Section A-Research paper
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Effect of Environmental Cyclic Aging on NMC and LFP 18650 Cylindrical Cell.

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Abstract— Lithium-ion batteries represent the overwhelming majority of the market. Because of their high energy density and long lifespan, they became the dominant solution. Currently, many different novels cell chemistries are under research for EVs. These lithium-ion cells undergo a variety of undesirable chemical and mechanical reactions inside the battery over a period of time that affect the different components of the cells, such as the anode, cathode (electrodes), electrolyte, separator, and current collectors, causing degradation of these parts and shrinking the performance. Hence It is important to understand battery degradation to manage both the performance of the systems and warranty liabilities. This project will focus on, characterization of LFP and NMC 18650 cells, to understand and compare degradation modes and mechanisms with respect to different electric parameters for fresh and cycle-ageing (long cycling at defined C rate) under environmental conditions. The cells will be characterized by using various nondestructive & destructive techniques such as EIS, Radiography, SEM-EDS & FTIR tests. In this project, a prominent focus is on understanding the degradation morphology and topography of LFP & NMC. Understanding the mechanism and modes of degradation to avoid thermal runaway and cell explosion will provide researchers and developers with useful data for EV applications.

Keywords — *Lithium-ion battery, Material analysis, SEM- EDS.*

Introduction:

Lithium-ion batteries are widely used in various applications, including portable electronic devices, electric vehicles, hybrid electric vehicles, and stationary energy storage systems. The use of batteries in EVs will increase in the coming years due to their eco-friendliness and reduced pollution. Most countries, including India, are aiming for 100 percent electric vehicles. The lithium-ion battery types NMC and LFP two that are frequently used for electric vehicles. Lithium-ion cell deterioration, which reduces their performance and longevity, is largely caused by cyclic ageing. Researchers have used cyclic ageing settings to conduct ageing studies on commercial lithium-ion cells to examine this phenomenon. Cyclic ageing, which results from repeated charging and discharging cycles, is one key aspect that affects the degeneration of lithium-ion batteries. The ageing behavior and characterization of lithium-ion batteries, such as the NMC and LFP batteries that are frequently used in electric vehicles (EVs), have been the subject of several studies [1]–[3]. In order to understand the materials and structure of lithium-ion batteries, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) are powerful techniques that can be used for material characterization of lithium-ion battery cells [4]. These methods can offer details on the morphology, structure, and chemical make-up of the electrodes, electrolytes, and separators, which can aid in figuring out the underlying causes of battery deterioration. The cathode material's particle size and surface area play a significant role in the degradation of lithium-ion batteries[5]. LiFePO4 particle size and surface area were discovered to have a significant impact on the performance of LiFePO4/graphite cells [6]. This research suggests that the performance and lifespan of lithium-ion batteries may be significantly impacted by the particle size and surface area of the cathode anode material. Vibration and nail penetration can also have an impact on the performance and longevity of lithium-ion batteries, in addition to cyclic ageing[7]. The impacts of these elements on the battery components can be studied, and the underlying mechanisms of battery degradation can be found using techniques for material characterization and analysis. FTIR spectroscopy is used to examine polymeric materials. The authors give a summary of FTIR spectroscopy and its uses in polymer science, including chemical composition analysis, structural characterization, and reaction monitoring. Additionally covered in the paper are numerous experimental issues and data analysis methods for FTIR spectroscopy in polymer research[8], [9]. Another effective method for assessing the ageing effects of lithium-ion batteries is electrochemical impedance spectroscopy (EIS) [10]. The electrochemical behavior of the battery's constituent parts can be revealed by EIS, which can aid in determining the underlying causes of battery deterioration. Lithium-ion battery ageing behavior and degradation mechanisms are highly reliant on operating parameters, including temperature, depth of discharge, and cycling conditions [5], [11]. Creating efficient battery management techniques requires a thorough understanding of these aspects and how they affect the battery's constituent parts. For an in-depth analysis and deep understanding of a battery cell, it is important to disassemble the cell. However, because safety hazards such as short circuits, health issues, and thermal runaways cannot be avoided, many manufactured products that do not disassemble the cell are recommended [12], [13]. In this disassembly procedure, the most recommended disassembly method for cells as well as safety precautions are taken.

Experimental Methods and Results:

The batteries used for this study were 18650 NMC capacity 3.3Ah, nominal voltage 3.6 V LFP with capacity 1.5Ah, nominal voltage 3.2 V, were undergo 100, 300 and 500 cycles. Below flow chart shows methodology for lithium-ion cell analysis.

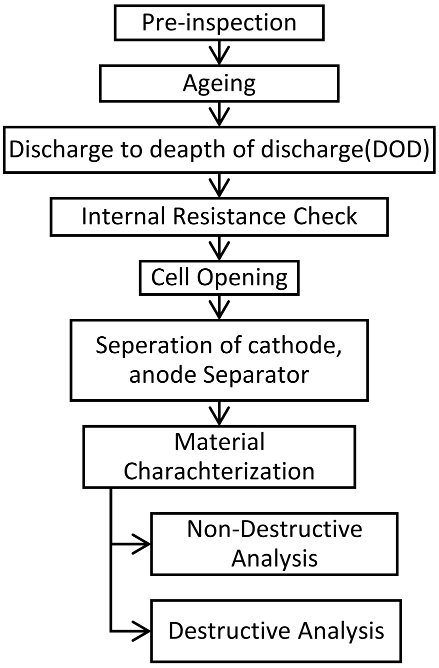


Figure 1: Flow chart for Li-ion cells analysis

Table 1:Commercial 18650-format lithium-ion battery Manufacturer-specified operating

Battery	NMC	LFP
Nominal Capacity (mAh)	3350	1550
Nominal Voltage (V)	3.6	3.2
Voltage Range (V)	2.5-4.2	2.5-3.65
Nominal Mass (g)	49	42
Internal resistance (mΩ)	≤ 35 mΩ	≤60mΩ
Working temperature	Charge: 0 ~ 45°C, Discharge: -20°C ~ 60°C	Charge: 0 ~ 55°C, Discharge: -20°C ~ 60°C

A. Non-Destructive testing:

Charge-Discharge Cycling of cells - When it comes to cycling these cells, it is important to understand that each cycle can have a different impact on their performance and lifespan. Generally, a full cycle (from 100% to 0% state of charge) will have a more significant impact. MCV™ – EV/ HEV Battery Cell Tester – Bitrode, was used for cycling of the batteries. Based on the datasheet from the battery manufacturer, charging and discharging cut-off voltages were set to (Table .1) 3.65 and 2.5 V for LFP and 4.2 and 2.5 V for NMC, and cycling was conducted at a rate of 1 C for both cell with current 1.5 A for LFP and 3.3 A for NMC, which was the standard charging \discharging rate stipulated by manufacturer.

1. Current Interrupt Test:

A battery cell's internal resistance is a critical parameter that determines its performance, efficiency, and durability. The current interrupt technique is commonly used to measure internal resistance, which involves briefly interrupting the current flowing through the cell and measuring the resulting voltage drop. A high internal resistance reduces the efficiency of the cell and increases its operating temperature, which can lead to thermal runaway. The current interrupt test is a quick and simple method of measuring the internal resistance of a battery [14], [15]. The test typically involves connecting a load to the battery, such as a resistor or an electronic load, and measuring the voltage across the load while a high current is flowing through it. Based on the above non-destructive method, during the cycling for this experiment, internal resistance is monitored. The fresh sample and after the 100, 300, and 500 cycles are noted.

For NMC (Figure 2), after 100 cycles, internal resistance has increased by 1.656 times its initial value, 1.973 times its initial value after 300 cycles, and 2.794 times its initial value after 500 cycles.

For LFP (Figure 3), after 100 cycles, internal resistance has increased by 1.307 times its initial value, 1.741 times its initial value after 300 cycles, and 2.082 times its initial value after 500 cycles.

The results show that the cell's internal resistance increased significantly after cycling. Internal resistance of an NMC and LFP cell has been measured before and after cycling, and the results indicate degradation of the cells. Furthermore, a destructive test is performed for a more detailed analysis.

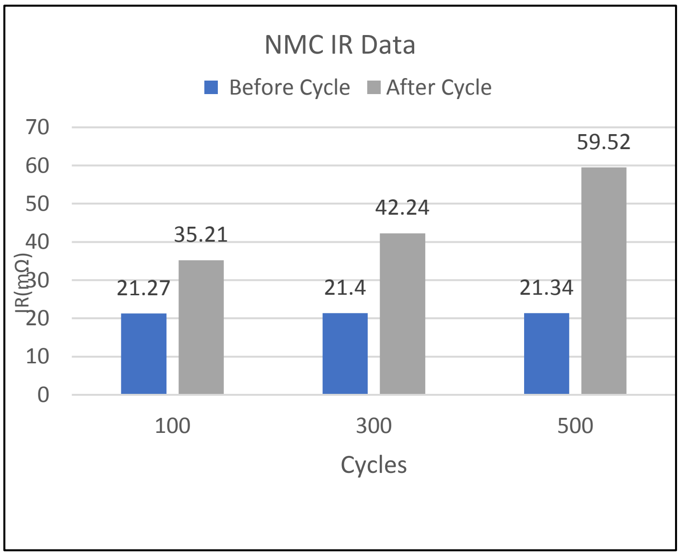


Figure 2: NMC No of cycles vs Internal Resistance

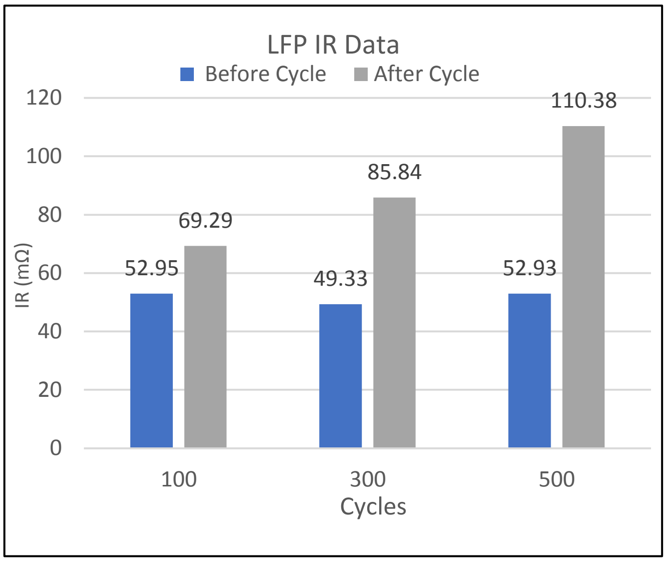
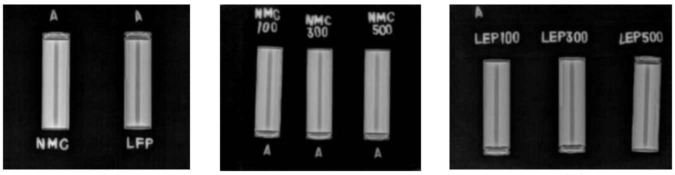


Figure 3: LFP No of cycles vs Internal Resistance

2. Radiography Test:

Radiography is a non-destructive testing method that produces images of an object's internal structure using X-rays or gamma rays. In the case of batteries, radiography can be used to inspect the internal components and detect any defects or damage that may impair the battery's performance or safety. Above result shows changes in the internal structure of the batteries by performing radiography on NMC and LFP batteries before and after 100, 300, and 500 charge and discharge cycles. This could assist you in identifying any degradation or damage that occurred during the cycling process, such as changes in the thickness or uniformity of the electrode layers or the formation of cracks or voids in the active material or gamma rays. In the case of batteries, radiography can be used to inspect the internal components and detect any defects or damage that may impair the battery's performance or safety. Result (Figure 4) shows changes in the internal structure of the batteries by performing radiography on NMC and LFP batteries before and after 100, 300, and 500 charge and discharge cycles. This could assist you in identifying any degradation or damage that occurred during the cycling process, such as changes in the thickness or uniformity of the electrode layers or the formation of cracks or voids in the active material.



(a) (b) (c)

Figure 4:Radiography Result (a) Fresh NMC and LFP (b) NMC 100,300,500 cycles (c) LFP 100,300,500 cycles

B. Destructive analysis:

Post-characterization of NMC and LFP cells is an important process for understanding the degradation mechanisms that occur during cycling and identifying ways to improve their performance and lifespan. After fully discharge the first step was to dismantled cell and remove the electrodes and separators from the both cells[16] .

1. SEM Analysis:

Microstructural analysis – In this step, the electrodes will be subjected to a microstructural analysis employing methods like scanning electron microscopy (SEM)- VEGA 3 LMU. MAKE: TESCAN machine; BSE (backscattered secondary electron detector) was utilized for compositional analysis and a secondary detector for morphological analysis.

NMC Cathode (Figure 5) - An aligned morphology of grains was discovered by analyzing the NMC cathode in the fresh cell (Figure 5a). The structure in the old cell, however, looked to be a mix of fine and coarse grains. The outcomes were consistent for new and 100 cycle cells (Figure 5b), but for 300 cycle (Figure 5c) and 500 cycle (Figure 5d) cells, it was clear that grains had been destroyed. 2000x magnification photographs were used to better comprehend this occurrence.

LFP Cathode (Figure 6) - The analysis of LFP Cathode material indicates that no significant changes observed in the fresh (Figure 6a), 100 (Figure 6b), and 300 (Figure 6c), cycle cells after SEM analysis. However, changes were observed in the cathode material after 500 (Figure 6d), cycles.

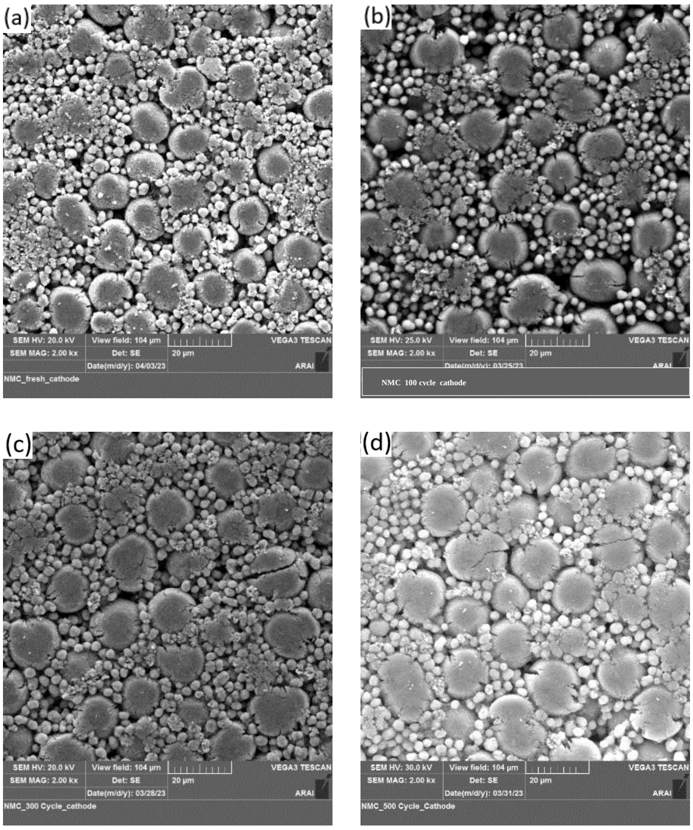


Figure 5:SEM Analysis of NMC Cathode electrode (a) Fresh (b)100 (c) 300 (d)500

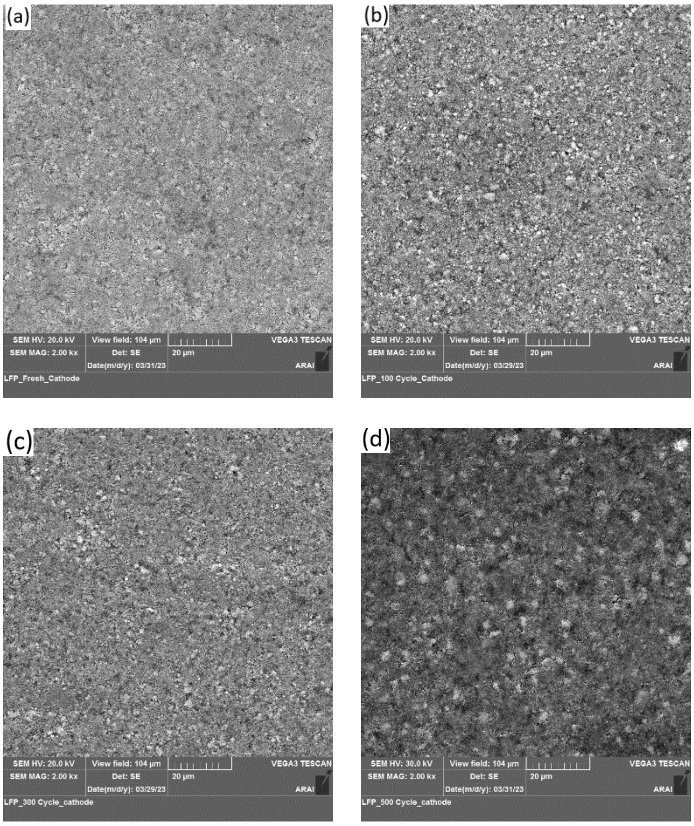


Figure 6: SEM Analysis of LFP Cathode electrode (a) Fresh (b)100 (c) 300 (d)500

NMC Anode (Figure 7) - The SEM analysis of the NMC anode reveals that there is no significant change in the morphology of the fresh cell (Figure 7a). However, for the 100 cycles (Figure 7b) and 300 cycles (Figure 7c) cells, the anode surface shows signs of degradation. For the 500 cycles (Figure 7d), the grains of the anode material are observed to have disintegrated into small spherical particles, which have formed agglomerates.

LFP Anode (Figure 8) - indicates that there are no significant changes observed in the fresh (Figure 8a) and 100-cycle (Figure 8b) cells. However, after 300 cycles (Figure 8c) and 500 cycles (Figure 8d), some cracks are visible in the anode material.

2. EDS Analysis:

EDS is an analytical method for figuring out a material's elemental makeup. EDS is particularly useful in supplying insightful information about the functionality and potential problems of battery cells, which is essential for creating and enhancing battery technologies. With the use of OXFORD software, an EDS analysis was carried out using a scanning electron microscope. EDS results obtained via SEM of the cathode and anode surface of fresh and aged cell with 100,300 and 500 cycles for both NMC and LFP battery material. Determination of Li in the sample cannot be done as the electron energies involved are out of the range of detector.

For NMC Cathode (Table 2a) Al, F, Co, Ni, P, and which confirm its chemistry. In comparison to other elements, Ni and Co have relatively large weight percentages. When the cathode material is fresh, Ni has the maximum weight percentage for fresh sample, after 500 cycles, it drops. The weight percentages range is low for Co element.

For NMC Anode (Table 2b) C, O, F, Si, P, Cu, and S which confirm its chemistry. Carbon (C) has the largest weight percentage of all the elements, and it falls as a cell ages. When the anode material is fresh, it is 90.82%; after 500 cycles, it is

81.18%. Compared to other elements, oxygen (O) has a relatively low weight percentage, and it changes dramatically during cycling. After 500 cycles, the weight proportion of oxygen (O) rises, indicating that the cell undergoes oxidation reactions during cycling. Following cycling, the weight percentages of additional elements, also exhibit some changes, suggesting potential impacts of the environment and cycling conditions on the anode material

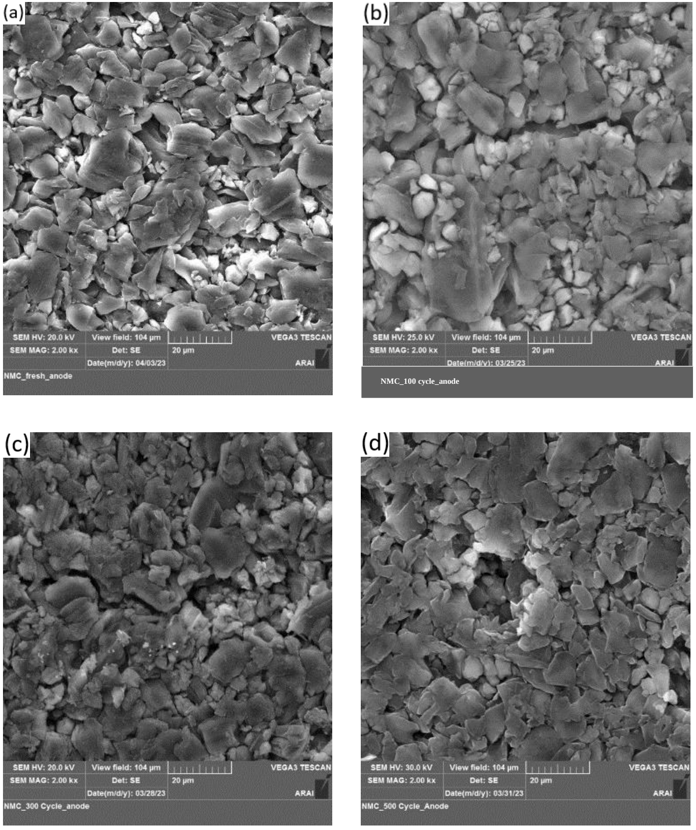


Figure 7: SEM Analysis of NMC Anode electrode (a) Fresh (b)100 (c) 300 (d)500

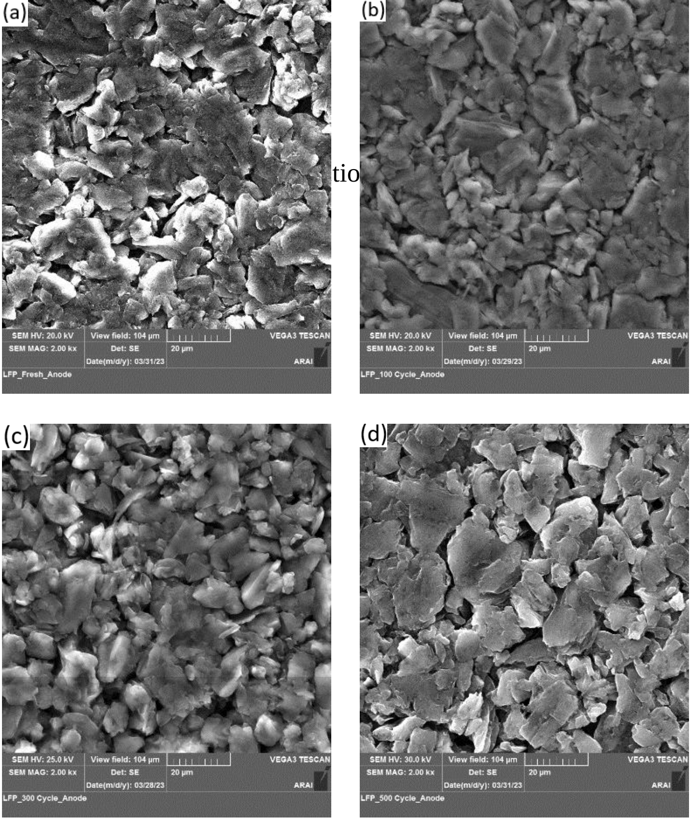


Figure 8: SEM Analysis of NMC Anode electrode (a) Fresh (b)100 (c) 300 (d)500

Table 2: EDS Analysis of NMC-: (a) CATHODE AND (b) ANODE MATERIAL

NMC Cathode				
Element	Weight %			
	Fresh	100 Cycle	300 Cycle	500 Cycle
C K	13.45	19.04	12.03	17.64
O K	32.1	28.4	34.42	32.01
F K	10.23	11.35	8.39	13.45
Al K	0.65	0.35	0.49	0.56
P K	0.73	0.26	0.44	0.29
Co K	4.08	4.84	5.27	4.43
Ni K	38.76	35.77	38.97	31.62
Total	100	100	100	100

(a)

NMC Anode				
Element	Weight %			
	Fresh	100 Cycle	300 Cycle	500 Cycle
C K	90.82	92.08	88.02	81.18
O K	5.6	4.25	4.16	11.19
F K	1.67	1.63	5.77	3.6
Si K	1.6	1.26		3.07
P K	0.31	0.29	0.36	0.38
Cu K	-	0.49	1.69	0.42
S K	-	-	-	0.18
Total	100	100	100	100

(b)

For LFP Cathode (Table 3a) C, O, P and Fe which confirm its chemistry. The weight percentage of Fe decreases as the cell ages, as can be observed from the decreasing values of iron content in the 100, 300, and 500 cycle columns. This suggests that there is a loss of iron from the LFP cathode as the cell undergoes cycles of charging and discharging.

For LFP Anode (Table 3b) C, O, F, P and Cu which confirm its chemistry. The weight percentage of carbon is initially high, but it decreases as the cell undergoes ageing. The other elements show little change in weight percentage.

Table 3: EDS ANALYSIS OF LFP (a) CATHODE AND (b)ANODE MATERIAL

LFP Cathode				
Element	Weight %			
	Fresh	100 Cycle	300 Cycle	500 Cycle
C K	17.08	13.27	17.23	17.67
O K	39.89	44.33	45	44.86
P K	15.02	16.34	14.28	14.42
Fe K	28.01	26.06	23.49	23.05
Total	100	100	100	100

(a)

LFP Anode				
Element	Weight %			
	Fresh	100 Cycle	300 Cycle	500 Cycle
C K	85.71	90.05	83.08	84.85
O K	8.45	5.64	10.43	9.13
F K	5.07	2.65	6.16	4.66
P K	0.77	0.5	0.34	0.55
Cu K	-	1.17	-	0.81
Total	100	100	100	100

(b)

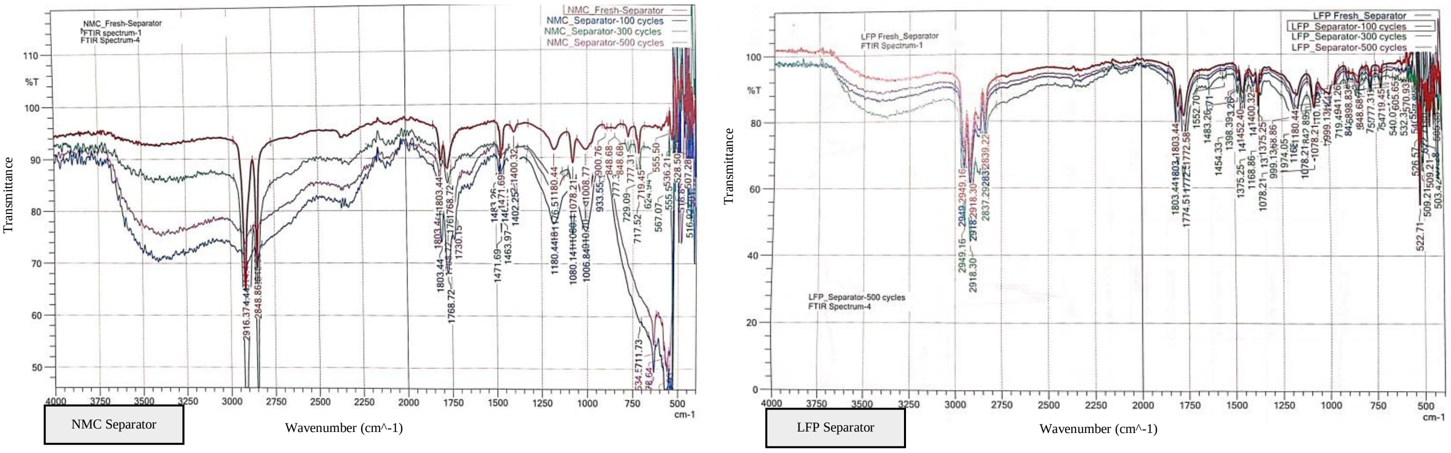
The materials clearly alter as the number of cycles rises, as shown by the tabular representations of the analysis on NMC and LFP cathodes and anodes. As the number of cycles rises, there is a noticeable increase in oxidation NMC cathode. On the other hand, as the cell ages, the iron content of the LFP cathode decreases. As the number of cycles rises, both NMC and LFP anodes exhibit material degradation with the appearance of cracks and the disintegration of grains.

3. FTIR Analysis:

FTIR (Fourier Transform Infrared spectroscopy) is an effective analytical technique for determining the properties of battery separator materials. SHIMADZU-IRAffinity-1S is a model is used for the test. Battery separators are thin, porous membranes that separate the electrodes in a battery cell; FTIR can be used to identify the functional groups in the separator material. FTIR can help identify potential separator material issues and improve the design and performance of battery cells by analyzing the composition of the separator material and any changes caused by ageing, thermal degradation, or electrolyte exposure. Overall, FTIR analysis is a valuable tool for improving battery safety and performance. Material group is found for NMC is Linear low-density Polyethylene (LLDPE) and for LFP is found Polypropylene (PP1) (Table 4). LLDPE excellent chemical and thermal stability, good mechanical properties, and low cost, it is a popular material for battery separators. It has good thermal stability and is chemically resistant, making it an ideal material for battery applications involving high temperatures and chemical exposure. Furthermore, LLDPE has good mechanical properties, allowing it to withstand punctures and tears that could cause short circuits. Polypropylene (PP1) is a thermoplastic material that is commonly used as a battery separator, especially in lithium-ion batteries. Because PP1 separators have a lower shrinkage rate, a higher melting point, and are highly resistant to corrosion and oxidation, they are an ideal material for battery applications requiring thermal stability, chemical resistance, and mechanical strength. PP1 separators are also relatively simple to manufacture and less expensive than other types of separators (Figure 9).

Table 4:FTIR Analysis for Separator Material NMC and LFP

Separator	Material Identified	Separator	Material Identified
NMC Fresh	Polyethylene	LFP Fresh	Polypropylene
NMC 100	Polyethylene	LFP 100	Polypropylene
NMC 300	Polyethylene	LFP 300	Polypropylene
NMC 500	Polyethylene	LFP 500	Polypropylene



NMC Separator

LFP Separator

Figure 9: Separator Material Identification

Conclusion:

I. EIS (IR) analysis showed that the NMC cells had 2.7 times higher internal resistance than LFP cells, indicating that LFP had better structural integrity. The range of internal resistance values for NMC was 21 mΩ to 59 mΩ (2.794 times its initial value), while for LFP it was 51 mΩ to 110 mΩ (2.082 times its initial value)
II. Radiography can be used to understand the basic construction of NMC and LFP cells.
III. SEM analysis revealed that the morphology of both cathode and anode materials degraded with increasing aging cycle, as evidenced by microcracking and disintegration of grains. However, compared to NMC, LFP showed better structural integrity.
IV. NMC cathode material was found to contain C, O, F, Al, P, Co, and Ni, with the presence of Nickel and Cobalt confirming a decrease in their percentage. For NMC anode material, C, O, F, Si, P, Cu, and S were detected, and the presence of carbon material was found to be high. However, carbon percentage decreased with increasing aging cycle. For LFP cathode material, C, O, P, and Fe were detected, with the presence of Phosphorous and Iron confirming the chemistry of LFP. Iron percentage decreased with increasing aging cycle. For LFP anode material, C, O, F, P, and Cu were detected, with the presence of carbon material being high. Carbon percentage decreased with increasing aging cycle.
V. Further evaluation of cell performance and degradation patterns is necessary with respect to increasing aging parameters and changing C rate of charge-discharge cycles.
VI. FTIR analysis showed that the separator material for NMC and LFP cells were composed of Polyethylene and Polypropylene, respectively.

Future Scope:

- XRD test can be conducted to analyze the phase composition of the anode and cathode materials in the battery.
- GCMS test can be performed to analyze the electrolyte composition of the anode and cathode materials in the battery.
- To further investigate the aging behavior of the battery, the environmental cycling can be increased to 1000 to 1500 cycles.
- To study the performance of the battery under different temperature conditions in different regions, it can be cycled at both ambient temperature (25°C) and high-temperature ranges (35 to 50°C).

Nomenclature:

NMC	Nickel Manganese Cobalt
LFP	Lithium Iron Phosphate
EV	Electric Vehicle
HEV	Hybrid Electric Vehicle
Li-ion	Lithium Ion
EIS	Electrochemical Impedance Spectroscopy

CV	Cyclic Voltammetry
SEM	Scanning Electron Microscope
EDS	Energy-Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
IR	Internal Resistance
CI	Current Interrupt
EIS	Electrochemical Impedance Spectroscopy

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