public and commercial transport [8]. Since power batteries are the core component of EVs they are also following an upsurge of growth [9]. Since LIBs exhibit high energy density, reliable charge-discharge stability and other fascinating properties when compared with other conventional rechargeable batteries such as Nickel-Cadmium (NiCd), and Pb-acid batteries, LIBs find their applications as power batteries in EVs [10].

LIB is composed of anode, cathode, electrolyte, separator and current collector. Separator functions as a barrier between anode and cathode reaction thereby allowing only the movement of Li+ ions through the electrolyte without any resistance. Practically in EVs, LIBs are connected in different configurations like cylindrical shape, pouch shape or prismatic shape as shown in Fig. 14 and are placed into a frame with control and safety circuitry, thereby preventing overheating and external shocks, to form a battery module. Then, a batch of modules is combined with additional control circuitries, a battery thermal management system (BTMS) and power electronics to form a battery pack as shown in Fig.15 [12].

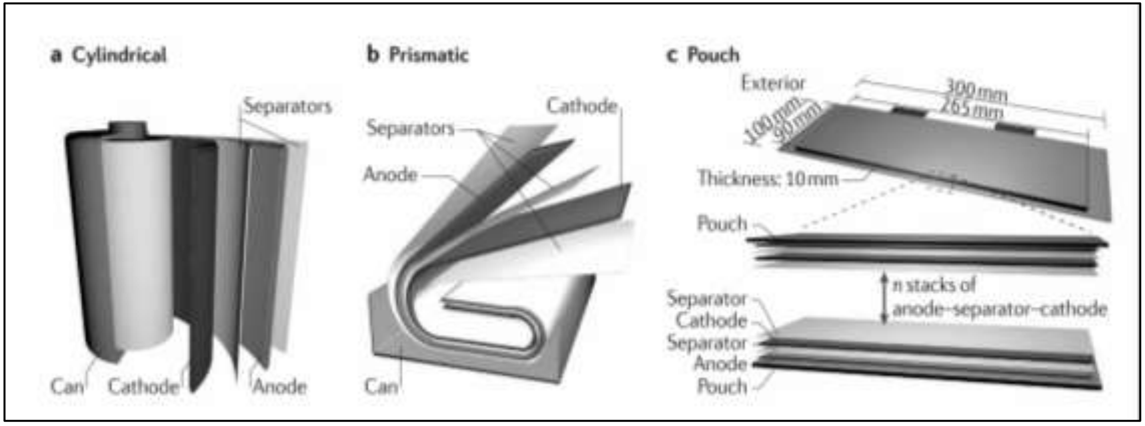

Fig. 14: Typical configuration of LIBs. [29]

Fig. 15 LIBs at different levels [14]

B. *Challenges*

Looking at the other side of the coin, the effective properties and performance of LIBs directly affect the running safety of EVs. Thermal issues caused due to overcharging, short circuit, overheating and other mechanical or electrical abuse limits the practical operation of lithium-ion batteries especially under harsh climatic conditions as shown in Fig. 16.

With the temperature rise, due to prolonged use of the battery, the separator starts expanding but on attaining a certain temperature it starts exhibiting an inverse effect by shrinking and ultimately leads to fracture causing a large-area internal short circuit (ISC). Additionally, the liquid electrolytes may begin to break down, releasing large amounts of heat eventually leading to thermal runaway [13][30].

Concerning the structure of storage batteries, various forms of development have been made and undoubtedly LIBs have shown the most promising results w.r.t capacity, power but efficient these batteries might be there is still demand for more power-dense batteries for electronic and hybrid vehicles.

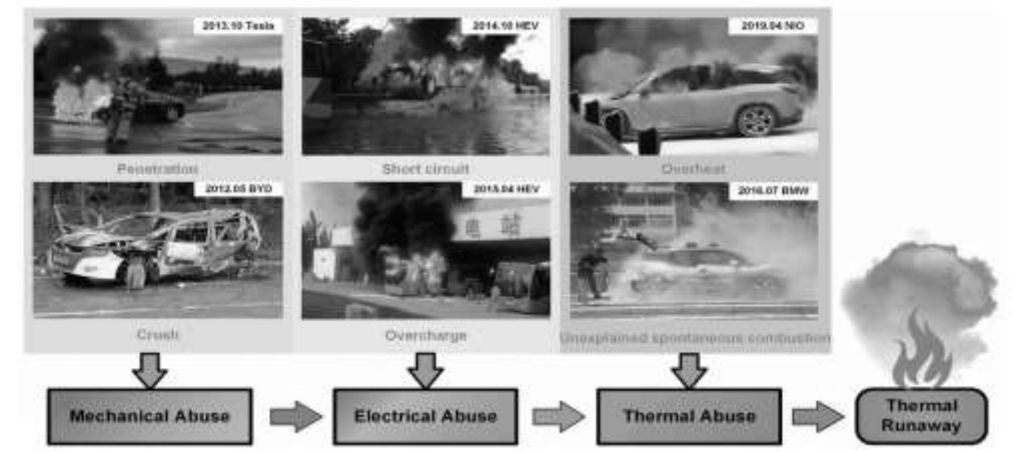

Fig. 16: Accidents related to power LIBs failure [14]

VI. NANOTECHNOLOGY IMPLEMENTATIONS

A. *Electrode improvement*

The inclusion of nanotechnology with battery technology is expected to allow higher storage densities of lithium when compared to standard electrodes as shown in Fig. 17. R&D has led to the formulation of various hypotheses [3].

- Researchers at Georgia Tech observed hollowing behaviour of anodes which was contrary to past studies, as past studies showed anodes undergo expansion and shrinkage during lithiation and delithiation when coated with oxide layers but in this research oxide-coated antimony nanocrystals were used which showed these exciting results. But, the use of antimony makes this implementation economically infeasible [4].
- Researchers at Purdue University have constructed electrodes using antimony, prepared in nanochain structure, which showed tremendous results in achieving higher storage capacity. But, this technique poses safety issues because, during charging, size expansion of electrodes (up to three times) is observed [4].
- Researchers at Rice University used CNT films to prevent any growth of dendrites on lithium metal anodes. This was done to prevent battery failure due to dendrite growth and also to achieve fast-charging Li-metal batteries [4].
- Researchers at USC are developing LIBs implementing silicon nanoparticles to achieve a high-capacity battery approximately holding 3 times the energy stored by graphite anodes and can be recharged within a timespan of ten minutes [4].
- Researchers at Stanford University have constructed Li anodes packed in a forest of tiny silicon nanowires which during battery operation undergoes expansion (up to 4 times the original size) but fracture does not take place. This was done to expand the storage capacity of LIBs up to ten times [4].

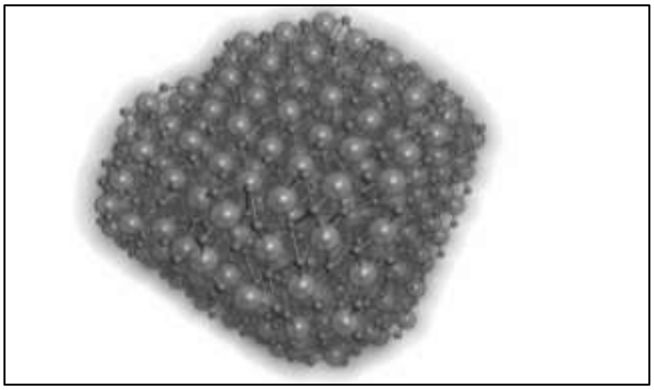

Fig. 17: Nanoparticle matrices in electrodes [3]

B. Electrolyte improvement

When nanoparticles such as Al_2O_3, and SiO_2 are added to the polymer gels, the conductivity and storage capacities of the batteries are found to significantly increase. Solid ceramics which show high-temperature resistance have also been explored for various high-stress applications.[5]

C. Improvement in storage capacity

It has been found that through the addition of single-walled carbon nanotubes (SWCNTs) in the electrodes, there is potential to improve the battery performance by almost 3 times. Thus, they are expected to replace the conventional carbon-based materials in LIBs. The advantages provided by the SWCNTs in battery components are increased depth of discharge, zero-volt state of charge, increased capacity, higher temperature operations and flexible geometrics.[6]

D. Improvement in battery storage

When a nanomaterial-based coating is provided to the electrodes, it acts as a barrier that separates the electrodes from the electrolyte when the battery is not in use. This electrode-electrolyte separation is important as the electrode and electrolyte materials may react with each other, causing a low-level discharge, which in turn reduces the shelf life of the battery [6].

E. Limitations of Nanotechnology with battery technology

- Nanoparticles have a low mass-volume ratio and high surface area. The high surface area results in surface-air interactions causing damage to the battery.
- The low density and the high interparticle resistance of nanomaterials can decrease the electrical conductivity of the material
- The production strategies and cost of nanomaterials are prohibitively high, making their implementation in today’s scenario questionable.

VII. SAFETY OF LIBS

Various situations may arise that can cause Li-ion batteries to leak, catch fire or even explode. Some of the causes that can cause the malfunction of LIBs to include-

- Overcharging and overheating of the battery
- Internal short circuit due to damage to the cell
- External short circuit due to improper wiring or during transportation [7]

Symptoms like excessive battery heating, strange odour and noises, leakage and colour and shape change indicate the faulty nature of batteries. In such situations, the use of the battery must be stopped immediately.

The following precautions could be followed to ensure the safe usage of LIBs-

- While recharging, combustible materials should not be used.
- The batteries must be maintained and stored in a dry environment at room temperature and away from direct sunlight.
- Their installation should be done properly.
- Their transportation and storage must be done with utmost care i.e., away from sharp objects and with proper packaging.
- The heat dissipated during charging and discharging should be properly thermally managed.
- Electronic protection must be provided based on the voltage threshold specifications.
- Risk assessment and safety analysis should be conducted during manufacture.
- Safety evaluation techniques such as Cyclic voltammetry, Differential scanning calorimetry and thermal ramp testing should be effectively carried out. [2]

VIII. CONCLUSION

A lithium-ion battery consists of a cathode, anode and an electrolyte. The cell works by the mechanism of a redox reaction which takes place inside of the cell. The performance of the battery was found to be dependent on the nature of the electrode, type of electrolyte and surface area of contact.

Improvising these factors can improve the overall performance and efficiency of the battery. We acknowledge nanotechnology to be one such science whose integration with battery technology can enhance the specific capacity, shelf life and battery performance. We conclude with the understanding that nanotechnology can undoubtedly help in the fabrication of LIB with well-designed characteristics which promotes the development of science and technology.

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