RESPONSE SURFACE METHODOLOGY (RSM) FOR PROCESS PARAMETERS OPTIMIZATION OF $LiFePO_4$ USING FLAME SPRAY REACTOR FOR Li-ION BATTERIES

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RESPONSE SURFACE METHODOLOGY (RSM) FOR PROCESS PARAMETERS OPTIMIZATION OF $LiFePO_4$ USING FLAME SPRAY REACTOR FOR Li-ION BATTERIES

by

NA YONG SIK

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There is a saying that goes “Rome wasn’t built in a day” and the meaning behind this is that important things take time which is certainly the case for this final year project as lots of effort, time and research has been put into completing it. Undoubtedly, the journey to completion wasn’t as smooth as what one would wish it to be, but it was certainly a journey worth looking back in the future. However, it would be a sin to take full credit for this FYP as there had been support and assistance from many different parties. First and foremost, I would like to convey my utmost gratitude to my beloved supervisor, Dr. NoorAshrina Binti A. Hamid for her invaluable guidance and endless support throughout this project. Her positivity was something to admire as there was never once in any discussion with her where she wouldn’t give me encouragement, which makes me extremely thankful to be under her wings for this project. Without all her guidance and encouragement, this project certainly wouldn’t have been completed on time. Next, I would like to sincerely thank my lovely family, fellow friends, respected lecturers and course mates for their support and assistance throughout the completion of this project. Finally, I would like to sincerely extend my gratitude towards Universiti Sains Malaysia (USM) and specifically, the School of Chemical Engineering for providing me with suffice equipment, licensed software, and conducive environment en route to completion of this project.

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Table of Contents

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
CCD	Central composite design
DOE	Design of experiment
FSP	Flame spray pyrolysis
GC	Glucose content
LIB	Lithium-ion batteries
LFP	Lithium iron phosphate, $LiFePO_4$
OFAT	One-factor-at-a-time
PRESS	Predicted residual error sum of squares
RSM	Response surface methodology
VIF	Variance Inflation Factor
USM	Universiti Sains Malaysia

KAEDAH PERMUKAAN TINDAK BALAS UNTUK OPTIMASI FAKTOR-FAKTOR LIFEPO$_4$ MENGGUNAKAN REAKTOR SEMBURAN API

ABSTRAK

Litium ferum fosfat ($LiFePO_4$) digunakan secara meluas disebabkan oleh kelebihannya iaitu kebolehbalikan yang sangat baik, faktor keselamatan (lebih selamat berbanding litium ion bateri yang lain) dan senang didapati pada harga yang murah. Dalam kajian ini, pengoptimuman faktor-faktor sintesis $LiFePO_4$ telah dijalankan secara kaedah permukaan tindak balas (RSM), iaitu salah satu teknik pengoptimuman yang mapan dan efektif dalam menganggar dan megoptimumkan proses. Perisian 'Design Expert' edisi ke-11 digunakan bagi tujuan RSM. Teknik pertama RSM yang digunakan adalah satu-fakor reka bentuk D-optimal untuk mengoptimumkan kepekatan pendahulu serta mendapatkan data-data statistik mengenai data yang telah digunakan di mana kepekatan optimum didapati adalah 0.35 M disebabkan saiz yang besar dibentuk dan secara tidak langsung, akan mempengaruhi kapasiti pengeluaran dikaju. Selepas itu, kesan suhu kalsinasi dan kandungan glukosa pada kapasiti pelepasan disiasat dan kesannya dikenal pasti melalui analisis varians (ANOVA). Rekabentuk komposit tengah (CCD) digunakan untuk simulasi tersebut dan kapasiti pengeluaran optimum tanpa melibatkan faktor-faktor adalah 160.417 mAh g^{-1}di suhu kalsinasi 689.395 ℃ dan kandungan glukosa 26.2079 % dan terdapat 99 lagi nilai optima yang unik. Setelah itu, krtieria telah dinyatakan iaitu apabila suhu kalsinasi minima, kandungan glukosa minima dan kedua-dua faktor minima dan kapasiti pengeluaran optima masing-masing adalah 158.447 mAh g-1, 153.103 mAh g-1, dan 151.515 mAh g-1 dan kesemuanya didapati mempunyai satu penyelesaian unik. Akhirnya, tiga jenis RSM iaitu, CCD, rekabentuk D-optimal dan rekabentuk data historik digunakan serta dibandingkan untuk mengenal pasti kaedah terbaik dari pandangan/sudut statistik.

RESPONSE SURFACE METHODOLOGY (RSM) FOR PROCESS PARAMETERS OPTIMIZATION OF LIFEPO$_4$ USING FLAME SPRAY REACTOR FOR LI-ION BATTERIES

ABSTRACT

Lithium iron phosphate, LiFePO$_4$ (LFP) is widely used due to the advantages it offers such as excellent reversibility, relatively safer than other lithium-ion batteries and its abundancy, which at the same time is inexpensive. In this final year project, the optimization of the process parameters for the synthesis of LFP via flame spray pyrolysis was done by implementing response surface methodology (RSM), a collection of mathematical and statistical techniques which is a well-established method useful for approximating and optimizing processes. Design expert V11 was the software utilized for RSM. The first design used was the 1-factor D-optimal design to optimize the precursor concentration and obtain the statistical data of the available data, in which the optimum concentration of precursor was 0.35 M it would form a large particle which will then indirectly affect the discharge capacity. Then, effect of the two process parameters, namely calcination temperature and glucose content on the discharge capacity were studied, and its significance was determined based on the analysis of variance (ANOVA). Central composite design (CCD) was applied for the simulation of it and the optimized discharge capacity based on no specific criteria of the parameters was 160.417 mAh g^{-1} at a calcination temperature of 689.395 ℃ and the glucose content 26.2079 % and there are another 99 unique solutions. Then, as the criteria was set as minimum calcination temperature, minimum glucose content and minimum of both factors, the discharge capacity was 158.447 mAh g^{-1}, 153.103 mAh g^{-1}, 151.515 mAh g^{-1} respectively, all with only one unique solution. Lastly, three types of RSM, specifically, CCD, D-optimal design and historical data design were implemented and compared on which method would yield the best results, statistically.

CHAPTER 1

INTRODUCTION

1.1 Research Background

A battery is a simple yet remarkable invention/device that converts chemical energy to electrical energy. In other words, batteries serve as an electrical storage system which is ubiquitous today in everyday life. Batteries can be categorised into two major groups based on its usability which are the single-use battery, termed as primary battery and the rechargeable battery also known as secondary batteries. Due to the attractiveness of secondary batteries in terms of ability to be reused, numerous studies have been conducted since the early 1860s. In the modern world today, lithium ion batteries are said to be one of the most advanced secondary batteries and is a powerhouse for modern day electronics where it is found in our everyday companions such as laptops, mobile phones, tablets, etc due to several benefits posed such as its large energy density, tremendous life cycle and superior coulombic efficiency (Blomgren, 2017; Loeffler et al., 2015). The working principle of lithium is based on the intercalation and deintercalation of lithium ion between the electropositive electrode (anode) and electronegative electrode (cathode).

Ever since the commercialization of the first ever lithium-ion batteries back in 1991 by Sony (Loeffler et al., 2015), the cathode material have always been one of the main focus of research as it is the component that determines the energy density, capability and unsurprisingly, cost (Yong Zhang et al., 2012). Lithium iron phosphate ($LiFePO_4$) has been extensively studied as the potential cathode material because of its remarkable advantages such as stability, safety, cost, environmental friendly and high theoretical capacity of approximately 170 mAh g^{-1} (W. J. Zhang, 2011; Yong Zhang et al., 2012). However, the questionable

downside of $LiFePO_4$ is the poor ionic and electronic conductivity which would deteriorate its rate performance.

Flame spray pyrolysis (FSP) is a versatile and promising technique in producing nanoparticles, particularly, nanoscale $LiFePO_4$ in a fast and continuous operation. As mentioned earlier, the drawbacks of $LiFePO_4$ are its low ionic and electronic conductivity but undoubtingly, it is possible to overcome this problem and further improve the conductivity of $LiFePO_4$. The fundamentals of how good the property of a material is always relating to the synthesis method. Solid-state reaction is then carried out following FSP. Hence, it is vital to investigate and optimize the process parameters of $LiFePO_4$ synthesised via FSP technology followed by solid-state reaction. Among the numerous parameters, precursor concentration, calcination time and glucose concentration (carbon content) are the keys to ascertain the electrochemical performance of $LiFePO_4$ via FSP.

Response surface methodology (RSM) is a well-established statistically based optimization strategy which would be useful in this context to investigate these effects of independent process parameters on the responding variable in our case, would be the discharge capacity. With RSM, we can easily determine the optimum conditions of all three parameters to be studied that would give $LiFePO_4$ the highest discharge capacity. Design Expert by Stat-Ease is the available software commonly used to perform RSM and optimize data.

1.2 Problem statement

Approximately 40-50 % of the total cost of a battery, specifically, lithium-ion battery is accounted by the cathode material. There are a variety of choices that could be the cathode material such as lithium cobalt oxide ($LiCoO_2$), lithium oxido (oxo) nickel ($LiNiO_2$) and, $LiFePO_4$. Among the three, it is undeniable that the latter have several distinct advantages over the former in which it is cheaper, safer, more eco-friendly, and high theoretical capacities. As

$LiFePO_4$ would exist as nanoparticles, it is ideal to synthesis it via flame spray pyrolysis as compared to other available techniques. As mentioned earlier, one of the major drawbacks of LFP is its low ionic and electric conductivity. Hence, it is vital to increase the conductivity of LFP as it would increase its potential for the best cathode material. The conductivity of LFP is related to the discharge capacity which is dependent on the process parameters of LFP synthesised by FSP followed by solid-state reaction, particularly two independent variables which are the calcination temperature and glucose (carbon) content. With the implementation of an optimization strategy, particularly, RSM, we can optimize the process easily. In this research, the discharge capacity of LFP was studied with the implementation of RSM to optimize of the three parameters.

1.3 Objectives

I. To analyse the effect of precursor concentration on the size of lithium ion based on RSM analysis (adequacy test and ANOVA).

II. To study the effect of calcination temperature and carbon content on the discharge capacity of LFP based on RSM analysis (adequacy test and ANOVA).

III. To optimize the process parameters of synthesis of LFP to obtain the maximum discharge capacity via RSM.

IV. To compare 3 different type of RSM, namely CCD, D-optimal design and historical data design from a statistical standpoint.

CHAPTER 2

LITERATURE REVIEW

This chapter presents the overview of this final year project topic, specifically on lithium-ion batteries, cathode material of lithium iron phosphate, $LiFePO_4$, LFP synthesis method of Flame Spray Pyrolysis, process parameters of calcination temperature and carbon content. Moreover, this chapter also covers the essential data needed for optimization of the process parameters by response surface methodology (RSM).

2.1 Lithium-ion battery

A battery is a mobile electro-chemical device functions to convert chemical energy to useful electrical energy. Adhering to the concept, lithium-ion batteries (LIB) were developed since the early 1860s but finally breaking out in the 1990s in which the first ever commercialized lithium-ion battery was produced by Sony in 1991. Fast forward to nearly 30 years later, lithium-ion battery is now on the verge of transforming the transportation sector by introducing the concept of electric vehicles and bicycles while still being a major part of our everyday life, powering our mobile phones and laptops.

Lithium is the lightest of all metals and debatably has the highest reduction potential (Ohzuku & Brodd, 2007) which means it has a high tendency to gain electrons and be reduced which these characteristics would directly attribute to lithium-ion batteries having one of the highest theoretical capacity in comparison with other rechargeable batteries, where Vincent, (2000) stated that the theoretical specific capacity of LIB is 3860 Ah kg^{-1} which is far more superior than zinc at only 820 Ah kg^{-1} and lead at 260 Ah kg^{-1}. Besides, Aravindan et al., (2013) had also made comparison on the rechargeable batteries and the data are tabulated in **Table 2.**

1 while Landi et al., (2009) highlighted the relationship between specific and volumetric energy density for different rechargeable batteries as displayed in **Figure 2. 1**.

Table 2. 1 Comparison among rechargeable battery system

	Magnesium	Lead	Ni	Li-ion
Specific energy density (theory) (W h kg^{-1})	135	170	220	226 – 560
Specific energy density (practical) (W h kg^{-1})	> 60	30 - 40	40 - 100	95 - 158

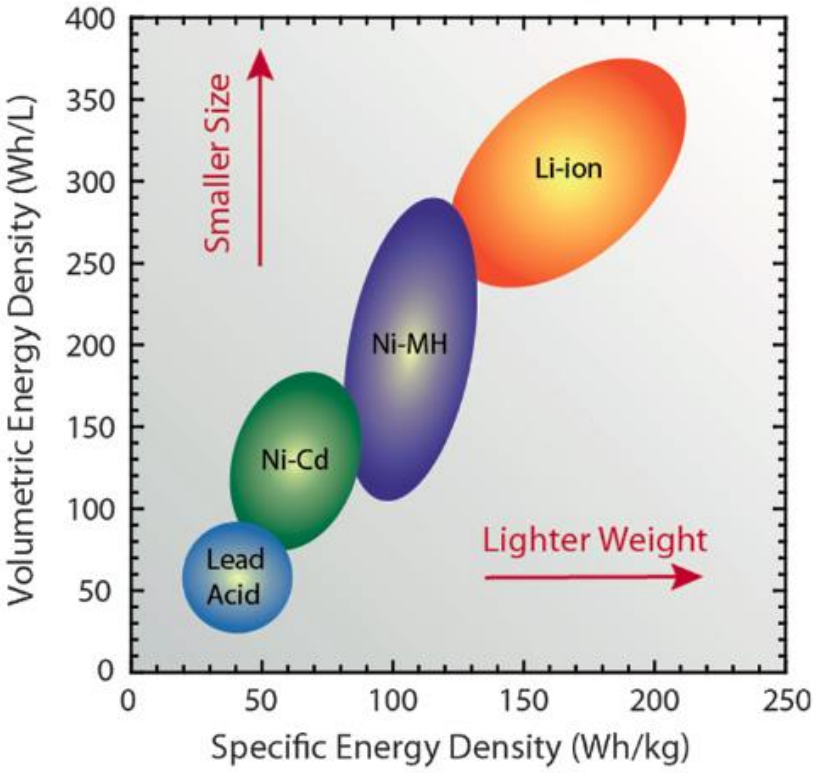

Figure 2. 1 Comparison of different rechargeable batteries as a function of volumetric and specific energy density (Landi et al., 2009)

Table 2. 1 shows the different values of both the theoretical and practical energy density for difference rechargeable batteries in which LIB have the highest energy density, both

theoretically and practically compared to magnesium, lead and nickel. Moreover, **Figure 2. 1** also depicts that LIB possess the highest volumetric and gravimetric energy density which makes LIB even more commendable. In fact, just two years ago, in the year 2019, three important pioneers and contributors of lithium-ion batteries, John B. Goodenough, M. Stanley Whittingham and Akira Yoshino were awarded the Nobel Prize in Chemistry (*Press Release: The Nobel Prize in Chemistry 2019 - NobelPrize.Org*, n.d.) for their endless contributions in the development of lithium-ion batteries which also further indicates the significance of lithium-ion batteries.

The working principle of lithium-ion battery is demonstrated in **Figure 2. 2** (P. Huang et al., 2015). Similarly, as all other fuel cells, the fundamental of LIB is based on redox reaction in which the reduction occurs at the cathode and oxidation at the anode. Typically for a discharge process, lithium ions are discharged from the anode and is intercalated to the cathode and vice versa for charging process. The terminology commonly for the discharge or deintercalation of a lithium ion from an electrode is delithiation.

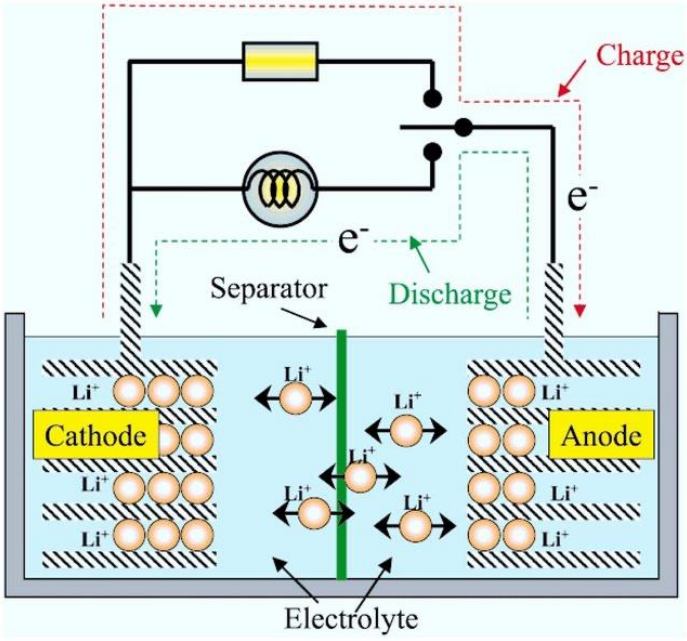

Figure 2. 2 Schematic diagram of working mechanism of lithium-ion battery during charge and discharge (P. Huang et al., 2015)

2.2 Cathode material - $LiFePO_4$

There had been a variety of cathode materials for lithium-ion batteries being researched since the establishment of lithium-ion batteries. The first cathode material introduced by Goodenough was lithium cobalt oxide ($LiCoO_2$) (*Press Release: The Nobel Prize in Chemistry 2019 - NobelPrize.Org*, n.d.) and until today, it had been studied extensively by various researchers (K. Wang et al., 2020; Xiao Wang et al., 2019) due to its excellent cycling performance, high specific capacity, and high working voltage. Despite these advantages, Sholichah et al., (2020) and K. Wang et al., (2020) has clearly stated the main concern of $LiCoO_2$ is the relatively short life span, low thermal stability, limited load capabilities. Economically, $LiCoO_2$ is also very expensive and is considered toxic. Hence, another popular cathode material that came into the discussion for high energy density is lithium nickel oxide ($LiNiO_2$) as it said to have a similar theoretical specific capacity as $LiCoO_2$ and is cheaper. It is still being researched as recently, Xu et al., (2016) did a study on the degradation mechanism of it. However, pure LiNiO2 cathodes are claimed to be unfavourable due to Ni^{2+} ions having a tendency to replace Li^+ sites during de-lithiation which would potentially block the Li diffusion pathway (Nitta et al., 2015; Rougier et al., 1996).

Ever since the first research on $LiFePO_4$ (LFP) by Padhi et al., (1997), it has then globally attract various researches globally to study $LiFePO_4$ as the cathode material. This was undoubtedly due to the cost of less expensive, toxic-free which release no harm to the environment, exhibits excellent reversibility and thermal stability, and all while still having a fairly decent theoretical capacity of 170 mAh g^{-1}. Not only that, but iron also (Fe) is abundant unlike other cathode material such as cobalt.

Generally, $LiFePO_4$ has an ordered olivine structure and orthorhombic space group of Pnma in which its systal constants are fixed at 1.044 μm, 0.601 μm and 0.4692 μm for a, b and c respectively (Borong Wu, 2018). As we know, during delithiation, Li^+ ions discharge

from the cathode forming $FePO_4$ in which the systal constants of its orthorhombic space group of Pnma differs in which the values are 0.976 μm, 0.574 μm and 0.476 μm for a, b and c respectively. The crystal structure of $LiFePO_4$ and $FePO_4$ is as shown below in which PO_4 is represented as tetrahedra.

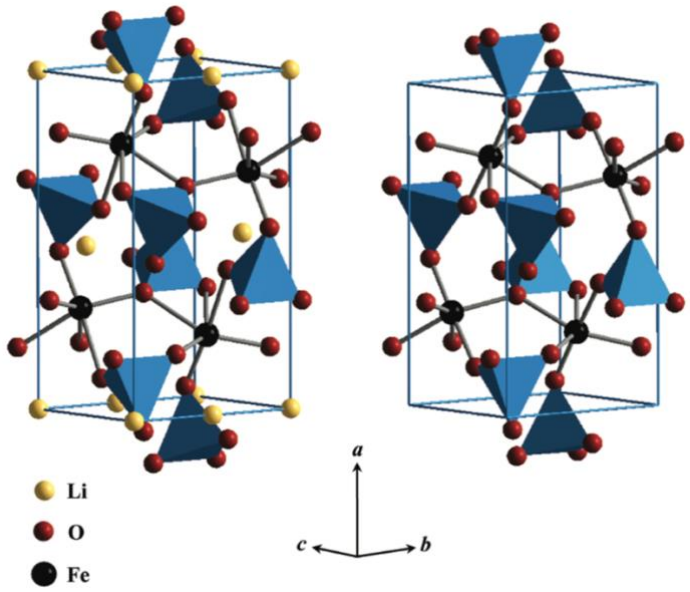

Figure 2. 3 Crystal structure of LiFePO4 and FePO4 (Castro et al., 2010)

However, as what was mentioned for the other cathode materials, there are also drawbacks of $LiFePO_4$ but perhaps manageable as it has a low electronic conductivity. This may be suppressed by varying the process parameters for method of synthesis for $LiFePO_4$ which the synthesis process is discussed in the next sub-section.

2.3 Flame-spray pyrolysis

There are various methods available to synthesise $LiFePO_4$ including carbothermal reduction (Shuqing & Kejie, 2011; Smecellato et al., 2017) , solid-state reaction (Kim et al., 2011) , mechano-chemical activation, hydrothermal processing (Wu et al., 2018) and also sol-gel process (Yingtang Zhang et al., 2018). However, despite the process mentioned were able to

obtain decent electrochemical results, the process tends to be quite complexed for large-scale production. Thus, to overcome this, $LiFePO_4$ was synthesised via flame spray pyrolysis (FSP) (Mallika Rani Parimi, 2018; Hamid et al., 2012) as this method was capable to produce large amount of nanosized $LiFePO_4$.

FSP is slowly establishing itself as a promising technology due to its rapid one-step synthesis, both at the laboratory and industrial scale. One of the most vital elements of FSP is the precursor in which the precursor molecules are decomposed/calcined at a high temperature over the flame spray (commonly ignited by fuel gas and oxygen) to produce the $LiFePO_4$ nanoparticles. As what mentioned by Mallika Rani Parimi, (2018), the possibility of FSP to produce nanoparticles makes it an even more commendable process as it will subsequently reduce the diffusion length leading to easy facilitation of the mobility of Li-ion from the active material. The schematic diagram of FSP can be observed as below (Hamid et al., 2012).

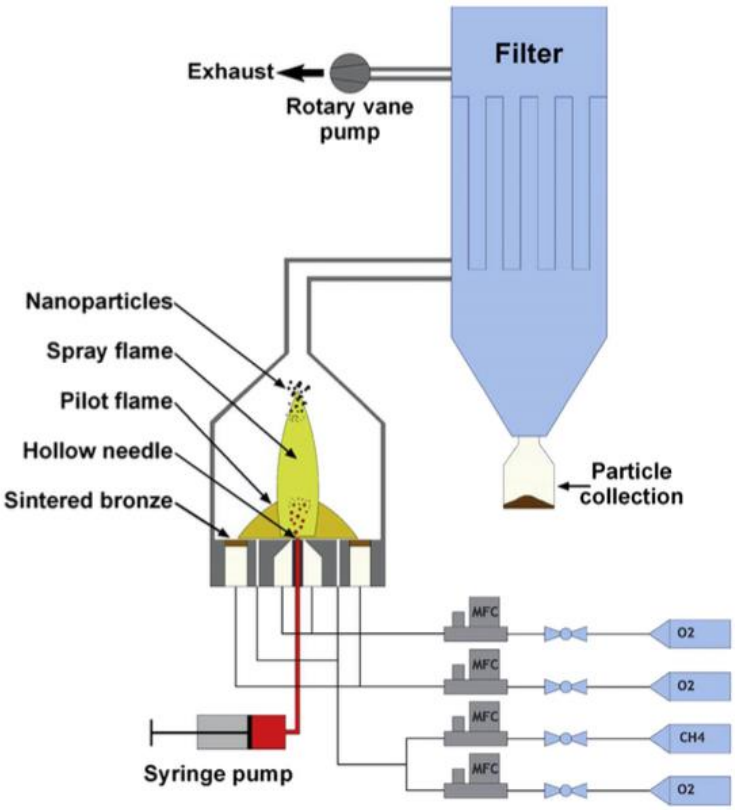

Figure 2. 4 Schematic diagram of flame spray pyrolysis (Hamid et al., 2012)

2.4 Process parameters of FSP

There are various parameters that can be manipulated to provide the optimum condition for $LiFePO_4$ to have the best electrochemical properties such as the discharge capacity and electronic conductivity. Halim et al., (2014) studied on the effect of fuel rate and annealing on the particle formation of $LiFePO_4$ using FSP in which it was discovered that an increase in fuel rate would lead to the decrease in particle size which would theoretically increase the electronic conductivity.

Meanwhile, the study of addition/implementation of carbon on $LiFePO_4$ was carried out by Bewlay et al., (2004) and Waser et al., (2011) and it was deduced that the conductivity of the particles were increased upon impregnation of carbon. As mentioned earlier on the importance of precursor, various researchers had also studied the effect of precursor solution in FSP (Bieber et al., 2019; Kashi et al., 2018; Saadatkhah et al., 2019). Bieber et. al (2019) recently studied the influence of precursor addition and the effect of varying precursor solution. They deduced that there is only a minimal effect on the spray formation with an increase in the concentration of precursor solution. However, the size of the particle agglomerate is directly affected when the precursor concentration varies. The presence of highly concentrated precursor would lead to a higher concentration of prime particles in the flame and subsequently increases the probability of particle collusion and agglomeration.

In this final year project, the two main process parameters to be varied and studied was the calcination temperature and amount of carbon content.

2.4.1 Calcination temperature

Generally, almost all LFP synthesis methods are affected by the temperature as it is known that an optimum temperature would yield LFP with desirable electrochemical properties, particularly a high discharge capacity. Halim et al., (2014) revealed that with the

increase in temperature, the particle size would decrease as they attributed this to the fact that the high temperature would cause solid evaporation that results in smaller particle. Meanwhile, another common LFP synthesis method which is carbothermal reduction also requires optimum calcination temperature as L. Wang et al., (2009) deduced that the discharge capacity would initially increase with calcination temperature from 500 to 650 ℃ due to their lower crystallinity and as the temperature is further increase (from 650 – 750 ℃), its discharge capacity experienced a drop, owing it to the abrupt increase in particle size where it has higher crystallinity and thus, prolonging the diffusion length.

Besides the aforementioned researchers, many other previous studies have demonstrated on the importance of the parameter of calcination temperature in the preparation of $LiFePO_4$. Thus, this will be evaluated and discussed further in this final year project.

2.4.2 Carbon content

Carbon has been added to $LiFePO_4$ in order to increase the electronic conductivity. Glucose, acetylene black, carbon black amongst common carbon source added in $LiFePO_4$.. Raj & Sil, (2018) revealed the effect of carbon content in LFP preparation by sol-gel method that the increase of carbon content leads to an increase in maximum discharge capacity where the optimum thickness of carbon required was 4.2 nm which produces discharge capacity of 148.2 mAh g^{-1} at calcination temperature of 700 ℃. On the other hand, perhaps due to the different method used, Xiaodong Wang et al., (2013) obtained the optimum carbon content at a value of 8.2 %, yielding a discharge capacity of 150.2 mAh g^{-1}.

Meanwhile, specifically for FSP, Hamid et al., (2012) investigated on the effect of increase of glucose content (source of carbon) on the electrochemical property. Specifically, the discharge capacity experiences a rise with the increase in carbon content as a higher content of carbon would effectively prevents the $LiFePO_4$ nanoparticles from sintering. In short, the

carbon content is of great essence and will also be studied alongside with the calcination temperature simultaneously via RSM.

2.5 Process optimization by response surface methodology

Optimization of both the process parameters of calcination temperature and carbon content were done using design of experiment (DOE). The most common and conventional optimization technique is the manipulation of one independent variable whilst fixing the other independent variable, also known as one-factor-at-a-time (OFAT) approach. However, this method is less efficient as it requires many test runs. Another strategy that is more of a trial-and-error method which is the best-guess approach which is not accurate and precise as it cannot guarantee the best solution.

Besides both OFAT and best guess approach, another common yet proficient technique of design of experiment (DOE) is response surface methodology (RSM). RSM is arguably the best optimization technique since its establishment back in the early 1950s by Box and Wilson (Şenaras, 2019). RSM is a collection of mathematical and statistical techniques useful for approximating and optimizing processes and most extensively applied in situations where there are few independent variables influencing the performance characteristic which fits the narrative of this project. RSM requires the experimental data as to develop a suitable approximation of the relationship between the performance measurement, particularly, discharge capacity and the respective independent variables of calcination temperature and carbon content. Specifically, RSM works by forming a polynomial equation that fits to the inputted data and subsequently describes the behaviour of the data and identifying the relationship of the responding variable to the manipulated independent variables.

There are few designs under RSM of the Design Expert software such as two/three-level factorial design, central composite design (CCD), Box-Behnken design, D-optimal design, and historical data. Among the three aforementioned designs, CCD is the most popular due to the lesser number of experimental works needed and also definitely because of its reliability. In fact, researchers had also done a comparison, i.e. Rakić et al., (2014) reported comparison between these three design methods and they deduced that both CCD and three-level factorial design created significantly better models compared to Box-Behnken. As there have been no available literature on RSM of process parameters of $LiFePO_4$ via FSP (solid-state reaction) which further indicates the motive of this research. Hence, this research is carried out to perform RSM for the process parameters, particularly, carbon content, and calcination temperature. CCD was first used to analyse the effects of the factors and then to both other two RSM of D-optimal design and historical data was also done to briefly compare the difference in the three statistical methods used.

2.5.1 Central composite design (CCD)

Central composite design, as mentioned earlier, is a type of response surface methodology which is said to require a lesser number of runs to optimize the data. There are literatures available on RSM, particularly via CCD, of process parameters of LFP but with different synthesis methods. The first being RSM of LFP synthesised via carbothermal reduction. Carbothermal reduction, as the name suggests, is the reduction of metal oxides to pure metal state, particularly lithium. In this case, the reduction process of the transition metal and the incorporation of lithium were both facilitated based on the transition of reaction of C to C_0 at a high carbothermal temperature (Barker et al., 2003). Yang et al., (2012) carried out RSM optimization of the process parameters of $LiFePO_4$ synthesised by carbothermal reduction and the model obtained provides the optimized parameters of the three variables

studied (carbon content, sintering time and sintering temperature) and the optimum conditions were determined to be 34.33 g mol^{-1}, 8.48 hours and 652 ℃. There has also been a study conducted by Huang et al., (2016) on the RSM optimization of process parameters of $LiFePO_4$ via solid-state method.

Besides that, another alternative route of synthesising LFP is via hydrothermal reduction and this method utilizes a supercritical hydrothermal system in which the source of lithium, iron and phosphate are all dissolved in water and subsequently heated at temperature ranging from 100 to 300 ℃ for few hours under specified conditions (Bodoardo et al., 2009). A very recent research on the RSM of LFP via hydrothermal reduction carried out by Z. Liu et al., (2020). The three parameters varied by Z. Liu et. al. in their study was the hydrothermal time, hydrothermal temperature, and the ascorbic acid dosage in which ascorbic acid is proven to be effective in ensuring Fe (II) species does not undergo oxidation during hydrothermal treatment (Nakano et al., 2008). With regards to earlier statement, the temperature range was indeed within the range as they varied the temperature range from the minimum of 150 to 210 ℃. The optimized value attained was at a hydrothermal temperature of 210 ℃, hydrothermal time of 9 hours and ascorbic dosage of 1.5 mmol. However, the discharge capacity was unable to reach close to the theoretical discharge capacity of 170 mAh g^{-1} as the discharge capacity attained was 152.5 mAh g^{-1}.

2.5.2 D-Optimal design

D-optimal design, similarly to CCD, is a type of RSM available in the Design Expert software. However, D-optimal design matrices are typically non-orthogonal and its effect estimates are correlated, unlike the other designs such as factorials and fractional factorials (*5.5.2.1. D-Optimal Designs*, n.d.). The very first practical algorithm for the establishment of optimal designs was developed by Mitchell, (1974).Typically, D-Optimal design are

implemented when standard designs are inapplicable to the research requirement of the problem, as mentioned by Johnson et al., (2011) but it can still be used generally.

Generally, there have been very less literature available on RSM of process parameters of LFP via D-Optimal design but there is a research conducted by Mathieu et al., (2017) on the implementation of D-Optimal design to the lithium battery for ageing model calibration, in which only 10 runs is proposed and a good absolute error of 1.08 % was attained as well as an accurate R^2 value of 0.96. Rest assure that D-Optimal design is still used widely but just not in the specific field of our topic of conduct as it is implemented in other application such as in the transesterification of waste cooking oil by El-Gendy et al., (2016) and a maximum predicted biodiesel yield of 100 % could be achieved at a methanol-to-oil molar ratio of 8.57:1, 3.99 wt% of catalyst, reaction time of 31 minutes and a mixing rate of 398.88 rpm.

2.5.3 Historical data design

Likewise, as central composite design and D-optimal design, historical data design is also a type of response surface methodology and simply just another feature available in Design Expert. Unlike the two aforementioned RSM techniques, historical data is able to accommodate all the data at hand (whether simulated or experimental data) into an empty design layout (Jeirani et al., 2013).

However, unlike CCD and D-optimal design, historical data design is probably the least go-to feature, as according to the official site of StatEase, they don't recommend for historical data to be used if there's a possibility of carrying out a designed experiment. (*Stat-Ease » V11 » Tutorials » Historical Data*, n.d.). Thus, relatively lesser research/literature are available regarding RSM via historical data, specifically for optimization of the process parameters of LFP. However, undoubtedly, there are still researchers who have implemented this method. Salam et al., (2018) studied the application of RSM via historical data design type for the

optimization of sand minimum transport condition in which R^2 achieved was very high at 0.9941. Besides that, in an article published by Nookaraju et al. in recent year of 2020, they've investigated on the optimization of hybrid wick heat pipe via RSM historical data design in which the ideal values of the parameters of mass stream rate, tilt angle and heat input are 0.04 kg/s, 15 ° and 176 watts respectively.

However, there is yet to be a RSM of process parameters of $LiFePO_4$ via FSP (solid-state reaction) which further indicates the motive of this research. Hence, this research is carried out to perform RSM for the process parameters, particularly, carbon content, and calcination temperature.

CHAPTER 3

METHODOLOGY

This chapter discloses information on the methods implemented in this final year project which includes the general research flow diagram and the project activities (timeline). **Figure 3. 1** displays the general research flow whilst the experimental design matrix for the 1-factor optimal design and central composite design (CCD) shown **Table 3. 1** and **Table 3. 4** individually. Meanwhile, the variables and coded variables levels were shown in **Table 3. 2** and **Table 3. 3** flaunts the variables involved and their respective units. Lastly, the experimental design matrix for the comparison of three different types of RSM were tabulated and as illustrated in **Table 3. 5**. The methodology is then briefly explained prior to the report.

3.1 Overview of research methodology

In order to optimize the two parameters of calcining temperature and carbon content, a mathematical and statistical analysis method, which is RSM was implemented along with the aid of a statistical software, known as Design Expert by StatEase. **Figure 3. 1** displays the general research flow.

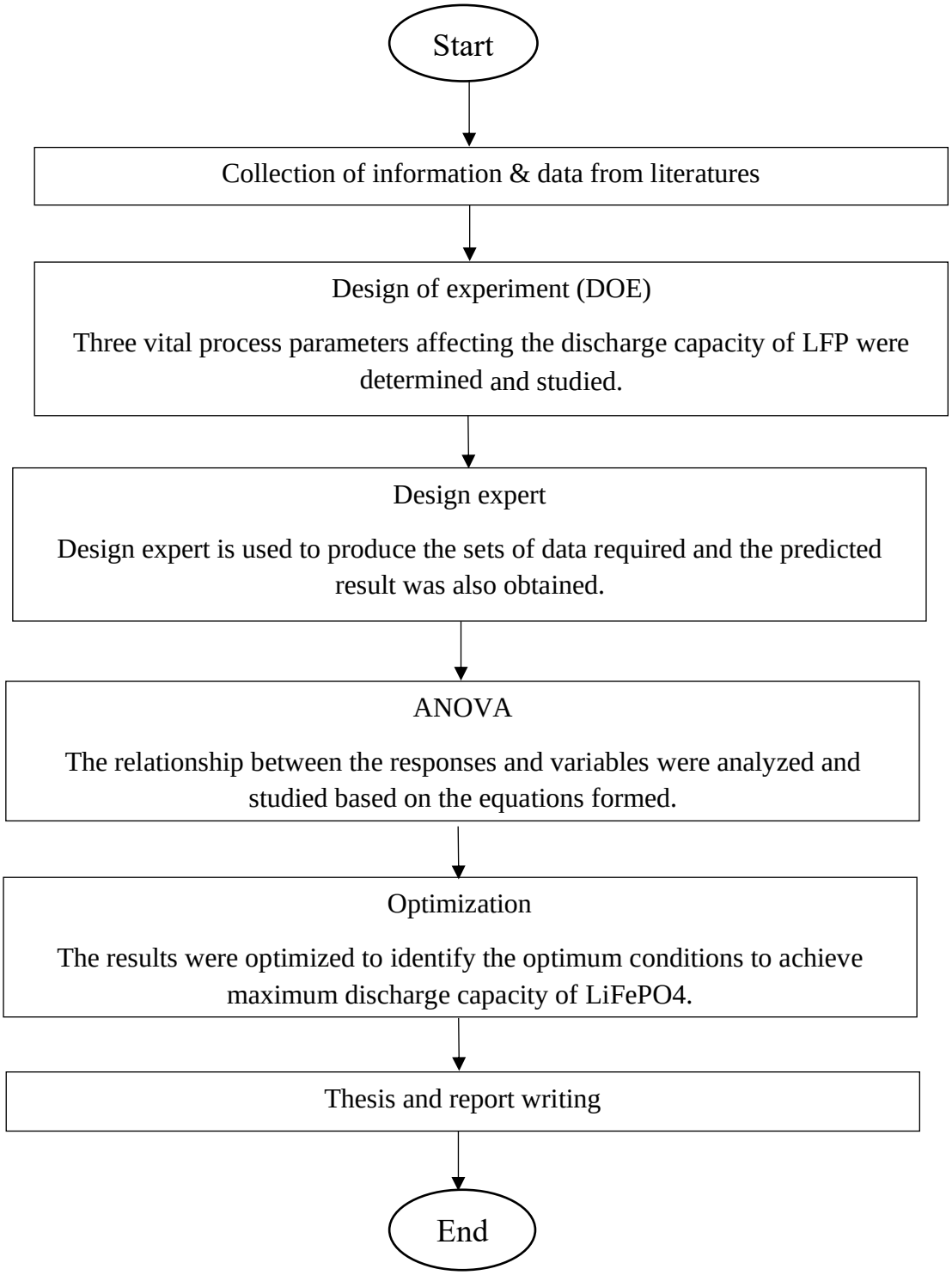

Figure 3. 1 General research flow diagram for this final year project

3.2 Collection of information & data from literature

A statistical software, known as Design Expert v11 was used to study the optimization of synthesis parameter of $LiFePO_4$. Thus, the data used with the software are vital in ensuring an accurate and trustworthy result. There are two details that will be used for the optimization which is:

i) Synthesis of $LiFePO_4$ via flame spray pyrolysis.

ii) Effect of calcination temperature and carbon content on discharge capacity.

Hence, the data are extracted from (Hamid et al., 2012, 2015):

- Hamid, N. A., Wennig, S., Hardt, S., Heinzel, A., Schulz, C., & Wiggers, H. (2012). High-capacity cathodes for lithium-ion batteries from nanostructured $LiFePO_4$ synthesized by highly-flexible and scalable flame spray pyrolysis.
- Hamid, N. A., Wennig, S., Heinzel, A., Schulz, C., & Wiggers, H. (2015). Influence of carbon content, particle size, and partial manganese substitution on the electrochemical performance of $LiFe_xMn_{1-x}PO_4$/carbon composites

3.3 Design of Experiment (DOE) & Design Expert

The first simulation done was the optimization of precursor concentration in which one of the features of Design Expert V11 to be used which is the 1-factor D-optimal design (one factor). The experimental design matrix generated by the software is as shown in **Table 3. 1**.

Table 3. 1 Experimental design matrix generated for precursor concentration

Runs	Factor
	Precursor concentration (M)
1	0.35
2	0.05
3	0.35
4	0.2
5	0.0125
6	0.0125
7	0.2
8	0.2
9	0.0125
10	0.2

Then, the optimization of the two main process parameters to are the calcination temperature and glucose content to yield the highest discharge capacity. A range of value from the minimum to the maximum was set for both the parameters and is implemented in Design Expert software. The design selected for RSM was Central Composite Design (CCD). **Table 3. 2** display the low and high levels of the variables whereas **Table 3. 3** shows the factors and its unit.

Table 3. 2 Variables and coded variable levels for CCD in DOE

Factor	Variable	Coded variable levels	
		-1	+1
A	Calcination temperature	600	800
B	Glucose content	10	30

Table 3. 3 Variables and unit

Variable	Coded variable levels
Calcination temperature	℃
Glucose content	%
Discharge capacity	mAh g^{-1}

Similarly, to the earlier simulation for precursor concentration, an experimental design matrix was generated by Design Expert and is as shown below:

Table 3. 4 Experimental design matrix generated by Design Expert (CCD)

Std	Run	Factor 1 A: Temperature (℃)	Factor 2 B: Glucose content (%)
2	1	800	10
1	2	600	10
5	3	600	20
12	4	700	20
4	5	800	30
11	6	700	20
8	7	700	30
3	8	600	30
6	9	800	20
7	10	700	10
13	11	700	25
10	12	700	20
9	13	700	20

Upon the optimization of the two parameters via CCD, 2 different optimization method which are D-optimal design and historical data design were applied to compare which simulation method would generate better results, statistically. Then, D-optimal design followed by historical data was selected in the system and the details required was keyed into the software respectively. As a comparison between different type of RSM would be made, particularly between CCD, D-Optimal design and historical data design, the design matrix for the two latter type of RSM would only require 7 and 8 minimal points which are as shown in **Table 3. 5** and **Table 3. 6** respectively.

Table 3. 5 Experimental design matrix generated by Design Expert (D-optimal design)

Run	Factor 1 A: Temperature (℃)	Factor 2 B: Glucose content (%)
1	800	10
2	600	30
3	600	20
4	700	20
5	700	30
6	800	30
7	600	10

Table 3. 6 Experimental design matrix generated by Design Expert (historical data design)

Run	Factor 1 A: Temperature (℃)	Factor 2 B: Glucose content (%)
1	800	10
2	600	10
3	600	20
4	700	20
5	800	30
6	700	20
7	700	30
8	600	30

3.4 Statistical Analysis

After keying in all the required data of both the independent and responding variables, it is only logical to analyze to analyze the result obtained and its validity. Hence, a built-in statistical analysis tool in Design Expert can be utilized. Particularly, the fitness of the equations/models obtained from the software can be assessed through the analysis of variance (ANOVA). This analysis is typically carried out to justify and verify the adequacy of the model. It is also essential in determining the influence of each independent variables attained from experimental results by DOE and interpret the data. Then, ANOVA is done via Design Expert software and typically the F-value (Fisher variation ratio) obtained is compared to the "Prob" whereby the value of Prob > F and less than 0.05 indicates that the model is significant. Hence, the models obtained were all validated and justified via this approach. Then, the responding variable of particle size and discharge capacity with the unit of nm and mAh g^{-1} of $LiFePO_4$

and where the former is influenced by the precursor concentration while the latter by the glucose content and calcination temperature will be fitted into a second-order polynomial regression model as below **(Eq. 1)**:

$$y = \beta_o + \sum_{i=1}^{n=1/2} \beta_i x_i + \sum_{i=1}^{n=1/2} \beta_{ii} x_i^2 + \sum_{i=1}^{n=1/2} \sum_{j=1+1}^{n=1/2} \beta_{ij} x_i x_j + \varepsilon$$

Where y is the predicted response of our response variable, either being the particle size or discharge capacity, β_o is the intercept coefficient, β_i is the coefficient of linear term, β_{ii} is the coefficient of quadratic term, ε is a term representing the other sources of variability that is not accounted by the response function (typically nil) and lastly n is indicating the number of parameters which for the case when the responding variable is the particle size, n = 1 and when the responding variable is discharge capacity, n = 2. The fitness of the polynomial model generated is normally conveyed based on the value of correlation coefficient, R^2. Besides the F-value mentioned in the earlier paragraph, another important indicator that demonstrates the significance and adequacy of the model is the p-value (probability value), adequate precision value, and also the value of predicted residual error sum of squares (PRESS).

3.5 Optimization for discharge capacity

The discharge capacity was optimized by applying central composite design (CCD) of one of the many designs of RSM. The optimized value of the responding variable was obtained by specifying the maximum and minimum limit (range) for the two manipulated variables. The optimized values can be obtained upon running the simulation and the results of graphs and tables such as the 3-D graph can be obtained and thus, proceeding to the final methodology.