Performance analysis of solid-state batteries in Electric vehicle applications

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Abstract. In recent years solid-state batteries, have emerged leading research focus, due to their distinct advantages over conventional batteries. Solid-state batteries, having solid electrolytes, offer higher energy and power density, enhanced safety features and longer lifespan. This makes them ideal in fulfilling demand for energy storage in electric vehicle, and smart grid applications. This study aims to evaluate various types of solid-state batteries, analysing their properties, advantages, and disadvantages, assessing their viability in EV applications. The objective is to identify and recommend the most effective solid-state battery that aligns with the specific demands and operational conditions of electric vehicles and conduct a comprehensive analysis of anode and cathode elements of one of the solid-state batteries in their fresh and damaged state using scanning electron microscopy (SEM).

1 Introduction

Electric vehicles (EV) are gaining popularity these days, as they are sustainable alternative for traditional fuel-based vehicles. Advancements in energy storage systems like battery have made EV formidable competitors to conventional batteries. Lithium-ion batteries have become the essential for the modern electric vehicle (EV) technology, powering an impressive majority of today's clean transportation options. According to statistics approximately 90% of today's electric vehicles are been powered up by Li-ion batteries (one of the popularly known liquid electrolyte battery). And it is also commonly used in mobile communication systems and portable electronics because of their high energy density, relatively long lifespan, and efficiency in recharging, high operating voltage etc.

Although these advantages, the liquid electrolytes (generally used in commercial LiBs) have serious safety problems. Charging, short circuit, corrosion high temperature

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decomposition, leakage and other issues likely to cause fire or explosion. Lithium dendrite growth is a prime issue, especially when exposed to extreme temperatures or improper charging practices, which leads to short circuits and thermal runaway due to exothermic reactions between the liquid electrolyte and the electrode. Because of all these issues, it ultimately reduces performance and efficiency of EV. To address these safety concerns, numerous research activities have been devoted to the development of electrochemical energy storage devices that meet performance, energy density, safety and cost targets for the future applications. Solid-state batteries are emerging as a promising solution to overcome many of these drawbacks associated with lithium-ion technology in electric vehicles. Unlike traditional lithium-ion batteries, solid-state batteries contain solid electrolyte instead of liquid electrolyte. This key difference significantly enhances their safety profile by virtually eliminate the risk of leaks and reduce the likelihood of thermal runaway. This makes solid-state batteries far less prone to catching fire or exploding under stress, addressing a critical safety concern.

Moreover, solid-state batteries, one of the most significant benefits is their simplified structure and reduced size. It additionally simplifies the manufacturing process. ASSBs can achieve higher energy density. The presence of solid electrolyte allows for the use of different electrode materials and configurations that are not compatible with liquid electrolytes, leading to improved energy storage capacity. This increase in energy density leads to longer driving ranges for EVs and more efficient performance in portable electronics. Despite the challenges, there is an immense potential for solid-state batteries to revolutionize the EV industry. However, ongoing research and investment in this area are promising, indicating that solid-state technology could become a viable and sustainable alternative in the near future, propelling the next generation of electric vehicle advancements.

2 Investigation on several types of solid-state batteries

Solid-state batteries are classified into distinct types based on type of electrolyte. But it is important to know working principle of electrolyte in solid-state battery. The main working principle of solid electrolyte is to allow transportation of ions between anode(negative) and cathode(positive) during charging and discharging process and electrons generated by the reaction are used to promote a load in external circuit [1]. Hence, solid electrolytes are prominent candidates to improve the overall performance of batteries with reduced size. There are diverse types of solid-state, one must analyse all types of solid-state batteries to conclude the best suited among all for the concerned application. The classification of solid-state batteries is shown in fig.1.

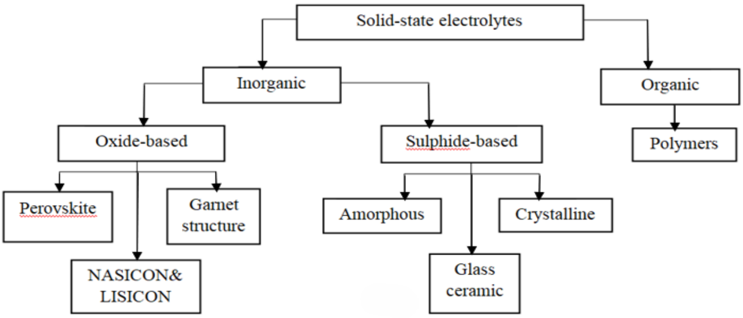


Fig. 1. Classification of solid-state batteries

2.1 Organic solid-state electrolytes

Polymer electrolytes have high molecular weight membranes which are composed of dissolution sats in a polymer matrix. They are easier to process and can be fabricated at low cost. But they possess low ionic conductivity for battery operation at room temperature. They are widely used in electrochemical devices. Batteries with polymer electrolyte have several advantages over conventional batteries. This is due to properties of polymer electrolyte such as transparency, light weight, highly flexible, increased ionic conductivity, easy to process and wide range in electrochemical window. Polymer electrolytes are further classified based on source and origin as natural and synthetic and based on physical state and composition is it divided as gel based, solid based and composite type polymer electrolyte. The classification is shown in the fig.2.

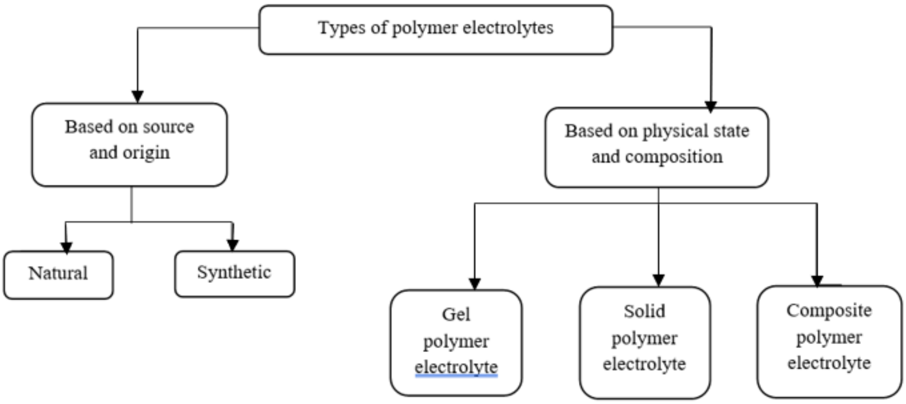


Fig. 2. Classification of polymer electrolytes

2.1.1 *Gel based polymer electrolyte*

Gel based polymer electrolyte indeed represent a notable advancement in battery technology particularly in comparison to traditional liquid electrolyte batteries as it has relatively higher efficiency. This electrolyte consists of polymer matrix, typically in the form of a gel, holding a liquid electrolyte [3]. This unique combination provides them stability and superior conductivity compared to conventional counterparts. The gel matrix provided structural integrity while allowing the electrolyte to flow freely, facilitating faster charging, and discharging. One of the standard features of gel-based polymer electrolytes is their enhanced safety profile. Unlike traditional solutions they are less corrosive, reducing risk of leakage of damage, especially crucial in applications like electric vehicles.

2.1.2 Solid polymer electrolyte

Solid polymer electrolyte is also known as solvent free polymer electrolyte. The key functionality lies in coordination of inorganic salt within polymer matrix. The active level of salt decides the performance of electrochemical cells utilizing solid-state polymer electrolyte. The activity influences the potential difference between different phases within the cell and dictates the efficiency of change transport through electrolyte. These factors collectively impact the overall performance, safety, and applicability across a range of industries, from energy storage to semiconductor manufacturing.

2.1.3 Composite polymer electrolyte

Composite electrolytes are compared of polymer matrices active inorganic fillers and lithium salts. Both polymer matrix and fillers are ion conductive. Their conductive behaviour is generally complex. Composite electrolyte can offer threshold ionic conductivity, can withstand high mechanical stress and strain and can provide strong connection between electrodes. All these characteristics shows improved performance when compared to battery with polymer-based electrolyte or inorganic electrolyte. Table-1 below shows the features of polymer batteries.

Table 1. Characteristics of all types of polymer electrolyte

Characteristics	**Gel-polymer electrolyte**	**Solid-polymer electrolyte**	**Composite polymer electrolyte**
Physical State	Gel (Semi-solid)	Solid	Solid/Gel mix
Ionic conductivity (S cm^{-1})	10^{-5} to 10^{-2}	10^{-7} to 10^{-4}	10^{-5} to 10^{-3}
Energy density (Wh/kg)	100 to 300	100 to 250	150 to 350
Power density (W/kg)	100 to 500	100 to 400	150 to 600
Advantages	Improved mechanical flexibility, enhanced ionic conductivity, good interfacial compatibility, high thermal stability.	Improved safety, high mechanical stability, wide electrochemical stability, minimal electrolyte leakage, ease of fabrication.	Enhanced mechanical strength, improved thermal stability, increased ionic conductivity, flexibility in design.
Disadvantages	Potential for electrolyte leakage, complex fabrication process, limited shell life, sensitive to temperature, potential for electrolyte drying.	Limited ionic conductivity, poor interfacial compatibility, hygroscopic nature, temperature sensitivity.	Complex synthesis process, potential for filler agglomeration, compatibility issues, expensive.

Though polymer electrolyte has several disadvantages it can be combined with Li anode and can be safely cycled even at high temperatures. But development of stable polymer electrolytes with Li metal which can be used commercially is still a change.

2.2 Inorganic solid electrolyte

Inorganic solid electrolytes as shown in fig.1 are classified based on chemical bonding with sulphur or oxygen as sulphide based and oxide based. Oxide based inorganic electrolytes are of many types but popularly used and has progressive results in research are very few, they are further divided as perovskite (CaTiO3), Lithium stuffed garnet type oxide

(Li7La3Zr2O12) and NASICON (acronym of solid super ion conductor) and LISICON (Lithium super ionic conductor). On the other hand, sulphide based are further classified based on the composition of that electrolyte as glass-ceramic, amorphous and crystalline. Inorganic electrolytes can in aggressive environment and elevated temperatures with high stability. Inorganic structures have sufficient vacancies and coordination defects which enables easy ion transportation. Table.2 is summary of characteristics of inorganic solid-state electrolytes.

Table.2. Summary of main characteristics of inorganic solid-state electrolytes

Characteristics	**NASICON**	**LISICON**	**Garnet-type**	**Perovskite-type**	**Sulphide**
Example	$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$	$Li_{14}Zn(GeO_4)_4$	$Li_7La_3Zr_2O_{12}$	$Li_{3.3}La_{0.56}TiO_3$	Li_2S-$P_2S_5Li_2SP_2S_5$ MS_X
Type	Crystalline	Crystalline	Crystalline	Crystalline, Amorphous	Glass-ceramic
Ionic conductivity ($S\ cm^{-1}$)	10^{-5} to 10^{-3}	10^{-5} to 10^{-3}	10^{-5} to 10^{-3}	10^{-5} to 10^{-3}	10^{-6} to 10^{-2}
Power density (W/kg)	100 to 300	200 to 400	300 to 500	250 to 450	150 to 50
Energy density (Wh/kg)	200 to 400	300 to 500	400 to 600	350 to 550	250 to 450
Advantages	High ionic conductivity, chemical stability, thermal stability, electrochemical stability	High mechanical strength	Crystalline in nature, high density	High electrochemical oxidation voltage	Easy operation, resistant to thermal conductivity, highly flexible and can withstand a sufficient range of stress and strain, highly conductive.
Disadvantages	Non-flexible synthesis, complexity, interface compatibility, expensive	Expensive large-scale production	Heterogeneous phase	Resistant to heat flow	Poor compatibility, sensitive to moisture and can easily form oxides and peroxides

Along with organic and inorganic electrolytes there is another type of electrolyte called hybrid electrolytes. Hybrid electrolytes are the combination of both organic and inorganic electrolytes. They present several disadvantages like complex manufacturing, interface issues, limited mechanical stability, thermal instability, and degradation over time.

3 Identifying Optimal solid-state battery for EV application

Researchers are ready to make huge investments in solid-state batteries since they are more reliable than Li-ion batteries. Sulphide and oxide batteries are more compatible as they can maintain stability in extreme conditions. Especially, lithium stuffed garnet type oxide electrolyte formulated as LLZO ($Li_7La_3Zr_2O_{12}$) is found out to be more compatible for electric vehicle applications.

The important characteristic of lithium stuffed garnet type oxide battery is high environmental stability which ensues longer lifespan, safety, and high performance of the battery. This stability also shows down the degradation process which increases durability.[5] Garnet type have high ionic conductivity which ranges between 10^{-4} to 10^{-3} S Cm^{-1}. Of course, there other electrolyte types such as LISICON and argyrodite which possess ionic conductivity more than LLZO, but they are less stable than LLZO. LLZO has an impressive electrochemical window of up to 6V. This enables operations at high voltages and enhanced energy density. Furthermore, LLZO is stable when Li metals are used as anode. This addresses a major problem with reactivity of electrolyte with Li metal anode. Reactivity of Li metal with electrolyte leads to formation of lithium dendrites which reduces efficiency of the battery. Lastly, LLZO exhibits compatibility with various cathode materials commonly used in lithium-ion batteries. This compatibility enables the design and fabrication of solid-state batteries with diverse electrode configurations, potentially expanding the range of application for these advanced energy storage devices.

These exceptional properties of lithium stuffed garnet type oxide electrolyte make them promising candidates for advancing the development of solid-state batteries, offering improved performance. Safety and versatility compared to traditional liquid electrolyte systems.

4 SEM Analysis

To achieve widespread commercial use, it is important to address few challenges like performance of the battery at extreme conditions, changes in the battery during different stages of charging and discharging. For this, it is important to know the electrochemical and mechanical changes of electrode materials and interfaces during battery operation. Scanning electron microscopy (SEM) is crucial tool for observing the concerned changes in a battery. SEM has ability to capture high resolution images with detailed insights into morphology, structure and composition of the battery materials and interfaces.

4.1 Specifications of sample

In this study lithium-ion polymer battery is presented as sample as it is easily available in commercial market than any other solid-state battery. The specifications of fresh and damaged states of lithium polymer battery are mentioned below in Table-3.

Table 3. Specifications of fresh and damaged Li-polymer batteries

	Fresh LiPo battery	**Damaged LiPo battery**
Rated capacity	1500mAh/5.7Wh	3900mAh
Rated Voltage	3.8V	3.85V
Limited charge voltage	4.35V	4.40V

Lithium polymer battery (LiPo) is a type of organic battery which uses lithium-ion battery technology paired with a semi solid(gel) polymer electrolyte. Lithium polymer battery, in

general, utilizes polyethylene oxide (PEO), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA) or polyvinylidene fluoride (PVDF) as electrolyte. In the considered sample cathode is lithium cobalt oxide (LiCoO2) and anode is of graphite. In the battery considered lithium ions move from positive electrode(cathode) through the electrolyte to the negative electrode(anode). During discharge lithium ions move from anode to cathode through the electrolyte, releasing energy that powers the device. In these reactions, 'x' represents the number of lithium ions that are intercalated (inserted) into or removed from the electrode material during charging or discharging.
Positive electrode reaction: $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$
Negative electrode reaction: $6C + xLi + xe^- \rightarrow Li_xC_6$
Total battery reaction: $LiCoO_2 + 6C \rightarrow Li_{1-x}CoO_2 + Li_xC_6$
And simplified electron transfer reactions for both anode and cathode can be written as follows,
$A^{n+} + xe^- \rightarrow An^{(n-x)+}$ and $A^{(n-x)+} \rightarrow An^+ + \ xe^-$ where $n > x$
$B^{m+}ye \rightarrow B^{(m+y)+}$ and $B^{(m+y)+} \rightarrow B^{m+} - ye^-$

4.2 Performing SEM Analysis

For performing the SEM analysis of the battery, safety precautions were taken while dismantling the battery. The fresh and damaged battery had been cut and each component of the battery is separated (anode, cathode, and electrolyte). Each separated component of fresh battery and damaged battery are subjected to SEM for detailed insights of elemental composition and microstructure surface. The fig.4 illustrates the flowchart of procedure for SEM analysis.

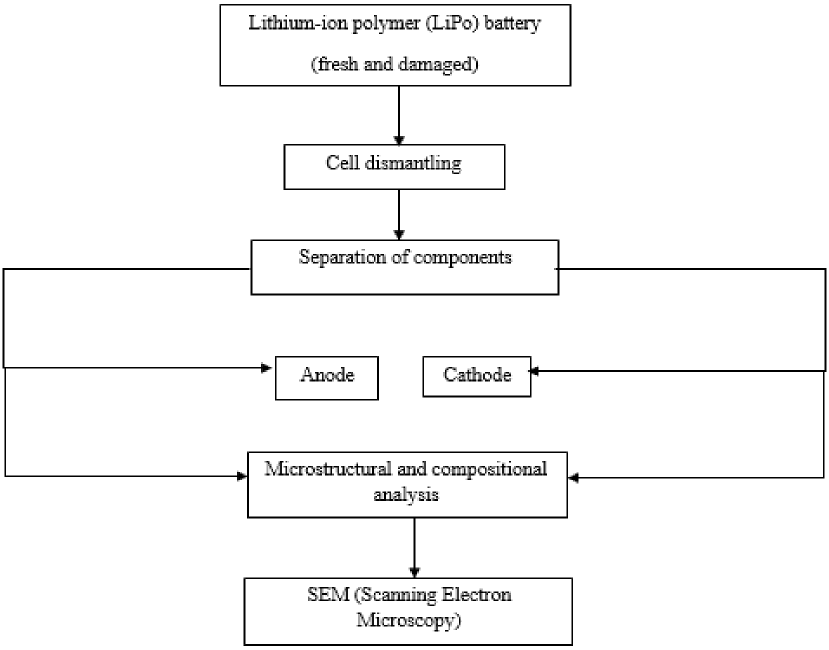


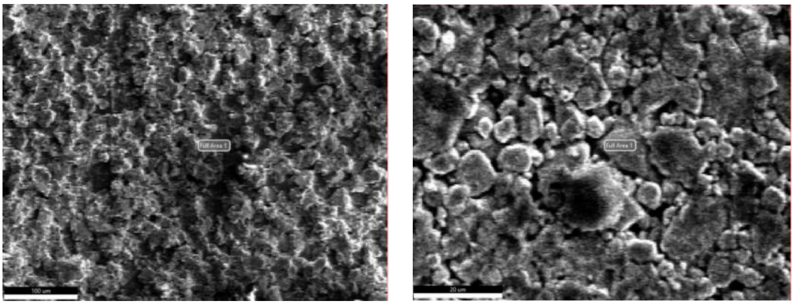
Fig. 4. Flowchart for the procedure of SEM analysis

5 Results and discussion

5.1 SEM Analysis of Cathode in Fresh and Damaged Samples

5.1.1 Microstructural analysis of fresh and damaged cathode samples

The microstructural findings of LiPo cathode specimens in their fresh and damaged state is illustrated in fig.5a&b.



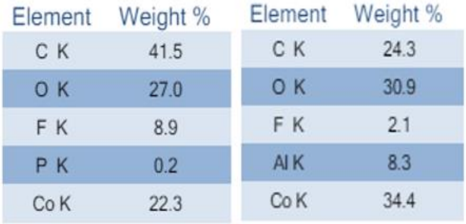
(a) (b)

Fig. 5a&b. Microstructural analysis of Li-polymer fresh and damaged specimen(cathode)

It is observed that, in the fresh cathode specimen, the particles may appear relatively uniform in shape and size, with smooth surface and well-defined edges. However, in the damaged specimen, the morphology is altered due to mechanical stress, which led to particle cracking, fracturing or fragmentation. Hence, this resulted in irregular shapes, rough surface, and the presence of agglomerates [7].

5.1.2 Elemental analysis of fresh and damaged cathode samples

Elemental analysis of fresh and damaged batteries is shown in fig.6a&b. The presence of intended cathode material component, such as transition materials (cobalt, nickel, manganese) and lithium are relatively uniform for fresh cathode specimen. On the other hand, for damaged cathode specimen it shows some changes. This indicated rigorous operations and degradation.



Element	Weight %
C K	41.5
O K	27.0
F K	8.9
P K	0.2
Co K	22.3

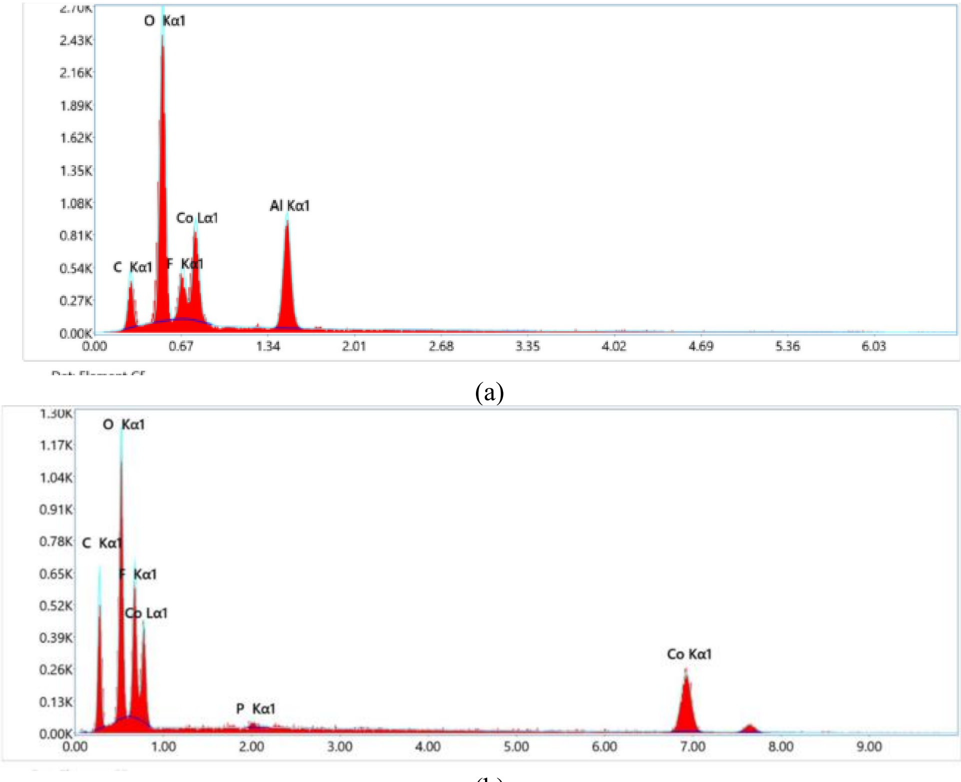
Element	Weight %
C K	24.3
O K	30.9
F K	2.1
Al K	8.3
Co K	34.4

(a) (b)

Fig. 6a&b. Elemental analysis of fresh and damaged Li-polymer batteries

As in the fig.6a&b transition metal percentage is relatively high and lithium content is also expected to be high. Lithium content cannot be displayed by as SEM cannot display elements with atomic number less than 4. Lithium content directly influences the capacity and energy density of the battery. Depending upon the specific cathode chemistry, additional elements such as oxygen, fluorine present in the smaller percentages as a part of active material or as components of coatings, additives, or impurities.

During battery cycling and degradation, the elemental percentages of transition metals within cathode material may change due to dissolution, migration, or redistribution processes. Even though, lithium cannot be observed, the electrochemical reactions, such as electrolyte decomposition, SEI formation, or side reactions with active materials, can lead to consumption or trapping of lithium ions, resulting in reduced lithium content within cathode material. Therefore, because of formation of degradation products can alter the elemental composition of the cathode material. These secondary phases may contain different elemental percentages compared to fresh state and can affect battery performance and stability.Fig.7a&b is graphical representation of quantity of elements in cathode in fresh and damaged states respectively.



(a)

(b)

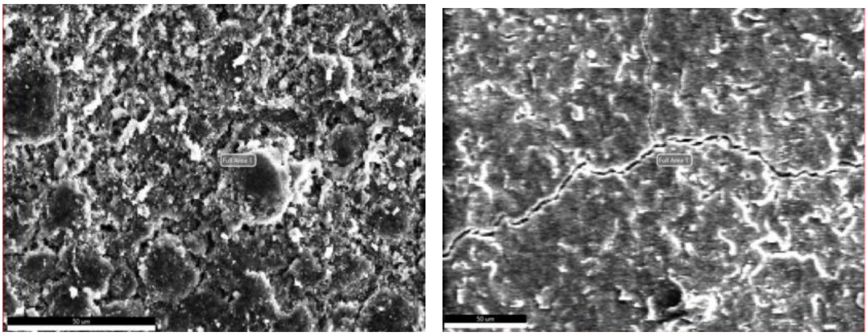
Fig. 7a&b Graphical representation of elements present in fresh and damaged cathode specimen

5.2 SEM Analysis of Anode in Fresh and Damaged Samples

5.2.1 Microstructural analysis of fresh and damaged anode samples

Fig.8a&b illustrates the microstructural findings of LiPo anode of fresh and damaged states. Similar to cathode, for anode material, the fresh state are typically smooth morphology facilitates efficient lithium-ion diffusion and promotes stable electrochemical performance. Whereas, in damaged state, the surface of the anode material become roughened or irregular due to the formation of surface films, SEI layers, and cracks. This roughening can increase surface area, alter surface chemistry, and also can affect electrode-electrolyte interactions.

But it is observed that dendrites formation is low or absent. But when it comes to lithium-ion battery, as battery's life is about expire, lithium dendrites and accumulation of lithium ions on surface of anode (graphite) is observed. This is due to few strategies which are used to suppress the dendrite growth like surface modification of the lithium metal, solid electrolyte doping, and mechanical constriction. Adding a lithium conducting layer where surface is insulated helps in contributing improved efficiency and battery lifespan.

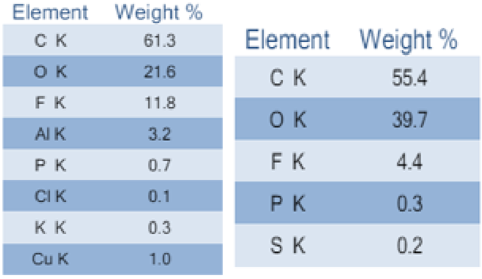


(a) (b)

Fig. 8a&b. Microstructural analysis of fresh and damaged Li-polymer battery(anode)

5.2.2 Elemental analysis of fresh and damaged anode samples

The each elemental percentages of anode specimen is shown in fig9a&b.



Element	Weight %
C K	61.3
O K	21.6
F K	11.8
Al K	3.2
P K	0.7
Cl K	0.1
K K	0.3
Cu K	1.0

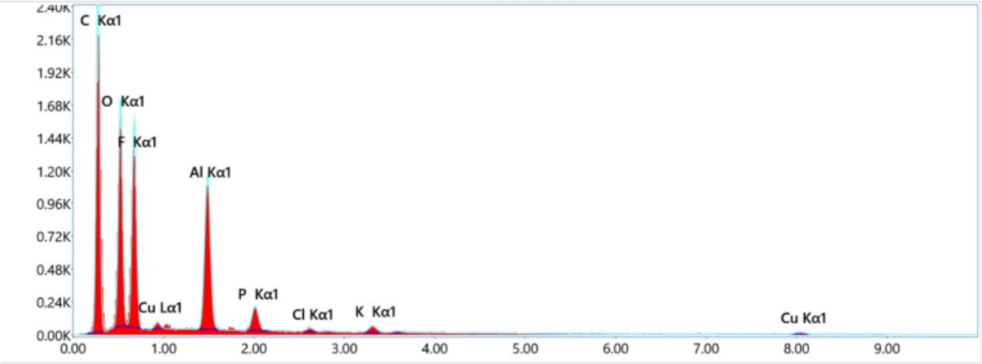
Element	Weight %
C K	55.4
O K	39.7
F K	4.4
P K	0.3
S K	0.2

(a) (b)

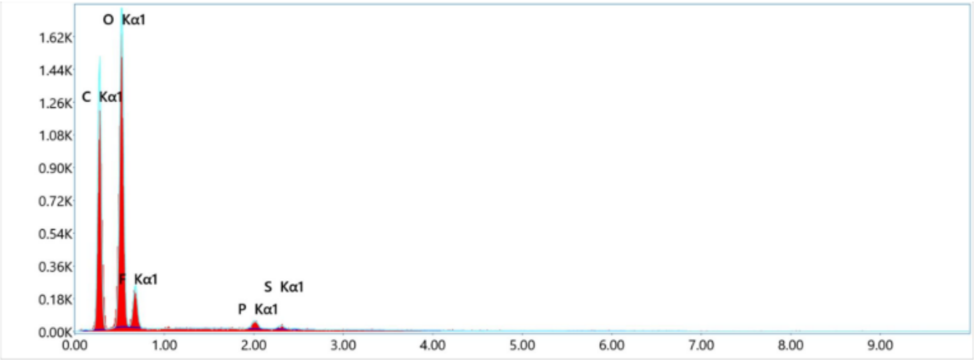
Fig. 9a&b. Elemental analysis of fresh and damaged Li-polymer battery(anode)

In fresh state, the elemental composition of graphite anodes primarily consists of carbon(C), which serves as the host matrix for intercalating lithium ions during charging. During battery cycling, graphite anode can undergo various degradation mechanisms, leading to changes in elemental composition. In other words, the repeated cycles can cause structural changes in graphite, such as formation of SEI layers, micro-cracks and surface roughening.

In operating conditions like overcharging, free lithium ions may deposit unevenly on the graphite surface, leading to lithium plating, which is the main cause of cracks in anode. Lithium plating is serious issue which can change the elemental composition if anode. It occurs when the anode surface is saturated positive lithium ions (Li+) [2]. To address this issue the anode's capacity is relatively larger than anode. Also charging current and operating temperature are limited to a threshold value. Fig.10a&b shows the quantity of éléments in anode material of fresh and damaged states respectively.[4]



(a)



(b)

Fig. 10a&b. graphical representation of elemental analysis of fresh and damaged anode specimen

Over all, SEM analysis allows for the detailed characterization of structural diffrences between fresh and damaged states of batteries, provides valuble insights into underlying mechanisms of électrodes in batteries. By understanding these diffrences, researches can develop stratergies to improve electrode design, materials selection and battery operation to enhance performance and durability.

6 Conclusion

Electric vehicles are sustainable future of the world. Hence it is important to do studies on it and make it as a competitive alternative for fuel-based vehicles. One of such research steps, is to power up electric vehicles using solid-state batteries instead of conventional lithium-ion batteries. In conclusion, this study explores wide range varieties of solid-state batteries and analyses their properties, composition of each battery, advantages, and disadvantages. This leads to identification of the most suitable solid-state battery for electric vehicle applications which is lithium stuffed garnet type oxide (LLZO). However, in order to move towards large scale manufacturing and broader utilization of solid-state battery under several conditions. Hence, these challenges are highlighted through SEM analysis. The micro-structural analysis of battery under SEM has given detailing about battery ensures the loss of ions (Lithium ions in this case) and accumulation of impurities in the surface. Therefore, SEM provides valuable information about additional processes occurring at batteries, that further helps in enhancing the energy density, power density, efficiency, life cycle of a battery.

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