SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CARBON COATED LIMnPO4 CATHODE MATERIALS FOR LITHIUM-ION BATTERIES



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JUNE 2024

DECLARATION

I declare that this project report entitled "Synthesis And Structural Characterization Of Carbon Coated LiMnPO₄ Cathode Materials For Lithium-Ion Batteries" is the result of my own work except as cited in the references.

Signature	:
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APPROVAL

I hereby declare that I have read this project report. In my opinion, it is sufficient in terms of scope and quality for the award of the Bachelor of Mechanical Engineering degree.

Signature	:
Name of Supervisor	· PM, Ir. Dr. Sivakumar A/L Dhar Malingam
Date	: <u>5 7 þ-</u> 4

DEDICATION

I dedicate this thesis to my parents, whose unwavering support and encouragement have guided me throughout my academic journey. I also want to express my gratitude to my mentors and advisors for their invaluable insights and guidance during the completion of this work. I am thankful to all the researchers whose contributions and dedication to the field have inspired me and laid the foundation for this study. Last but not least, I want to acknowledge my friends and colleagues for their camaraderie and collaboration, which have made this endeavour a truly rewarding experience. This work is a testament to the collective support and inspiration of all those who believed in me.

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ABSTRACT

Lithium-ion batteries (LIBs) have transformed the energy storage industry, with widespread use in portable electronics, electric vehicles, and renewable energy systems. Extensive research efforts have been directed towards developing highperformance LIBs with increased energy density, enhanced safety, and longer cycle life. Lithium manganese phosphate (LiMnPO₄) has emerged as a promising cathode material among the various electrode materials. It possesses high theoretical capacity (170mAh g⁻¹), excellent thermal stability, and operates at a high voltage (4.1 vs. Li⁺ /Li). However, its capability is capped by low intrinsic electronic conductivity and surface degradation. This study uses the carbon coating method to analyze its structural properties as the carbon content varies. The sol-gel method was employed for the carbon coating process with organically derived glucose as the cost-effective carbon source. The carbon-coated samples were characterized using X-ray diffraction (XRD), Raman spectroscopy and field emission scanning electron microscope (FESEM) with energy dispersive X-ray (EDX). The results of the qualitative and quantitative analyses indicate that 15wt% C-LiMnPO4 exhibits the best structural properties that may contribute to the best electrochemical properties based on a comparison of previous studies. An optimized carbon coat may provide improved electronic conductivity and structural stability while maintaining its desired crystal structure. Overall, this study utilized an eco-friendly and cost-effective improvement technique that enhances the structural characteristics and may improve the cathode material's electrochemical properties.

ABSTRAK

Bateri litium-ion (LIB) telah mengubah industri penyimpanan tenaga, dengan penggunaan meluas dalam elektronik mudah alih, kenderaan elektrik dan sistem tenaga boleh diperbaharui. Usaha penyelidikan yang meluas telah diarahkan ke arah membangunkan LIB berprestasi tinggi dengan peningkatan ketumpatan tenaga, keselamatan yang dipertingkatkan dan hayat kitaran yang lebih lama. Litium mangan fosfat (LiMnPO \neg 4) telah muncul sebagai bahan katod yang menjanjikan di kalangan pelbagai bahan elektrod. Ia mempunyai kapasiti teori yang tinggi (170mAh g-1), kestabilan haba yang sangat baik, dan beroperasi pada voltan tinggi (4.1 lwn. Li+ /Li). Walau bagaimanapun, keupayaannya dihadkan oleh kekonduksian elektronik intrinsik yang rendah dan degradasi permukaan. Kajian ini menggunakan kaedah salutan karbon untuk menganalisis sifat strukturnya kerana kandungan karbon berbeza-beza. Kaedah sol-gel digunakan untuk proses salutan karbon dengan glukosa yang diperoleh secara organik sebagai sumber karbon yang kos efektif. Sampel bersalut karbon telah dicirikan menggunakan pembelauan sinar-X (XRD), spektroskopi Raman dan mikroskop elektron pengimbasan pelepasan medan (FESEM) dengan sinar-X penyebaran tenaga (EDX). Keputusan analisis kualitatif dan kuantitatif menunjukkan bahawa 15wt% C-LiMnPO4 mempamerkan sifat struktur terbaik yang mungkin menyumbang kepada sifat elektrokimia terbaik berdasarkan perbandingan kajian lepas. Lapisan karbon yang dioptimumkan boleh memberikan kekonduksian elektronik dan kestabilan struktur yang lebih baik sambil mengekalkan struktur kristal yang diingini. Secara keseluruhan, kajian ini menggunakan teknik penambahbaikan mesra alam dan kos efektif yang meningkatkan ciri-ciri struktur dan boleh meningkatkan sifat elektrokimia bahan katod.



vii

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TABLE OF CONTENTS

DECLA	RATIO	DN	ii
APPROV	AL		iii
DEDICA	TION	ſ	iv
ABSTRA	СТ		v
ABSTRA	K		vi
ACKNO	WLE	DGEMENT	viii
TABLE	OF CO	DNTENTS	ix
LIST OF	TAB	LES	xi
LIST OF	' FIGU	JRES	xii
LIST OF	ABB	REVIATIONS	xiv
СНАРТИ	ER 1 I	NTRODUCTION	1
	1.1	Background	1
	1.2	Problem Statement	4
	1.3	Objective	5
	1.4	Scope of Project	5
СНАРТИ	ER 2 I	ITERATURE REVIEW	6
	2.1	Lithium-Ion Battery	6
	2.2	Phospho-olivine LiMPO4 compound (M = Fe, Mn, Co, or Ni)	7
	2.3	Cathode Material Improvement	8
	2.4	Carbon Coating	9
	2.5	Coating Material Source	10
	2.6	Coating Method	11
	2.7	Characterization	14
		2.7.1 XRD	15
		2.7.2 FTIR	18
		2.7.3 FESEM, SEM and EDX	19
		2.7.4 Raman Spectroscopy	20
	2.8	Summary of Literature Review	22
СНАРТИ	E R 3 N	IETHODOLOGY	24

ix

3.1	Introduction	24
3.2	Project Workflow	25
3.3	Synthesize Carbon Coated LiMnPO4 samples	27
3.4	Characterization of Carbon-coated LiMnPO4 samples	29
CHAPTER 4 R	RESULTS AND DISCUSSION	31
4.1	XRD	31
4.2	Raman Spectroscopy	33
4.3	FESEM and EDX	35
4.4	Effects of Carbon Coating and its Coating Method LiMnPO ₄	on 42
4.5	Potential Samples Characteristics Contributing to Enhance	ced
	Electrochemical Performance	46
CHAPTER 5 C	CONCLUSION AND RECOMMENDATIONS	49
NN 5.1	Conclusions	49
.5.2 مارك	Recommendations for Future Study	50
REFERENCES		51
APPENDIX A		62
APPENDIX B		63
APPENDIX C		64
APPENDIX D		65
APPENDIX E		66

LIST OF TABLES

Table 2.1 Advantages and disadvantages of various synthesis techniques	12
Table 3.1 Samples Details	26
Table 4.1 Average Crystallite Size	32
Table 4.2 Summary of FESEM morphology of all samples	44



UNIVERSITI TEKNIKAL MALAYSIA MELAKA

LIST OF FIGURES

Figure 1.1 The Basic demonstration of LIB	4
Figure 2.1 Postmortem analysis of NMC622; (a) X-ray Diffractometer pattern and (b) FTIR spectra	15
Figure 2.2 XRD diffraction patterns of the $LiMn_xFe_{1-x}PO_4$ (x = 0, 0.02, 0.04, 0.08)	16
Figure 2.3 XRD patterns of the LFMP-A, LFMP-B and LFMP-C materials	17
Figure 2.4 X-ray diffraction pattern	17
Figure 2.5 FTIR spectra of the sample; (a) LMO, (b) LCO, (c) NMC 333, (d) NMC424, (e) NMC442	18
Figure 2.6 FTIR spectra of carbon-coated LiMnPO ₄ material	19
Figure 2.7 SEM and SEM-EDX images of cycled (aged) graphite	20
Figure 2.8 (a) and (b) SEM images of sintered LiFePO ₄ -LATP composite at two magnifications. (c) EDX mapping showing the carbon distribution (bright areas) in the LiFePO ₄ -LATP composite	20
Figure 2.9 Schematic representation of Rayleigh, stokes, and anti-stoke scattering.	21
Figure 2.10 (a) Fourier transform infrared and (b) Raman spectra	22
Figure 3.1 The flowchart shows the entire project workflow.	26
Figure 3.2 Magnetic stirring with heating process	27
Figure 3.3 Sintering process in Furnace	27
Figure 3.4 Grinding process using pestle and mortar	28
Figure 3.5 Bottled with label samples	28
Figure 3.6 XRD testing system: Miniflex 600, Rigaku	29
Figure 3.7 Raman testing system (UniRAM-3500)	29
Figure 3.8 FE-SEM testing system with EDX, S-5000 HITACHI	30
Figure 3.9 Sputter coater (SC77620 Quorum)	30

Figure 4.1 XRD patterns; (a) 0wt% C-LiMnPO ₄ , (b) 5wt% C-LiMnPO ₄ , (c)	
10wt% C-LiMnPO4, (d) 15wt% C-LiMnPO4, (e) 20wt% C-	
LiMnPO ₄	33
Figure 4.2 Raman Spectra patterns; (a) 0wt% C-LiMnPO4, (b) 5wt% C-	
LiMnPO ₄ , (c) 10wt% C-LiMnPO ₄ , (d) 15wt% C-LiMnPO ₄ , (e)	
20wt% C-LiMnPO ₄	34
Figure 4.3 FESEM images; bare LiMnPO ₄	37
Figure 4.4 EDX result; LiMnPO ₄ elemental composition	37
Figure 4.5 FESEM images; 5wt% C-LiMnPO ₄	38
Figure 4.6 EDX result; 5wt% C-LiMnPO ₄ elemental composition	38
Figure 4.7 FESEM images; 10wt% C-LiMnPO ₄	39
Figure 4.8 EDX result; 10wt% C-LiMnPO ₄ elemental composition	39
Figure 4.9 FESEM images; 15wt% C-LiMnPO ₄	40
Figure 4.10 EDX result; 15wt% C-LiMnPO ₄ elemental composition	40
Figure 4.11 FESEM images; 20wt% C-LiMnPO ₄	41
Figure 4.12 EDX result; 20wt% C-LiMnPO ₄ elemental composition	41
Figure 4.13 Graph of Average Crystallite Size of Carbon Coated LiMnPO4 vs	
Carbon Content (wt%)	42

LIST OF ABBREVIATIONS

LIB	Lithium-ion battery
EV	Electric Vehicle
redox	Electrochemical Oxidation-Reduction
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
XRD	X-ray Diffraction Microscopy
FTIR	Fourier-Transform Infrared Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
Cu K-α	Copper K – alpha
FWHM	Full width at half maximum
Ag	Silver metal
CNTs ERS	Carbon nanotubes MALAYSIA MELAKA

CHAPTER 1

INTRODUCTION

1.1 Background

A battery is a device that stores and provides electrical energy through electrochemical reactions. It consists of one or more electrochemical cells, in an enclosed system containing electrodes, electrolytes, and a separator. When a battery is connected to an external circuit, a chemical reaction occurs within each cell, leading to the generation of electric current. The chemical reaction is specifically known as electrochemical oxidation-reduction (redox) reaction where the electrons are transferred from one material to another in an electric circuit. Figure 1. 1 shows the basic demonstration of how the charging and discharging process occurs in lithium-ion batteries (LIB). Batteries can be mainly classified into two categories which are rechargeable and non-rechargeable batteries. Non-rechargeable batteries are mostly used in low-power devices such as watches, remote controls, etc., as they have low C-rates. A rechargeable battery is more suitable for used highpower devices and long-term usage devices or machines such as laptops, power tools, etc.

The development of emerging technologies requires rechargeable batteries to be integrally involved in the process of unlocking new possibilities in technological advancement. The crucial role of the rechargeable battery can be observed in various fields such as electronics, transportation, renewable energy, etc. Various types of rechargeable batteries are used in those fields. The common types of batteries are the lithium-ion battery (LIB), nickel-metal hydride batteries (NiMH), and lead-acid batteries. Lithium-ion battery is the most preferred to be used in electronic devices and electric vehicles because it has high operating voltage, and relatively high capacity (Ramasubramanian et al., 2022) Researchers from worldwide are interested in the olivine-type lithium metal phosphates, LiMPO₄ (M = Fe, Mn, Co & Ni) because it is a promising cathode material for lithium-ion batteries (EL Khalfaouy et al., 2019). The LiMnPO₄ has a theoretical capacity of around 170 mAh g⁻¹ which is similar to LiFePO₄ but higher operating voltage (4.1 vs. Li⁺/Li) than LiFePO₄ material (3.45 V vs. Li⁺/Li) (Bibi et al., 2022).

LiMnPO₄ cathode material has an excellent electrochemical property but it is still facing some issues such as low intrinsic electronic conductivity, Jahn-Teller lattice distortion of Mn³⁺ ions, the surface energy barrier for Li diffusion, meta-stable nature of the delithiated phase (Wani & Suresh, 2021). The lifespan of a battery is often affected by cathode materials that experience surface degradation after extended or frequent cycling (Cheng et al., 2022). To produce high-efficiency LIB, it is important to utilize the maximum energy density of LIB. The energy density of LIBs is often limited by the low electrochemical capacity of cathode materials (<200 mAh g⁻¹) and the poor rate performance of the electrodes (Ramasubramanian et al., 2022). The battery's cathode determines the energy density, capacity, stability, lifespan, and also affects the charging and discharging rate (T. Chen et al., 2023). Therefore, the battery cathode should undergo some enhancement process to overcome those issues that cap the limits of the battery's cathode to achieve its best performance.

The cathode material can be protected by a surface coating which improves the specific capacity, thermal stability, and electrochemical stability of LIB (Z. Chen et al., 2022). (P. Zhang & Liu, 2023) have conducted a study on how carbon coating

affects lithium iron phosphate (LiFePO₄) and found that the carbon coating enhances the electrical conductivity, structural stability, and electrochemical performance of LiFePO₄. The electronic conductivity of LiMnPO₄ can be effectively improved by carbon coating (Han et al., 2022). The improvement in the electrochemical performance of LiMnPO₄ cathode material is possible with conductive carbon coating because it increases the lithium-ion diffusion kinetics and conductivity (Ragupathi et al., 2019). Carbon coating enhances surface electronic conductivity by preventing metal ion dissolution which avoids direct contact with electrolytes and acts as a reducing agent to suppress the oxidation of Mn²⁺ to Mn³⁺ during the sintering process (Nwachukwu et al., 2023). Based on the review of previous studies on the enhancement of LiMnPO₄, it can be seen that carbon coating can improve the rate performance and cycle stability of LiMnPO₄.

The carbon coating layer thickness has an important impact on the performance of cathode materials such as the specific capacity and cycling stability of LIB (Z. Chen et al., 2022). The specific capacity of carbon-coated LiFePO4 with 10 wt% glucose addition is the highest compared to other glucose amounts (0 wt%, 5 wt%, 20wt%) (P. Zhang & Liu, 2023). The hydrothermal method can allow large-scale production of carbon-coated cathode material in a single reaction (T. Chen et al., 2023). The hydrothermal method can be an appropriate choice for producing carbon-coated cathode material that satisfies the high demand for LIB. The optimum amount of coating material will also give the cathode material the best performance. In this project, glucose will be used as the carbon source because it is an eco-friendly, readily available, and inexpensive carbohydrate. Different amounts of glucose will be used to coat LiMnPO4 using the hydrothermal method to find its impact on structural characteristics that reflect its electrochemical properties.



Figure 1.1 The Basic demonstration of LIB (Mahmud et al., 2022)

1.2 Problem Statement

Advances in technology that largely rely on battery power have led to a huge spike in the demand for Lithium-Ion Batteries (LIB). This covers a variety of items, such as renewable energy storage systems, portable electronics, electric cars, and more. Because of their high energy density and adaptability, LIB is the go-to option for a wide range of applications.

One major problem impacting lithium-ion battery performance is cathode deterioration. The two primary causes of this deterioration are high temperatures and structural instability. The cathode material may undergo physical and chemical alterations as a result of a battery's many cycles of charging and discharging and environmental influences. The integrity of the material may be lost due to structural instability, and high temperatures can hasten chemical processes that aid in deterioration.

To create lithium-ion batteries that are incredibly robust, cost-effective, and efficient, it is imperative to overcome the difficulties related to cathode materials. To do this, one must have a thorough grasp of the structural characteristics and synthesis of coated cathode materials. Coating the cathode materials can stabilize them, reduce degradation, and increase overall battery performance. Research and development efforts are concentrated on optimizing the synthesis methods and formulations to attain the required attributes of coated cathode materials.

In conclusion, technical developments are driving the demand for lithium-ion batteries (LIBs). However, to create more efficient and affordable LIBs, issues including cathode degradation, low energy density, and short lifespans must be resolved. To increase the structural stability and general performance of LIBs, researchers are investigating various methods, such as using carbon-coated cathode

1.3 **Objective**

materials.

The objectives of this project are as follows:

- 1. To synthesize carbon-coated LiMnPO₄ cathode materials with different glucose amounts.
 - 2. To study the structural properties of carbon-coated LiMnPO₄ cathode materials.

1.4 Scope of Project

The scopes of this project are:

- 1. To prepare carbon-coated lithium manganese phosphate (LiMnPO₄/C-0, LiMnPO₄/C-5, LiMnPO₄/C-10, LiMnPO₄/C-15, LiMnPO₄/C-20) cathode.
- To perform structural characterization on carbon-coated LiMnPO₄ cathode by using x-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDX).

CHAPTER 2

LITERATURE REVIEW

2.1 Lithium-Ion Battery

Lithium-ion batteries are electrochemical devices widely used as power sources in electronic devices that need to be portable. Lithium-ion batteries are regarded as an important energy storage solution in multiple applications, making advancements in their performance necessary (P. Zhang & Liu, 2023). Fossil fuel consumption impacts the economy of the entire world by causing damage to the ecosystem. Lithium-ion batteries were an alternative option that got attention as they offer high capacity and structural stability compared to other types of batteries (B & M.K., 2022). The growing number of electrochemical energy storage devices operating in extremely low temperatures poses a significant challenge to the existing lithium-ion battery technology. (Yang et al., 2023). The electric vehicle development has been rapidly growing and therefore the requirement for lithium-ion batteries with longer cycle life, higher energy density and better safety performance is rising (Feng et al., 2023). In order to comply with that requirement, the development of lithiumion batteries should have high energy density cathode materials to unlock longer driving range capability, however, lithium-ion batteries commonly operate at high potential and experience surface degradation which affects the performance degradation under extended cycling (Cheng et al., 2022). Other than that, lithium-ion batteries are in demand due to technological advancements in the electronics industry, and thus expanding the battery supply chain with improved electrochemical performance is an important thing (Ramasubramanian et al., 2022). The olivine-type lithium metal phosphates, LiMPO₄ (M = Fe, Mn, Co & Ni), have attracted the interest of many researchers from all around the world because it is a promising cathode material for lithium-ion batteries and it results in their various studies conducted to unleash a new possibility (Wani & Suresh, 2021). The energy density of a lithium-ion battery is mainly influenced by the specific capacity of the cathode material and that is the key factor determining the usage time of battery-powered devices such as range of electric vehicles (B. Wang et al., 2021).

2.2 Phospho-olivine LiMPO4 compound (M = Fe, Mn, Co, or Ni)

In 1997, Goodenough proposed that olivine-type LiMPO₄ ($M = \frac{1}{4}$ Fe, Mn) materials are suitable to be a cathode material for lithium-ion batteries, and phosphate materials have drawn extensive attention of researchers (Padhi et al., 1997; Xie et al., 2021). Most of the compounds of the phospho-olivine type LiMPO₄ (M = Fe, Co, Ni, and Mn) have been studied in-depth after the discovery of LiFePO₄ in order to build an optimized and promising cathode material with improved electrochemical properties (Ragupathi et al., 2019). The phospho-olivine type $LiMPO_4$ (M = Fe, Co, Ni, and Mn) has considerably many advantages as compared to other layered oxides, $LiMO_2$ (M = Co, Ni) (L. Wang et al., 2022). Compared to other members of olivine phosphate family, LiMnPO₄ is a good choice for high structural stability and high energy density cathode material for lithium-ion batteries as it can offer higher operational voltage (4.1 V vs. Li/ Li⁺) than LiFePO₄ material (3.45 V vs. Li/Li+), even though they have similar capacity and exhibits a theoretical energy density of 700 Whkg⁻¹ (J. Zhang et al., 2021). LiMnPO₄ also has more safety features due to the presence of a strong P-O covalent bond, but, low ionic and electronic conductivities (Nwachukwu et al., 2023). Lithium manganese phosphate, LiMnPO₄ has 20% higher redox potential than LiFePO₄ and it makes consideration of LiMnPO₄ cathode material to be the replacement of LiFePO₄ for lithium-ion hybrid batteries (Han et al., 2022; Sharmila & Parthibavarman, 2021). LiMnPO₄ have drawbacks such as worse electrode kinetics due to extremely low electrical conductivity and lithium-ion diffusion rate (Han et al., 2022). Another structural weakness that affects LiMnPO₄ is the Jahn-Teller effect and mechanical degradation (Nwachukwu et al., 2023). Jahn-Teller effect is a collapse of the cathode material's structure that results in capacity fade during cycling (Z. Chen et al., 2022; Wani & Suresh, 2021; Xie et al., 2021).

2.3 Cathode Material Improvement

The cathode material is the main component of a lithium-ion battery because it absorbs lithium-ion during the discharging process, and its characteristics greatly impact the battery's performance (Mahmud et al., 2022). Cathode materials are essential in determining the lithium-ion battery's overall performance because its capacity, energy density, and stability rely on it (T. Chen et al., 2023). When the charging-discharging process occurs, structural deterioration happens mainly due to the unstable structure of the cathode material. Accordingly, different modifications have been widely employed to improve structural stability, such as microstructure design, surface engineering, and element doping (Feng et al., 2023)Particle agglomeration should be avoided in the cathode material morphology because it affects the cathode materials' transfer resistances (Rct) by providing irregular accessibility for Li+ insertion or extraction(Patil et al., 2019).

The energy density of lithium-ion batteries is often capped by the poor electrochemical capacity of the cathode materials. Therefore, carbon materials can be employed to improve their cyclic stability and specific capacity (Ramasubramanian et al., 2022). The surface coating of cathode material is a common and effective method to eliminate cathode material degradation and increase the cycling performance of lithium-ion batteries (Cheng et al., 2022). The cathode material must be structurally stable to intercalate or deintercalated lithium ions frequently. It requires a high electronic conductivity to maintain high-rate capacity or high-power density (Wani & Suresh, 2021). Improving the operation potential of lithium-ion cathode material is a popular strategy to enhance the cell voltage and, thus, the power of batteries and specific energy (Kasnatscheew et al., 2019). The improvised electrochemical performance may be accredited to these three aspects: (i) The crystal size minimization reduces the transfer distance of Li⁺ ions and improves the specific surface area (ii) Carbon coating can significantly increase the electronic conductivity, broadens the interface between LiMnPO4 nano-crystallites and also may decrease the activation energy of migrating Li⁺ ion which enhances the ionic conductivity. (iii) The negative impact of detrimental defect areas on Li⁺ ions (Han et al., 2022).

2.4 Carbon Coating

Surface modification has been proven to be a cost-effective solution and applicable method for increasing the cathode material of lithium-ion battery's performance with the alteration of the physiochemical properties or producing a protective layer to reduce the excessive interaction between the electrodes and the electrolyte (Pratheeksha et al., 2019; Ramasubramanian et al., 2022). Carbon materials have drawn significant attention because they provide a larger surface area, strong heat resistance, high electrical conductivity, and high structural integrity, enhancing lithium-ion batteries' performance (Liu et al., 2019). The result of specific

capacity highlights the positive influence of carbon coating, where the sample with 10 wt.% glucose exhibits significant enhancements compared to 0 wt%, 5 wt%, and 20 wt %, indicating an optimized electronic conductivity and Li⁺ ion diffusion kinetics (P. Zhang & Liu, 2023). The nanostructure, amorphous carbon, and 6 nm ultra-thin carbon coating of carbon-coated lithium vanadium phosphate (LiVPO₄) have been discovered to contribute to exceptional electrochemical performance (Yang et al., 2023). Carbon coating may curb undesirable side reactions, facilitate improved electrochemical performance, reduce the electrode materials' chargetransfer impedance, and enhance cathode materials' conductivity and electrochemical properties (Z. Chen et al., 2022; Xie et al., 2021). Particularly at high temperatures, the carbon-coated lithium-ion phosphate (LiFePO₄) reduces this passivation and mitigates against iron dissolution (Liu et al., 2019; L. Wang et al., 2022). Furthermore, the carbon coating lessens the ions' breakdown into electrolytes, confirming that the carbon coating significantly improves the electrodes' performance (Sharmila & Parthibavarman, 2021). The carbon layer coating on the surface of LiMnPO₄ crystallites can improve the poor electrical conductivity of bare LiMnPO₄ and rapidly grow the electrochemical activity (Han et al., 2022).

2.5 Coating Material Source

Carbon can be obtained from multiple sources, such as carbon nanotubes, polymer, graphene, glucose, and sucrose (Z. Chen et al., 2022). Variations in carbon's chemical origins and structures lead to distinct features that influence electrochemical and interfacial interactions (Ramasubramanian et al., 2022). Since glucose is an inexpensive and widely accessible substance, it may be used as a carbon source (P. Zhang & Liu, 2023). The characteristics of the carbon-coated

cathode material are mostly determined by the selected carbon source; the cathode materials should be inexpensive, nontoxic, and simple to handle and synthesise (Wani & Suresh, 2021). The lithium iron manganese phosphate matrix material's low conductivity was successfully resolved using an organic carbon source, and more significantly, the environment depends on using greener synthetic procedures (Xie et al., 2021).

2.6 Coating Method

Several preparation methods have been employed to prepare LiMnPO₄ cathode material, such as spray pyrolysis, polyol process, a sol-gel technique, hydrothermal synthesis, and solid-state method (Wani & Suresh, 2021). The lithium iron phosphate (LiFePO₄), which was coated with an organic carbon layer using the hydrothermal technique, has an evenly distributed layer of carbon coating through a regulated synthesis process (P. Zhang & Liu, 2023). The consistently distributed carbon layer can provide a good interface between the active particles' surfaces, increasing the particles' surface conductivity (Yang et al., 2023). Even though adding a carbon layer may improve the conductivity of lithium iron phosphate, too excessive or thick carbon may resist the Li^+ ion transport (Ramasubramanian et al., 2022). Furthermore, carbon layer thickness is one of the most important factors affecting lithium-ion batteries' specific capacity and cycling stability (Z. Chen et al., 2022). The sol-gel method can effectively synthesize carbon-coated LiMnPO₄ cathode material (Bibi et al., 2022). The temperature of the heating treatment process or calcination process must be considered because it influences the morphologies, the quality of carbon coating, and the electrochemical properties (Huynh et al., 2019; Välikangas et al., 2020). Researchers have highlighted the synthesis procedure as critical to managing the material's size and shape, leading to higher electrochemical performance, among the tactics used to increase the rate performance of LiMnPO₄ cathode material (Nwachukwu et al., 2023). Various conventional methods are utilized for synthesizing the LiMnPO4 cathode material, including spray pyrolysis, polyol process, sol-gel, and solution combustion (EL Khalfaouy et al., 2019). Based on Table 2.1, the sol-gel method allows the synthesis of LiMnPO₄ with a regulated process, which is essential to meeting the optimized production conditions.

Synthesis Method	Advantages	Disadvantages
Sol-gel	• Simplest, cheap, reliable, •	Relatively longer
	reproducible and the reaction	reaction time which
	is controllable from its	increases the cost of
	beginning.	fabrication.
	• Produces powders with •	It is impossible to attach
	precise stoichiometry control,	a thick layer of
	high purity, uniform structure	nanoparticles to the
	and very small size.	substrate.
	• Films are easily anchored on	
	the substrate bearing the	
	complicated shapes and large	
	surface area.	
	• It enables synthesis at a low	
	temperature.	
	• It enables small quantities of	
	dopants to be introduced in	
	the solvent and end up	
	uniformly dispersed in the	

final product.

• It is easy to perform in the laboratory.

Hydrothermal/	The ability to synthesize • High cost of equipment.
Solvothermal	substances that are unstable • Safety issues during the
	when close to the melting reaction process.
	point.
•	The ability to produce large
	crystals of high quality.
WALAYSIA MA	Precise and easily adjust the
	size, shape distribution, and
	crystallinity of the final
	product by regulating the
	parameters, such as reaction
	temperature, reaction time,
	solvent type, surfactant type,
	and precursor type.
INIVERSITI TE	Highly homogeneous nanoparticles can be
	obtained.
Solid-State •	Solid-state reactions are • Hard to control particle
	exothermic, efficient, and growth.
	scalable. Solvent-free. • Less homogeneity of
•	Low cost, process simplicity. products.
•	Conventional method for • High Temperature is
	large-scale production in less required.
	time.
•	Smaller size products.
•	Eco-friendly.

Spray Pyrolysis • Spray pyrolysis is cost- • Coatings are not uniform

	effective.	in thickness.
•	Operates at atmospheric	
	pressure, well-controlled	
	stoichiometry and	
	homogeneity.	
•	Films deposit over large	
	surface area, low operational	
	cost, purity of products.	
•	Spray pyrolysis deposition	
	leads to relatively uniform	
	and high-quality coatings.	
·	No high temperatures are	
	required during processing	
	(up to 500°C).	
· .	Films deposited by spray	
	pyrolysis are reproducible,	
	giving it potential for mass production.	
	Low processing temperature.	

2.7 Characterization

The characterization of lithium iron phosphate (LiFePO₄) cathode material has been utilizing scanning electron microscopy (SEM), and X-ray diffraction analysis XRD, to identify the electrochemical improvement of the cathode material (P. Zhang & Liu, 2023). The cathode material's structural conformity can be conducted using XRD and Fourier transform microscopy (FTIR) (Kumar et al., 2021). The structural degradation can be found through both XRD or FTIR analysis and it can be observed in Figure 2.1 where cycled cathode material causes the formation of Li₂CO₃ (Nisa et al., 2022).



Figure 2.1 Postmortem analysis of NMC622; (a) X-ray Diffractometer pattern and (b) FTIR spectra (Nisa et al., 2022).

2.7.1 XRD

The crystal structure of the cathode material can be detected by X-ray diffraction (XRD) with Cu K-a radiation, and the produced XRD patterns can assist in confirming that the addition of carbon does not alter the ideal crystal structure (P. Zhang & Liu, 2023). Based on an XRD pattern of a cathode material LiFePO₄, which is displayed in Figure 2.2, the sharp peaks indicate a good crystallinity of the material, and all of the diffraction peaks match with pure LiFePO₄ PDF card (JCPDS Card No.40-1499), showing that the cathode material is an ordered olivine structure indexed to orthorhombic with a space group of Pnma (Yang et al., 2023). XRD testing is required to identify the structure and phase of the cathode material of lithium-ion batteries (Kumar et al., 2021). According to Figure 2.3, the diffraction peak of the three samples is basically identical and completely directed to the LiMnPO₄ orthorhombic olivine structure standard card (JCPDS: 33-0804) (Xie et al., 2021). Moreover, XRD testing is essential to know the purity of the synthesized electrode samples (Sharmila & Parthibavarman, 2021). For example, Figure 2.4 shows the characteristic peaks of (020), (011), (120), (111), (121), (131), (211) and (222) planes, which aligned perfectly with the JCPDS file no. 74-0375 with no other

additional or secondary peaks observed in the XRD patterns, revealing the high purity of the lithium manganese phosphate (LiMnPO₄) material (Ragupathi et al., 2019). XRD pattern also assists in identifying the structural properties of coating material (Sanchez et al., 2021). Furthermore, an XRD pattern with a narrow halfpeak width and strong diffraction peaks means the high crystallinity of synthesized materials (J. Zhang et al., 2021).



Figure 2.2 XRD diffraction patterns of the $LiMn_xFe_{1-x}PO_4$ (x = 0, 0.02, 0.04, 0.08) (Han et al., 2022)





2.7.2 FTIR

Certain vibrational modes of molecules, such as those found in modern lithium-ion battery's cathode material are unique and it represented by a specific absorption band in infrared (IR) spectra. Therefore, Fourier-transform infrared spectroscopy (FTIR) is utilized to analyze the lattice dynamics of the as-prepared lithium-ion battery's cathode material (Kumar et al., 2021). Furthermore, the study on quick charging batteries can be performed with FTIR because it can make fast measurements (Meyer et al., 2021). FTIR spectrum analysis can find any presence of anionic impurities on the surface of cathode material samples and based on figure 2.5 it displays the presence of carbonate compound (~900/cm and ~1400/cm) (Nisa et al., 2022). FTIR can be utilized to identify phosphate functional group (Lv et al., 2020). Figure 2.6 shows the FTIR spectra of carbon-coated LiMnPO4 material and the presence of the PO4³⁻ group can confirmed with the FTIR band at 989, 1068 and 1137 cm⁻¹ which corresponds to the asymmetric stretching P-O vibration in the PO4 group (Ragupathi et al., 2019).



Figure 2.5 FTIR spectra of the sample; (a) LMO, (b) LCO, (c) NMC 333, (d) NMC424, (e) NMC442 (Nisa et al., 2022).



Figure 2.6 FTIR spectra of carbon-coated LiMnPO₄ material (Ragupathi et al., 2019).

2.7.3 FESEM, SEM and EDX

An analysis of the materials' microstructure and elemental composition can be done with a scanning electron microscopy (SEM) (Sharmila & Parthibavarman, 2021). SEM analysis discovers the fine and uniform particle sizes which correlate to the increased contact area and advancement in electrochemical interfaces (P. Zhang & Liu, 2023). Alternatively, aged graphite-based electrodes (after 100 cycles) are visualized with SEM under inert circumstances and shown in Figure 2.7 to demonstrate the existence of Li metal dendrites (Klein et al., 2021). Combining Energy Dispersive X-ray analysis (EDX) with Scanning Electron Microscopy (SEM) is used to examine the cathode material's microstructure, recognize phases, and display the distribution of carbon particles on cathode materials, as seen in Figure 2.8, which affects the cathode material's electrochemical characteristics (Ihrig et al., 2022). The Field Emission Scanning Electron Microscope (FESEM) is an instrument that provides a wide variety of information from the sample surface, similar to the

SEM, but with higher resolution and a much greater energy range (Lewczuk & Szyryńska, 2021).



Figure 2.8 (a) and (b) SEM images of sintered LiFePO₄-LATP composite at two magnifications. (c) EDX mapping showing the carbon distribution (bright areas) in the LiFePO₄-LATP composite (Ihrig et al., 2022).

2.7.4 Raman Spectroscopy

Raman spectroscopy is a non-destructive spectroscopic technique to analyze a material. Nobel laureates Chandrasekhara Venkata Raman (Raman, 1953) and Grigorij Samuilovič Landsberg (Landsberg, 1928) independently developed Raman spectroscopy in the first half of the 20th century. However, it was not formally

established until the second half of the century when laser light-equipped spectrometers were introduced (Hendra & Stratton, 1969; Platonenko, 1964). In addition to its historical and scientific background, the Raman effect offers various sophisticated techniques for studying the physics and chemistry of molecules in different physical systems, depending on their specific utility and requirements. Figure 2.9 illustrates the characteristic shift (Stokes and anti-Stokes) observed in the scattering medium, and the corresponding Stokes (anti-Stokes) lines provide valuable insight into the system's vibration modes (Rambadey et al., 2023).

Raman spectroscopy can be utilized to investigate phosphate materials (Lv et al., 2020). Both internal and exterior modes can express olivine vibrations in this way. The vibrational modes of PO_4^{3-} anions are sensitive to the presence of lithium ions in the crystal structure. Raman spectroscopy may be used to monitor the process of lithium intercalation and deintercalation into the olivine structure.



Figure 2.9 Schematic representation of Rayleigh, stokes, and anti-stoke scattering.


Figure 2.10 (a) Fourier transform infrared and (b) Raman spectra

2.8 Summary of Literature Review

A lithium-ion battery is the best option for an electrochemical energy storage system and power source because of its many good qualities, including lightweight, high power and energy density, high current discharge, and extended service life (Cheng et al., 2022). The energy density of lithium-ion batteries is often capped by the poor electrochemical capacity of the cathode materials. Therefore, carbon materials can be employed to improve their cyclic stability and specific capacity (Ramasubramanian et al., 2022). Carbon coating may effectively curb undesirable side reactions, facilitate improved electrochemical performance, reduce the electrode materials' charge-transfer impedance, and enhance the conductivity and electrochemical properties of cathode materials (Z. Chen et al., 2022; Xie et al., 2021). Furthermore, carbon layer thickness is one of the most important factors that affect the specific capacity and cycling stability of lithium-ion batteries (Z. Chen et al., 2022). Therefore, different amounts of glucose will be used to find an optimized

coating material with the best physiochemical properties and electrochemical performance. The cathode material's structural conformity can be conducted using XRD (Kumar et al., 2021) and Raman Spectroscopy. The Field Emission Scanning Electron Microscope (FESEM) provides high-resolution imaging and a broader energy range compared to the SEM(Lewczuk & Szyryńska, 2021). Therefore, FESEM will be used in this project for better results. Moreover, the combination of energy-dispersive X-ray analysis (EDX) with field emission scanning electron microscopy (FESEM) is used to examine the cathode material's microstructure, recognize phases, and display the distribution of carbon particles on cathode

materials.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The method employed to perform the synthesis of carbon-coated LiMnPO₄ in powder form is a sol-gel method. The sol-gel method allows the synthesis of LiMnPO₄ with a regulated process, which is essential for finding the optimized condition to produce it (Wani & Suresh, 2021). The obtained dry gel will be grounded to improve the distribution of carbon coating further (Z. Chen et al., 2022). Based on a study conducted on lithium iron phosphate (LiFePO₄), the weight percentage of glucose from 0 wt.%, 5 wt.%, 10 wt.%, and 20 wt.% has been used to find the carbon coating effect, and the result shows the sample with 10 wt.% exhibits the best structural characteristic (P. Zhang & Liu, 2023). This project will use the same approach to find a suitable carbon coating for the LiMnPO₄ cathode material. Then, the obtained samples will be calcined at 300°C because a previous study has found that the best electrochemical performance was shown by LiMnPO₄ calcined at the temperature of 700°C for 3 hours (Wani & Suresh, 2021). After the calcination process, the samples are ready for the characterization process to discover their physical properties, which reflect their electrochemical properties. XRD, FTIR, and SEM with EDX will be utilized for the characterization process. The cathode material's structural conformity can be determined using XRD and Raman spectroscopy. The microstructure of cathode material and distribution carbon coating can be analyzed using FESEM with EDX. The result of the characterization process will then be used to analyze its structural properties, which reflect its electrochemical properties.

3.2 **Project Workflow**

This project starts by reviewing the topic-related study material to obtain appropriate insight into this project and valid data to solve and achieve the objective of this project based on the problem statement. Figure 10 shows the flowchart of the entire project's workflow. The literature review mainly focuses on lithium-ion batteries or, more specifically, on lithium manganese phosphate (LiMnPO₄) cathode material. After a proper literature review has been done, it will be a guide to prepare the carbon-coated LiMnPO₄ cathode material. A prefabricated LiMnPO₄ precursor will be used to do carbon coating. The carbon coating will be done with different amounts of coating material, as shown in Table 2, where every sample contains 2 g of LiMnPO4 precursor, and the glucose amount depends on the weight percentage (0 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%). After all samples are synthesized, they will undergo a characterization process where XRD, FTIR, and SEM with EDX will be used to find the structural properties of the samples. If any irrelevant result is obtained, such as impurities in the prepared sample, the carbon coating process will be repeated with an improved experimental procedure until relevant data is produced. The appropriate result will be the green light to analyze and identify the effects of carbon-coating on LiMnPO₄ cathode material. After completing all the above tasks, a report with all in-depth details can be written.

25



Figure 3.1 The flowchart shows the entire project workflow.

Wt.% of Glucose	Amount of Glucose (g)	Amount of LiMnPO ₄ (g)
0	0	2
5	0.1053	2
10	0.2222	2
15	0.3529	2
20	0.5	2

Table 3.1 Samples Details

3.3 Synthesize Carbon Coated LiMnPO₄ samples

a) Sol-Gel Method:



Figure 3.2 Magnetic stirring with heating process

The sol-gel method dissolves glucose in distilled water under magnetic stirring at 90°C. To serve as the carbon source, glucose is added to this solution in varying amounts (0wt%, 5wt%, 10wt%, 15wt%, and 20wt%). Then, the LiMnPO₄ precursor is gradually added under continuous magnetic stirring. After a wet gel is formed, it is dried at 180°C until it yields a powder.

b) Sintering:



Figure 3.3 Sintering process in Furnace

All samples were sintered separately in a furnace at 700°C for 3 hours. Subsequently, each sample was allowed to cool down in the furnace overnight, undergoing a slow cooling process.



Figure 3.5 Bottled with label samples

Post-sintering, the samples are ground using a pestle and mortar to achieve fine powders. Later, all samples were labelled and kept in an air-tight container with a desiccant to avoid moisture absorption.

3.4 Characterization of Carbon-coated LiMnPO₄ samples

a) X-ray Diffraction (XRD):



Figure 3.6 XRD testing system: Miniflex 600, Rigaku

X-ray diffraction (XRD; Miniflex 600, Rigaku) testing was performed on all samples using Cu K α radiation of 0.15406 nm at a scan rate of 0.05° s⁻¹ in the 2 θ angular (5°–80°). The used machine is shown in the



Figure 3.7 Raman testing system (UniRAM-3500)

Raman spectra were recorded on a Raman Microscope (UniRAM-3500, Micro Raman system) using a 532 nm laser excitation. c) Field Emission Scanning Electron Microscopy (FESEM):



Figure 3.8 FE-SEM testing system with EDX, S-5000 HITACHI



Figure 3.9 Sputter coater (SC77620 Quorum)

The samples' particle morphology and microstructure were examined using field emission scanning electron microscopy (FE-SEM, S-5000 HITACHI) at an accelerating voltage of 5.0 kV. Before imaging with FE-SEM, the samples were coated with silver (Ag) using a sputter coater (SC77620 Quorum). The elemental composition has also been documented using EDX.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 XRD

X-ray diffraction (XRD; Miniflex 600, Rigaku) testing was performed using Cu K α radiation of 0.15406 nm at a scan rate of 0.05° s⁻¹ in the 20 angular (5°–80°). The powder X-ray diffraction testing has been carried out to characterize the structure and crystallite size of the cathode material, LiMnPO₄ samples with different carbon coating amounts (0wt%, 5wt%, 10wt%, 15wt%, 20wt%). The XRD patterns of the samples are plotted using graphing software (OriginPro, 2019b) presented in Figure 4.1. The diffraction peaks in the five samples perfectly match JCPDS PDF card 33-0804, which assigned the materials as an ordered olivine structure indexed to orthorhombic with the Pnma (62) space group (Xie et al., 2021). No peaks of the impurities are detected in the XRD patterns (Sharmila & Parthibavarman, 2021). In addition, there are no peaks corresponding to carbon signals because the carbon may exist in the amorphous state in all samples (Ragupathi et al., 2019). Comparing the differences in peak intensity at specific positions.

The 5wt% carbon-coated LiMnPO₄ sample has high intensity and sharp peaks compared to the other samples. According to the Scherrer equation, it shows that the crystallite size is larger than that of the other samples. The crystallite size is an important property that determines the electrochemical performance of the cathode material because a small crystallite size reduces charge transfer resistance (R_{ct}) by providing a larger surface area (Moazzen et al., 2020). Therefore, the XRD pattern was utilised to calculate the crystallite size of the samples using the Scherrer equation (Equation 4.1) (Disha et al., 2024; Ronduda et al., 2020).

Equation 4.1: Scherrer's Equation

 $D=\frac{k\lambda}{\beta_{hkl}\cos\theta_{hkl}}$

D =	Crystallite size, nm
k =	Shape factor
$\lambda =$	X-ray Wavelength
$\beta_{hkl} =$	Half-width of the diffraction band (FWHM)
	radians
$\theta_{hkl} =$	Bragg – diffraction angle at peak, radians

For that, the Full width at half maximum (FWHM) of peaks found on the XRD pattern is determined. The FWHM value and diffraction angle of the peak are then substituted into Equation 4.1 to obtain the crystallite size. The multiple crystallite sizes are used to find the average crystallite size of the material, as shown in Table

Table 4.1 Average Crystallite Size				
4.1.				
4 1				

Samples	Average Crystallite Size (nm)
0wt% C – LiMnPO ₄	44
$5wt\% \ C - LiMnPO_4$	73
10wt% C – LiMnPO ₄	48
15wt% C – LiMnPO ₄	45
20wt% C – LiMnPO ₄	58



Figure 4.1 XRD patterns; (a) 0wt% C-LiMnPO₄, (b) 5wt% C-LiMnPO₄, (c) 10wt% C-LiMnPO₄, (d) 15wt% C-LiMnPO₄, (e) 20wt% C-LiMnPO₄.

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4.2 Raman Spectroscopy

Raman spectra were recorded on a Raman Microscope (UniRAM-3500, Micro Raman system) using a 532 nm laser excitation. Raman spectroscopy was utilized to investigate phosphate materials (Sanchez et al., 2021) and identify the presence of impurities (Kong et al., 2020). Herein, olivine vibrations can be expressed in internal and external modes. The observed internal modes resemble PO₄ tetrahedron oscillations, whereas external modes correspond to Li⁺, Mn²⁺, and PO₄³⁻ ions. The vibrational mode and frequency band corresponding to the phosphate functional group were determined by referring to the Raman spectra of the previous study. The Raman spectra data are plotted using graphing software (OriginPro,

2019b) and presented in Figure 4.2. Based on the plotted Raman spectra, the intramolecular symmetric vibrations of the PO_4^{3-} anion, or the A_g mode of v_1 , are responsible for the sharp band seen at 950 cm⁻¹, while the two weaker bands at 1010 cm⁻¹ and 1070 cm⁻¹ are associated with the PO_4^{3-} anion's asymmetric stretching modes (v_3) (Jenkins et al., 2021). The symmetric A_gv_2 mode also has a wide peak at 438 cm⁻¹, which can be observed clearly in all samples but is almost unnoticeable in the bare sample. The remaining 590 cm⁻¹ and 625 cm⁻¹ peaks correspond to symmetric A_gv_4 modes (EL Khalfaouy et al., 2019). The Raman spectra have no other peaks that may represent impurity (Kong et al., 2020).



Figure 4.2 Raman Spectra patterns; (a) 0wt% C-LiMnPO₄, (b) 5wt% C-LiMnPO₄, (c) 10wt% C-LiMnPO₄, (d) 15wt% C-LiMnPO₄, (e) 20wt% C-LiMnPO₄.

4.3 **FESEM and EDX**

The particle morphology and microstructure of the samples were examined using field emission scanning electron microscopy (FE-SEM, S-5000 HITACHI) at an accelerating voltage of 5.0 kV. Before imaging with FE-SEM, the samples were coated with silver (Ag) using a sputter coater (SC77620 Quorum). A conductive coating is required to prevent specimen charging when using an electron beam for FESEM imaging. The deposition process with Ag nanomaterial does not alter the morphological integrity of the cathode materials (Valerini et al., 2021). The FESEM images of all samples, 0wt% C-LiMnPO₄, 5wt% C-LiMnPO₄, 10wt% C-LiMnPO₄, 15wt% C-LiMnPO₄, and 20wt% C-LiMnPO₄ are shown in Figure 4.3, Figure 4.5, Figure 4.7, Figure 4.9, and Figure 4.11 respectively. Every sample has been observed at three magnification levels: x5000, x10,000, and x30,000. The elemental composition has also been documented using EDX. Based on morphological analysis performed on the bare sample, LiMnPO₄ exhibits particles with irregular sizes measuring up to 1.5µm. The particles show grain boundaries at x30,000 magnification, indicating nanoscale crystallite sizing. The primary particles are uniformly dispersed and clustered to form micro-sized secondary particles. Many nanoparticles are also present and have agglomerated with microparticles, forming an unevenly distributed secondary particle. The morphology of 5wt% carbon-coated LiMnPO₄ has a very high crystallinity structure. A combination of quasi-spherical and irregular shape particles is formed in this sample. This sample may have a large crystallite size as a small quantity of nanoparticles can be observed, mostly microparticles sizing up to 1.3µm. Almost single crystalline morphology may have formed with micron-sized primary particles with evenly distributed nano-sized crystallite and fewer defects such as grain boundaries.

The prepared 10wt% carbon-coated LiMnPO₄ particles exhibit a wide size distribution, which forms non-uniformity in the particle size distribution. The micron-sized particles measure up to 1.8µm. Most of the particles exhibit irregular particle shape. This sample's morphology depicts the agglomeration between major microparticles and a few nanoparticles. The microparticles have high crystallinity, a smooth surface, and almost no grain boundaries visible at a high magnification level, x30,000.

For 15wt% carbon-coated LiMnPO₄, the FESEM images show a non-uniform particle size distribution and irregularly shaped particles. The nanoparticles agglomerate together with microparticles. The microparticle has a size measuring up to 1.6µm. Some micron-sized particles have visible grain boundaries, which depicts an aggregation of nanoparticles that have formed it, but certain micron-sized particles have high crystallinity with smooth surfaces. Overall, this sample may have been dispersed on average by nanoscale crystallite size.

UNIVE The sample, 20wt% carbon-coated LiMnPO₄, shows a morphology with wide rage particle size distribution and irregular particle shape. The nanoparticles appearing on the surface of the microparticles showing agglomeration has happened. Meanwhile, the microparticles seem to be formed by aggregation of smaller microparticles. The smaller microparticle may have nanosized crystallite because the grain boundaries are visible at a high magnification level.

The Energy-dispersive X-ray spectroscopy (EDX) analysis confirms the purity of all samples, with no impurities detected. This thorough morphological and compositional evaluation underscores the varied structural characteristics induced by different carbon coatings on LiMnPO₄, which may significantly impact the material's performance in practical applications.



Figure 4.3 FESEM images; bare LiMnPO₄



Figure 4.4 EDX result; LiMnPO₄ elemental composition



Figure 4.5 FESEM images; 5wt% C-LiMnPO₄



Figure 4.6 EDX result; 5wt% C-LiMnPO₄ elemental composition



Figure 4.7 FESEM images; 10wt% C-LiMnPO₄



Figure 4.8 EDX result; 10wt% C-LiMnPO₄ elemental composition



Figure 4.9 FESEM images; 15wt% C-LiMnPO₄



Figure 4.10 EDX result; 15wt% C-LiMnPO₄ elemental composition



Figure 4.11 FESEM images; 20wt% C-LiMnPO₄



Figure 4.12 EDX result; 20wt% C-LiMnPO₄ elemental composition

4.4 Effects of Carbon Coating and its Coating Method on LiMnPO₄

The impact of carbon coating on LiMnPO₄ was examined in terms of morphology and crystallite size in each sample, as it was found to influence the cathode material in previous studies (Han et al., 2022; P. Zhang & Liu, 2023). Moreover, this analysis is crucial for evaluating the effectiveness of the coating technique and understanding the advantages of carbon coating on the structural properties of the cathode material, LiMnPO₄.

The XRD results indicate that all samples exhibit an orthorhombic olivine structure (JCPDS: 33-0804). This suggests that the presence of carbon or the carbon coating method did not alter the structure of LiMnPO₄. Additionally, the carbon content may be too low or exist in an amorphous form, which could explain why no diffraction peaks corresponding to carbon are observed in the XRD pattern (Ragupathi et al., 2019). By using Scherrer's equation, the average crystallite size was found to change when the amount of carbon changes in LiMnPO₄, as shown in

the Figure 4.13. TEKNIKAL MALAYSIA MELAKA



Figure 4.13 Graph of Average Crystallite Size of Carbon Coated LiMnPO₄ vs Carbon Content (wt%)

The 5wt% carbon coating yielded the largest crystallites (73 nm). This may have happened due to increased thermal stabilization that happens after molten glucose causes large particle agglomeration and promotes particle growth(Henriksen et al., 2020). A low carbon content may not be enough to encapsulate the particles uniformly and act as a barrier that controls particle growth. When the carbon uniformly coats the surface of the particles, it can effectively prevent particle growth (Liu et al., 2020; P. Zhang & Liu, 2023). Therefore, as the carbon content increases beyond this point, it may be enough for uniform coating and act as a barrier restricting crystallite growth, resulting in smaller crystallites. This is evident in the decreased crystallite sizes for the 10wt% and 15wt% samples. However, at 20wt% carbon, the crystallite size increases again (58 nm), likely due to particle aggregation and complex interactions during sintering. The existence of carbon may also affect samples' cooling rate after sintering, which influences particle growth. This may indicate that adding carbon to LiMnPO₄ can influence crystallite size due to its thermal stability and the resulting effects on heat distribution during the sintering and cooling process of samples after sintering. For samples exhibiting smaller crystallite size, the sufficient glucose amount as the carbon source melts during sintering, and the molten glucose flows and tries to adhere to the precursor's surface. Carbon coating may be a physical barrier between the particles or crystallite (Sim et al., 2020). Therefore, after carbon decomposition occurs, the particle surface is coated, and particle growth is effectively prevented. However, different carbon coating content may cause different impacts based on its coat uniformity. Mechanical processing, such as grinding with a pestle and mortar, can also affect the shape and size of particles, resulting in uneven particles due to the lack of control over applied mechanical energy (Pagola, 2023). Therefore, effective grinding methods, such as ball milling, should be employed for uniform particle size distribution (Jaafar et al., 2024; Nwachukwu et al., 2023). The right amount of carbon and the synthesis technique is crucial to get the desired particle size and uniform shape. The variation and new characterization results of carbon-coated samples may contribute to the enhanced performance of LiMnPO₄ in lithium-ion batteries.

The FESEM images were observed to identify its morphology. An overview of FESEM morphology can be found in Table 4.2. It shows that the morphology varies as the carbon content changes. The changes in particle size might be caused by the addition of carbon content, which can form a protective layer around the particles, increasing their overall observed particle sizes (Jaafar et al., 2024). The FESEM and XRD results seem to be aligned properly, further supporting the characterization analysis. Furthermore, based on the crystallographic result obtained using XRD, it was found that there was no change in carbon-coated LiMnPO4 material structure when compared to bare LiMnPO4, which is an ordered olivine structure indexed to orthorhombic with the Pnma (62) space group. This shows that the synthesis method was effective and efficient, but none of the samples achieved uniform particle distribution. This might be caused by the inconsistent powder grinding performed using a pestle and mortar because particle uniformity was found to rely majorly on the grinding process in the previous study (Esmezjan et al., 2019; Suprunchuk et al., 2024).

Samples	Particle Size & Shape	Particle Distribution	Crystallite Size
0wt%	Irregular particles	Non-uniform;	<100nm
C-LiMnPO ₄	size up to 1.5µm	Large microparticles formed	(Nano-

Table 4.2 Summary of FESEM morphology of all sample

		by nanoparticle aggregation; some nanoparticles were found agglomerate randomly with microparticles	sized)
5wt%	Quasi-spherical and	Non-uniform;	<100nm
C-LiMnPO ₄	irregular sizes up to	Highly crystallinity large	(Nano-
	1.3µm	microparticles have formed; few nanoparticles agglomerate	sized)
		with microparticles;	
10wt%	Irregular particles	Non-uniform;	<100nm
C-LiMnPO ₄	size up to 1.8µm	Large microparticles formed	(Nano-
		by nanoparticle aggregation;	sized)
		some nanoparticles were found	
		agglomerate randomly with	
		microparticles	
15wt%	Irregular particles	Non-uniform; microparticles	<100nm
C-LiMnPO ₄	size up to 1.6µm	majorly formed by	(Nano-
		nanoparticle aggregation;	sized)
		Large microparticles form by	
		smaller microparticle	
		aggregation; few nanoparticles	
		found agglomerate randomly	
		with other particles	
20wt%	Irregular particles	Non-uniform: microparticles	<100nm
C-LiMnPO ₄	size up to 5um	are formed by nanoparticle	(Nano-
		aggregation, and those	sized)
		microparticles agglomerate,	*
		forming larger microparticles	

4.5 Potential Samples Characteristics Contributing to Enhanced Electrochemical Performance

An optimized carbon coating significantly impacts the properties of LiMnPO₄. By analyzing the structural properties of samples, we can gain insight into the electrochemical performance of carbon-coated LiMnPO₄. The material's electrochemical performance is affected by its crystallite size, morphology, phase purity, and coating quality (Ihrig et al., 2022). Carbon coating can improve discharge capacities, rate capability, and cyclability (Yu et al., 2019).

The crystallite size of LiMnPO₄ significantly affects its electrochemical properties. When the synthesized particle size is smaller, the contact area between the particles and the electrolyte increases, and the diffusion distance of lithium ions within the particles decreases, benefiting the material's electrochemical performance. This study determined crystallite sizes using X-ray Diffraction (XRD) and the Scherrer equation, revealing that bare LiMnPO₄ has a crystallite size of 44 nm. Upon carbon coating, crystallite sizes varied, with the 5wt% carbon-coated sample showing a significant increase to 73 nm, which may be due to enhanced heat distribution during sintering. However, as carbon content increased, the crystallite size decreased, with the 10wt% sample at 48 nm, the 15wt% sample at 45 nm, and the 20wt% sample at 58 nm. The 15wt% carbon-coated sample, with a crystallite size of 45 nm, strikes a balance between promoting and restricting growth, essential for high electrochemical activity. Moreover, its morphology is majorly covered by nanoparticles, which can significantly increase its contact area with the electrolyte.

Field Emission Scanning Electron Microscopy (FESEM) provided insights into the particle size, shape, and distribution of LiMnPO₄ samples, correlating to increased contact area and advancement in electrochemical interfaces (P. Zhang & Liu, 2023). A small particle size and uniform morphology can significantly enhance electronic conductivity by reducing impedance and shortening diffusion distance (Gou et al., 2024). The 15wt% carbon-coated LiMnPO₄ consist of majorly nanosized crystallites and extensive nanoparticle aggregation forming secondary particles. This morphology, characterized by a balance of microparticles and nanoparticles, ensures a high surface area and efficient Li⁺ ion diffusion paths, which are beneficial for electrochemical performance (T. Chen et al., 2023). However, agglomeration is still found among the microparticles in 15wt% carbon-coated LiMnPO4, but it can be improved by performing the grinding method more effectively (Suprunchuk et al., 2024). The agglomeration of LiMnPO₄ increases the diffusion path length of Li-ions, negatively impacting their transport (Z. Chen et al., 2022). The 15wt% C-LiMnPO4 has the smallest crystallite size among the other carbon-coated samples, and the presence of the nanoparticles may enhance its electrochemical capability.

Based on the Energy Dispersive X-ray (EDX) analysis, all samples exhibited phase purity with no impurities. This was further confirmed by the Raman spectra. It is important to verify the absence of impurities, as their presence could lead to surface corrosion or structural degradation, ultimately affecting the electrochemical properties adversely (L. Wang et al., 2022). In addition, defects in the LiMnPO4 crystallites, such as impurity phases, can hinder the migration of Li⁺ ions over long distances (Han et al., 2022). The phase purity ensures consistent performance, and the high-quality carbon coating improves electrical conductivity and structural integrity. Therefore, all carbon-coated samples may demonstrate consistent electrochemical behaviour and long-term stability.

Furthermore, an optimized amount of carbon coating process is crucial for developing high-performance LiMnPO₄ cathodes because it can improve electronic

47

conductivity (Yang et al., 2023). The appropriate carbon content increases the Li-ion and electron transfer and protects the cathode materials from side reactions at the electrolyte (Sim et al., 2020). The balance between sufficient coating thickness and uniform application is essential to maximize structural integrity and electrochemical performance. An excessive carbon coating layer thickness impedes lithium ions' deembedding process (G. Zhang et al., 2023). Uniform coatings enhance conductivity, reduce internal resistance, and improve the overall efficiency and stability of the cathode material during charge-discharge cycles (Sharmila & Parthibavarman, 2021). Non-uniform coatings may lead to inconsistent performance and reduced battery life. Carbon coating enhances electrical conductivity and mitigates particle agglomeration, which can be beneficial in overcoming the defects found in the carbon-coated samples. The 5wt% carbon-coated sample exhibited the smallest average crystallite size and many nanoparticles, indicating effective carbon coating. This balance is essential for maintaining a high surface area and ensuring uniform electrochemical reactions across the material.

The LiMnPO₄ sample with a 15wt% carbon coating shows excellent characteristics that enhance its electrochemical performance. With further refinement of its morphology, it may exhibit a well-balanced combination of crystallite size, morphology, phase purity, and coating quality to ensure the material's high performance, stability, and efficiency in real-world applications. These results highlight the significance of precise material engineering in creating highperformance cathode materials for the next generation of lithium-ion batteries.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The objectives of this thesis were successfully met by synthesizing carboncoated LiMnPO₄ cathode materials with varying glucose amounts and studying their structural properties. An organic-derived carbon source, glucose, was used for carbon coating on a LiMnPO₄ precursor. The carbon-coated LiMnPO₄ was synthesized using the sol-gel method and sintered at 700°C for 3 hours in a furnace. Following the sintering process, the samples were allowed to undergo cooling within the furnace and later subjected to grinding using a pestle and mortar. The obtained LiMnPO₄/C-5, samples (LiMnPO₄/C-0, $LiMnPO_4/C-10$, $LiMnPO_4/C-15$, LiMnPO₄/C-20) were structurally characterized using X-ray diffraction (XRD), Raman spectroscopy, and field emission scanning electron microscopy (FESEM) with energy dispersive X-ray analysis (EDX). All the obtained samples contain no impurity, as confirmed by XRD, Raman spectra, and EDX. By using Scherrer's Equation, the average crystallite size was 44nm, 73nm, 48nm, 45nm and 58nm for LiMnPO4/C-0, LiMnPO4/C-5, LiMnPO4/C-10, LiMnPO4/C-15, LiMnPO4/C-20 respectively. The FESEM morphology of samples provided a great insight into the effect of carbon coating where LiMnPO₄/C-15 have morphology majorly dispersed with nanoparticles compared to other carbon-coated samples. However, a wide range of particle size distributions has been found, which might be caused by the ineffective grinding method of samples, and it has been proven in many previous studies.

Both the qualitative and quantitative analysis revealed that the carbon coating significantly changes cathode materials' structural properties, enhancing the

electrochemical performance of the LiMnPO₄ cathode materials. Among the variants, the sample with 15wt% carbon coating (LiMnPO₄/C-15) exhibited the most promising potential for optimization. This improvement may be attributed to the optimal balance of conductivity and structural integrity the carbon coating provides, which facilitates better electron transport and structural stability during charge-discharge cycles of lithium-ion batteries.

5.2 **Recommendations for Future Study**

Future experimental work will include an analysis of the electrochemical properties of the samples, such as electrochemical impedance spectroscopy (EIS). EIS will determine the effect of carbon coating on LiMnPO4's electronic conductivity (Wani & Suresh, 2021). This will further validate the analysis based on the structural properties of LiMnPO4. The doping method should also incorporate the carbon coating process as it provides further benefits to improve lithium-ion battery performance. It has been revealed that chromium (Cr) doping enhances the performance of LiMnPO4 in electronic devices, as Cr-doped LiMnPO4 unveiled an improved dielectric loss (Bibi et al., 2022). Carbon nanotubes (CNTs) can be included to improve morphology and suppress the nanoparticle aggregation that forms microparticles (Duan et al., 2020). To fully understand the impact of sample morphology on electrochemical performance, it is essential to conduct galvanostatic charge/discharge tests (Wu et al., 2020). These suggestions are vital for future study and could unlock the immense potential of carbon-coated LiMnPO4 as a cathode material for lithium-ion batteries.

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No.	Pos. [°2Th.]	FWHM Left [°2Th.]	Crystallite Size [nm]
1	16.8909	0.1378	58.26
2	20.4405	0.1082	74.58
3	22.2897	0.0984	82.25
4	23.6381	0.2165	37.47
5	25.1324	0.1082	75.19
6	29.1371	0.1574	52.13
7	31.7495	0.1673	49.35
8	35.0319	0.0689	120.86
A9 S	35.8762	0.1082	77.14
10	37.3176	0.1771	47.33
11	38.8344	0.2362	35.65
12	39.2722	0.1673	50.40
13	41.6402	0.2952	28.78
14	43.6591	0.4133	20.70
15	44.3002	0.492	17.43
16	45.7605	0.6298	13.69
17	47.4235	0.3149	27.54
18	48.3965	0.3346	26.02
19	49.3927	0.2657	32.90
20	51.6685	0.3149	28.02
21	54.1681	0.1574	56.67
22	54.6525	0.1574	56.79
23	55.6151	0.2657	33.79
24	56.7642	0.2854	31.63
25	57.2193	0.2362	38.30
26	60.4711	0.1574	58.40
27	61.1174	0.2755	33.47
28	64.5751	0.4822	19.48
29	65.5691	0.4231	22.33
30	66.474	0.6888	13.78
		Average Crystallite Size:	44.01

APPENDIX A

Crystallite Size Calculation (Scherrer Eq.) for Bare LiMnPO₄

No.	Pos. [°2Th.]	FWHM Left [°2Th.]	Crystallite Size [nm]
1	16.8799	0.1378	58.26
2	20.4488	0.0984	82.01
3	22.2892	0.1279	63.28
4	23.6071	0.1673	48.49
5	25.1304	0.0984	82.68
6	29.1337	0.059	139.07
7	31.7519	0.0787	104.91
8	35.0469	0.059	141.15
-9-S	35.883	0.0689	121.15
10	37.3261	0.0984	85.18
11	38.7422	0.0787	106.96
12	39.2316	0.0787	107.12
13	41.6475	0.1771	47.97
14	43.5911	0.1673	51.12
15	44.3379	0.3149	27.23
n 16	45.5933	0.4723	18.24
17	48.3963	0.1574	55.31
18	49.3521	0.1181	74.00
19	49.8198	0.0787	111.25
20	51.6619	0.0787	112.11
21	54.1681	0.0787	113.33
22	54.6718	0.096	93.12
23	55.6211	0.096	93.52
24	56.746	0.288	31.34
25	57.2362	0.12	75.39
26	60.4929	0.12	76.61
27	61.0851	0.384	24.01
28	63.0574	0.372	25.04
29	64.5574	0.396	23.72
30	65.3643	0.12	78.62
31	66.4759	0.528	17.98
		Average Crystallite Size:	73.88

APPENDIX B

Crystallite Size Calculation (Scherrer Eq.) for 5wt% C-LiMnPO₄

-	No.	Pos. [°2Th.]	FWHM Left [°2Th.]	Crystallite Size [nm]
-	1	16.8742	0.0984	81.59
	2	20.43	0.0984	82.00
	3	22.2896	0.1574	51.42
	4	23.6082	0.2066	39.27
	5	25.1097	0.1378	59.04
	6	29.1299	0.1673	49.04
	7	31.7395	0.1181	69.91
	8	33.9062	0.2362	35.15
	A9 S	35.0377	0.0492	169.26
	10	35.8664	0.1181	70.67
	11	37.2947	0.1181	70.97
	12	38.829	0.2362	35.65
	13	39.2559	0.1574	53.56
	14	41.6394	0.3542	23.99
	15	43.6588	0.4133	20.70
	16	44.2988	0.4625	18.54
	17	45.7246	0.6298	13.68
	18	48.4489	0.3444	25.28
	19	49.3677	0.2558	34.17
	20	50.0691	AL 0.3542 SIA	24.74
	21	51.6477	0.1378	64.02
	22	54.1778	0.187	47.70
	23	54.6655	0.1574	56.79
	24	55.6445	0.1181	76.03
	25	56.7709	0.3346	26.98
	26	57.219	0.1181	76.59
	27	60.4859	0.246	37.37
	28	61.1132	0.2558	36.05
	29	63.4955	0.8266	11.30
	30	64.5954	0.492	19.09
	31	65.3574	0.1771	53.27
	32	66.2341	0.925	10.25
_			Average Crystallite Size:	48.25

APPENDIX C

Crystallite Size Calculation (Scherrer Eq.) for 10wt% C-LiMnPO₄

No.	Pos. [°2Th.]	FWHM Left [°2Th.]	Crystallite Size [nn
1	16.8792	0.2165	37.08
2	20.4304	0.1181	68.32
3	22.2806	0.1082	74.80
4	23.6719	0.2362	34.35
5	25.1105	0.187	43.51
6	29.1496	0.187	43.88
7	31.749	0.1673	49.35
8	33.8742	0.3149	26.36
ALA9 SI	35.0321	0.1771	47.02
10	35.8689	0.1673	49.89
11	37.2959	0.1476	56.78
12	38.8442	0.2362	35.65
13	39.2427	0.1279	65.92
14	41.6386	0.2657	31.98
15	43.5446	0.3542	24.14
1/Nn 16	44.2967	0.4723	18.15
17	45.4589	0.492	17.50
	48.3956	0.1673	52.04
19	49.3609	0.2558	34.17
/ER 20	50.0691	0.3542	24.74
21	51.6428	0.0984	89.65
22	52.6804	0.3641	24.34
23	54.1676	0.1378	64.73
24	54.6711	0.0787	113.59
25	55.5962	0.2362	38.01
26	57.2238	0.0787	114.94
27	60.4786	0.1574	58.40
28	61.1094	0.3149	29.28
29	63.459	0.7282	12.82
30	64.928	0.5117	18.39
31	65.4078	0.3641	25.92
32	66.2081	0.8659	10.95
		Average Crystallite Size:	44.90

APPENDIX D

65

-	No.	Pos. [°2Th.]	FWHM Left [°2Th.]	Crystallite Size [nm]
-	1	16.8703	0.1279	62.77
	2	20.4198	0.1082	74.57
	3	22.2627	0.1279	63.28
	4	23.6395	0.1968	41.23
	5	25.1019	0.0787	103.37
	6	29.1157	0.0984	83.38
	7	31.7295	0.1279	64.55
	8	35.0279	0.0787	105.81
	9S	35.8681	0.0984	84.82
	10	37.3127	0.1771	47.33
	11	38.823	0.2362	35.65
	12	39.2132	0.1181	71.38
	13	41.588	0.246	34.53
	14	43.659	0.2263	37.80
	15	44.2676	0.2362	36.30
	16	47.4144	0.3149	27.54
	17	48.4087	0.1771	49.16
	18	49.3326	0.1968	44.40
	19	49.7744	0.187	46.81
	20	51.6431	0.0984	89.65
	21	54.1604	0.0984	90.64
	22	54.6605	0.0787	113.58
	23	55.611	0.0984	91.24
	24	56.7699	0.2854	31.63
	25	57.2157	0.1673	54.07
	26	60.4857	0.2558	35.94
	27	61.1126	0.0984	93.72
	28	63.121	0.4625	20.15
	29	64.6016	0.5904	15.91
	30	65.5665	0.4428	21.33
	31	66.4671	0.3838	24.74
_			Average Crystallite Size:	57.98

APPENDIX E

Crystallite Size Calculation (Scherrer Eq.) for 20wt% C-LiMnPO₄

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