SYNTHESIS AND CHARACTERIZATION OF LITHIUM IRON PHOSPHATE NANOWIRES FROM SAGO PITH WASTE CELLULOSE NANOFIBRIL AEROGEL

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UNIVERSITI TEKNOLOGI MALAYSIA
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A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Philosophy

Faculty of Chemical and Energy Engineering
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To my beloved father and mother,
ACKNOWLEDGEMENT

First and foremost, I thank God for leading me in this research journey. Next, I would like to express my gratitude to my supervisors, Dr. Lai Jau Choy and Dr. Lim Teck Hock for giving me an opportunity to complete this thesis under their supervision. I am very grateful to receive their constant guidance and time in completing this research.

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This project aimed to produce highly crystalline lithium iron phosphate coated aerogel (LiFePO₄ nanowires) via coating and sintering LiFePO₄ on the surface of an aerogel template prepared from cellulose nanofibril (SPCNF) extracted from sago pith waste (SPW). The effects of SPCNF aerogel quantity (Xₚ), sintering duration (Xₜ) and sintering temperature (Xₜ) on the quality of LiFePO₄ were studied. Specifically, SPCNF were first extracted from SPW through combined chemical and mechanical treatments, followed by a freeze-drying step to produce an aerogel. The resulting white and spongy SPCNF aerogel was characterized to elucidate its morphology, crystallinity, and thermal resistance using field-emission scanning electron microscopy, powder x-ray diffraction (PXRD) and thermogravimetric analysis, respectively. Results showed that the morphology of SPCNF aerogel resembled that of a web-like structure with the diameters of each SPCNF measured to be within 15-30 nm. The degree of crystallinity of the aerogel was approximately 88.38% and its thermal degradation temperature was in the range of 260-350 °C. The aerogel was then coated with LiFePO₄ through direct coating on aerogel by applying a uniform solution containing Li⁺, Fe²⁺ and PO₄³⁻ in 1:1:1 molar ratio and followed by calcination and sintering. The final product, LiFePO₄ nanowires had wire-like structure with the diameters between 15-30 nm, and the PXRD and transmission electron microscopy verified the nanowires were covered with LiFePO₄. Results from design of experiment of full-factorial design showed that the three parameters are significant and the coating quality, Y can be correlated with the following equation: Y = 5.662 + 7.23875Xₚ + 7.23875Xₜ + 5.60125XₚXₜ + 7.23875XₚXₚXₜ + 5.60125XₜXₚXₚXₜ + 5.60125XₚXₜXₚXₜ.
ABSTRAK

Projek ini bertujuan untuk menghasilkan kristal litium besi fosfat bersalut aerogel (nanodawai LiFePO₄) melalui penyalutan ke permukaan templat aerogel nanofibril selulosa (SPCNF) yang diekstrak daripada hampas sagu (SPW). Kesan kuantiti aerogel SPCNF (Xₚ), tempoh pensinteran (Xₜ) dan suhu pensinteran (Xₜ) ke atas kualiti LiFePO₄ telah dikaji. Secara khusus, SPCNF diekstrak daripada SPW melalui gabungan rawatan kimia dan mekanikal, diikuti oleh pengeringan secara pembekuan untuk menghasilkan aerogel. Aerogel SPCNF yang bertekstur lembut dan berwarna putih dicirikan dari segi morfologi, darjah penghabluran dan rintangan haba, masing-masing melalui kaedah bidang pelepasan mengimbas mikroskopi elektron, pembelauan sinar-x serbuk (PXRD) dan analisis termogravimetri. Hasil ujian menunjukkan bahawa morfologi aerogel SPCNF adalah dalam struktur bentuk web dengan diameter SPCNF dalam lingkungan 15-30 nm. Darjah penghabluran aerogel SPCNF adalah sebanyak 88.38% dan degradasi termal berlaku pada suhu antara 260-350 °C. Aerogel tersebut kemudian disaluti dengan LiFePO₄ melalui penyalutan langsung ke atas aerogel dengan menggunakan satu larutan homogen yang mengandungi ion Li⁺, Fe²⁺ dan PO₄³⁻ dalam nisbah molar 1:1:1 dan diikuti oleh proses pengkalsinan dan pensinteran. Produk terakhir, nanodawai LiFePO₄ mempunyai struktur bentuk dawai dengan diameter dalam lingkungan 15-30 nm, dan analisis PXRD dan transmisi elektron mikroskopi mengesahkan nanodawai telah diliputi dengan LiFePO₄. Keputusan daripada rekabentuk eksperimen faktorial penuh menunjukkan bahawa ketiga-tiga parameter tersebut adalah penting dan boleh dihubungkaitkan dengan kualiti salutan, Y melalui persamaan berikut: 

\[ Y = 5.662 + 7.23875X_p + 7.23875X_t + 5.60125X_T + 7.23875X_pX_t + 5.60125X_pX_T + 5.60125X_tX_T + 5.60125X_pX_tX_T. \]
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
<td></td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
<td></td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
<td></td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
<td></td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS AND SYMBOLS</td>
<td>xiv</td>
<td></td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xvii</td>
<td></td>
</tr>
</tbody>
</table>

1 INTRODUCTION
1.1 Background of the Study 1
1.2 Problem Statement 3
1.3 Objectives 5
1.4 Significance of the Study 5
1.5 Scope of the Study 6

2 LITERATURE REVIEW
2.1 Sago Pith Waste 7
2.2 Cellulose 8
2.3 Nanocelluloses 10
   2.3.1 Cellulose Nanocrystal 12
   2.3.2 Cellulose Nanofibril 14
2.3.3 Mechanical Treatments 15
  2.3.3.1 Grinding Process 15
  2.3.3.2 Blender 16

2.4 Energy Consumption and New Processes 16

2.5 Pre-treatments 17
  2.5.1 Enzymatic Pre-treatment 17
  2.5.2 2,2,6,6-tetramethyl-1-piperidinyloxy-Mediated Oxidation 18

2.6 Effects of the Production Methods on the Morphology of Cellulose Nanofibril 19

2.7 Aerogel 20

2.8 Nanocellulose Aerogel from Cellulose Nanofibril 22

2.9 Lithium Iron Phosphate as Cathode Material 24

2.10 Lithium Iron Phosphate 26

2.11 Methods for Synthesizing Lithium Iron Phosphate 28
  2.11.1 Solid State Method for Synthesizing Lithium Iron Phosphate Powders 28
    2.11.1.1 Solid State Synthesis 28
    2.11.1.2 Microwave Heating 29
  2.11.2 Solution-Based Methods for Synthesizing Lithium Iron Phosphate Powders 30
    2.11.2.1 Hydrothermal Synthesis 30
    2.11.2.2 Sol-Gel Synthesis 31

2.12 Approaches to Improve the Electrochemical Performance of Lithium Iron Phosphate 32
  2.12.1 Carbon Coating 32
  2.12.2 Reduction of Lithium Iron Phosphate Particle Size 33

2.13 Nanowires 34
2.14 Lithium Iron Phosphate Nanowires 35
2.15 Summary 38

3 METHODOLOGY 40
3.1 Raw Material and Chemicals 40
  3.1.1 Sago Pith Waste 40
  3.1.2 Chemicals and Reagents 41
3.2 Sago Pith Waste Cellulose Nanofibril Extraction and Sago Pith Waste Cellulose Nanofibril Aerogel Formation 43
3.3 Synthesis of Lithium Iron (II) Phosphate Precursors 43
3.4 Synthesis of Lithium Iron (II) Phosphate Nanowires 44
3.5 Lithium Iron (II) Phosphate Quality Optimization via Design of Experiment 44
3.6 Characterization Sago Pith Waste, Sago Pith Waste Cellulose Nanofibril and Sago Pith Waste Cellulose Nanofibril Aerogel 46
  3.6.1 Fourier Transform Infra-Red Spectroscopy 46
  3.6.2 Thermo-gravimetric Analysis 47
3.7 Characterization Lithium Iron (II) Phosphate Nanowires 47
  3.7.1 Simultaneous Thermo-gravimetric Analysis 47
  3.7.2 Powder X-Ray Diffraction 47
  3.7.3 Field Emission Scanning Electron Microscopy 48
  3.7.4 Transmission Electron Microscopy 48

4 RESULTS AND DISCUSSIONS 50
4.1 Characterization of Sago Pith Waste Cellulose Nanofibril Aerogel 50
4.1.1 Field Emission Scanning Electron Microscopy 51
4.1.2 Fourier Transform Infra-Red Analysis 53
4.1.3 Powder X-ray Diffraction 56
4.1.4 Thermo-gravimetric Analysis 58
4.2 Simultaneous Thermo-gravimetric Analysis of Lithium Iron (II) Phosphate Powder 61
4.3 Characterization of the Synthesized Lithium Iron (II) Phosphate Nanowires 63
4.4 Modelling and Simulation of Quality Lithium Iron (II) Phosphate Nanowires 68
4.5 Validation of Predicted Quality of Lithium Iron (II) Phosphate Nanowires Model 73

5 CONCLUSIONS AND RECOMMENDATIONS 78
5.1 Conclusion 78
5.2 Recommendations 80

REFERENCES 81
Appendices A-C 103-108
## LIST OF TABLES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Chemicals used for the experiments</td>
<td>41</td>
</tr>
<tr>
<td>3.2</td>
<td>Solvents used for the experiments</td>
<td>42</td>
</tr>
<tr>
<td>3.3</td>
<td>Parameter levels of the experimental design</td>
<td>45</td>
</tr>
<tr>
<td>3.4</td>
<td>The formulation table arrangement</td>
<td>46</td>
</tr>
<tr>
<td>4.1</td>
<td>Major peaks in the FTIR spectra of SPW and SPCNF aerogel</td>
<td>54</td>
</tr>
<tr>
<td>4.2</td>
<td>Thermal parameters obtained from TG and DTGA curves of SPW and SPCNF aerogel</td>
<td>60</td>
</tr>
<tr>
<td>4.3</td>
<td>Experimental results for the quality LiFePO$_4$ nanowires (%)</td>
<td>69</td>
</tr>
<tr>
<td>4.4</td>
<td>Example of calculation the yield of LiFePO$_4$ nanowires using Image J</td>
<td>71</td>
</tr>
<tr>
<td>4.5</td>
<td>Summary of Fit of the Developed Model for Quality LiFePO$_4$ nanowires</td>
<td>72</td>
</tr>
<tr>
<td>4.6</td>
<td>Comparison between predicted and experimental values for quality LiFePO$_4$ nanowires</td>
<td>74</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Relationships between the polymorphs of cellulose.</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Hierarchical structure from plant to cellulose chains.</td>
<td>10</td>
</tr>
<tr>
<td>2.3</td>
<td>Hierarchical relationship of nanocellulose terms.</td>
<td>12</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic illustration of CNC and CNF production via mechanical and chemical treatments, respectively.</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>Cellulose aerogel.</td>
<td>21</td>
</tr>
<tr>
<td>2.6</td>
<td>Application fields for aerogel products.</td>
<td>21</td>
</tr>
<tr>
<td>2.7</td>
<td>Effect of CNF content on the microstructure of aerogels.</td>
<td>23</td>
</tr>
<tr>
<td>2.8</td>
<td>The crystal structure of olivine LiFePO₄.</td>
<td>26</td>
</tr>
<tr>
<td>2.9</td>
<td>(a) Ge (b) GaN (c) ZnO nanowires.</td>
<td>34</td>
</tr>
<tr>
<td>2.10</td>
<td>Synthesis of LiFePO₄/ CNTs nanowires using atomic layer deposition.</td>
<td>36</td>
</tr>
<tr>
<td>2.11</td>
<td>Triaxial LiFePO₄ nanowires.</td>
<td>36</td>
</tr>
<tr>
<td>3.1</td>
<td>Overall flow for the synthesis of LiFePO₄ nanowires.</td>
<td>49</td>
</tr>
<tr>
<td>4.1</td>
<td>(a) SPW, (b) A cellulose fibre suspension after chemical and mechanical treatments and (c) SPCNF aerogel after freeze-drying.</td>
<td>51</td>
</tr>
<tr>
<td>4.2(a)</td>
<td>FE-SEM micrograph of SPCNF aerogel produced after freeze-drying SPW (10,000 X).</td>
<td>52</td>
</tr>
<tr>
<td>4.2(b)</td>
<td>Freeze-dried SPCNF aerogel (100,000X).</td>
<td>52</td>
</tr>
<tr>
<td>4.3</td>
<td>FTIR spectra of SPW and SPCNF aerogel. Red boxes indicate signals originated from lignin and hemicelluloses which were not no longer observed in the SPCNF aerogel.</td>
<td>53</td>
</tr>
<tr>
<td>4.4</td>
<td>Simple schematic diagram after chemical treatment of lignocellulosic fibres.</td>
<td>55</td>
</tr>
<tr>
<td>4.5</td>
<td>X-Ray Diffractogram of (a) SPW and (b) SPCNF aerogel.</td>
<td>57</td>
</tr>
<tr>
<td>4.6</td>
<td>Mass loss curves and derivatives mass loss curves of SPW and SPCNF aerogel.</td>
<td>59</td>
</tr>
</tbody>
</table>
4.7 STA analysis of a control sample of LiFePO₄ prepared without SPNCF aerogel template. 62

4.8 FE-SEM micrograph and EDX spectrum of thermally annealed SPCNF aerogel without LiFePO₄ as a control. Au signals arisen from the coating process to reduce charging effect. 65

4.9 FE-SEM micrograph and EDX spectrum of LiFePO₄ nanowires. 66

4.10 TEM image, EDX spectrum and XRD pattern (matched with standard LiFePO₄, Li₃PO₄ and Fe₃O₄) of LiFePO₄ nanowires. 67

4.11 Images of LiFePO₄ nanowires at different smoothness (a) very smooth (b) smooth (c) rough. 70

4.12 Optimization graph of the quality of LiFePO₄ nanowires. 74

4.13 FE-SEM micrographs of experimental samples of LiFePO₄ nanowires. 76

4.14 Comparison XRD patterns of experimental samples of LiFePO₄ nanowires at different sintering temperature and time. 77
## LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>1-Dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>2-Dimensional</td>
</tr>
<tr>
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<td>3-Dimensional</td>
</tr>
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<td>AGU</td>
<td>Anhydroglucose Unit</td>
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<tr>
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</tr>
<tr>
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</tr>
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<td>Carbon atom</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>Toluene</td>
</tr>
<tr>
<td>-C-C</td>
<td>Carbon-carbon</td>
</tr>
<tr>
<td>CFs</td>
<td>Carbon Fibers</td>
</tr>
<tr>
<td>-CH</td>
<td>Methyl group</td>
</tr>
<tr>
<td>CH(_3)COOLi</td>
<td>Lithium Acetate</td>
</tr>
<tr>
<td>CMC</td>
<td>Cellulose Microcrystal</td>
</tr>
<tr>
<td>CMF</td>
<td>Cellulose Microfibril</td>
</tr>
<tr>
<td>CNC</td>
<td>Cellulose Nanocrystal</td>
</tr>
<tr>
<td>CNF</td>
<td>Cellulose Nanofibril</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>-C–O</td>
<td>Carbon-Oxygen Bond</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>DoE</td>
<td>Design of experiment</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of Polymerization</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Analysis</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>EVs</td>
<td>Electric Vehicles</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe(CH₃COO)₂</td>
<td>Iron (II) Acetate</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>Iron (II) ion</td>
</tr>
<tr>
<td>Fe₂P</td>
<td>Iron Phosphide</td>
</tr>
<tr>
<td>FeC₂O₄·2H₂O</td>
<td>Iron (II) Oxalate Dihydrate</td>
</tr>
<tr>
<td>FeC₂O₄·H₂O</td>
<td>Iron (II) oxalate monohydrate</td>
</tr>
<tr>
<td>FeCl₂·4H₂O</td>
<td>Iron (II) chloride tetrahydrate</td>
</tr>
<tr>
<td>FeO₆</td>
<td>Iron Oxide</td>
</tr>
<tr>
<td>FePO₄</td>
<td>Iron (III) Phosphate</td>
</tr>
<tr>
<td>FePO₄(H₂O)₂</td>
<td>Iron (III) Phosphate Dihydrate</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>HEVs</td>
<td>Hybrid Electric Vehicles</td>
</tr>
<tr>
<td>HIUS</td>
<td>High Intensity Ultrasonication</td>
</tr>
<tr>
<td>HSO</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Lithium ion</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>Lithium Carbonate</td>
</tr>
<tr>
<td>Li₄P₂O₇</td>
<td>Lithium Pyrophosphate</td>
</tr>
<tr>
<td>LiBs</td>
<td>Lithium Ion Batteries</td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>Lithium Cobalt Oxide</td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium Fluoride</td>
</tr>
<tr>
<td>LiFePO₄</td>
<td>Lithium Iron Phosphate</td>
</tr>
<tr>
<td>LiFePO₄/C</td>
<td>Lithium Iron Phosphate Coated Carbon</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>Mn-based spinels lithiated transition metal oxides</td>
</tr>
<tr>
<td>LiMO₂</td>
<td>lithiated transition metal oxides</td>
</tr>
<tr>
<td>LiO₆</td>
<td>Lithium Oxide</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>Lithium hydroxide monohydrate</td>
</tr>
<tr>
<td>LiₓMᵧ(XO₄)₂</td>
<td>polyanion-type lithiated transition metal oxides</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
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</tr>
<tr>
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<td>Tin Oxide</td>
</tr>
<tr>
<td>SPCNF</td>
<td>Sago Pith Cellulose Nanofibril</td>
</tr>
<tr>
<td>SPW</td>
<td>Sago Pith Waste</td>
</tr>
<tr>
<td>STA</td>
<td>Simultaneous Thermal Analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-Tetramethyl-piperidin-1-yl)oxy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TMP</td>
<td>TEMPO-Mediated Oxidation</td>
</tr>
<tr>
<td>wt %</td>
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</tr>
<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Preliminary Test Results</td>
<td>103</td>
</tr>
<tr>
<td>B</td>
<td>Calculation the Density of Sago Pith Cellulose Nanofibril Aerogel</td>
<td>105</td>
</tr>
<tr>
<td>C</td>
<td>The Peak Matching Results of the XRD Diffractogram for LiFePO$_4$ Nanowires which were Synthesized at Different Temperatures (423, 460 and 500 °C) and Sintering durations (136, 163 and 180 minutes)</td>
<td>106</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Malaysia is the world’s third largest exporter of sago starch with a total sago palm plantation area of 68,000 ha, after Indonesia (1,843,278 ha) and Papua New Guinea (1,020,000 ha) (Ahmad, 2014). Each year, a large amount of agro-residue termed sago pith waste (SPW) or hampas by the locals, is generated during the processing of the rasped pith of the sago palm trees. Improper handling of this agro-waste can eventually cause environmental problems (Toh et al., 2011). To date, different works have been done in order to turn the SPW into value-added products. For example, as an alternative substrate for fermentable sugars production (Linggang et al., 2012), bioethanaol production (Saravana et al., 2014) and etc.

Aerogel is a highly porous material with high specific surface area, low density and low thermal conductivity. It can be used as thermal insulators, super adsorbents, batteries and more. Kitsler (1932) published the first report on aerogel prepared from inorganic gels. The main drawback of these inorganic aerogel is their poor mechanical properties (brittle and fragile) and thus, organic aerogels were introduced (Kim et al., 2011). Cellulose nanofibril (CNF) aerogel is a strong organic aerogel. The fibrillar morphology of and strong mutual hydrogen bonds in CNF facilitate the mechanical ductility and flexibility of the aerogel (Chen et al., 2011 and Pääkkö et al., 2008). Due to their mechanical robustness, CNF aerogels can be used in various applications such
as templates for synthesizing inorganic hollow nanotubes (Korhonen et al., 2011) and cobalt-ferrite nanoparticles (Olsson et al., 2010).

Lithium iron phosphate (LiFePO₄) has been identified as the most promising cathode material for making lithium ion batteries because of its low cost, high theoretical capacity (170 mAh g⁻¹) and long cycle life (Zhang, 2010). LiFePO₄ in the form of nano-sized particles has a higher surface electrochemical reactivity, shorter diffusion length for electrons and Li-ions and thus, better electrochemical performance (Yamada et al., 2001, Jamnik et al., 2003, Dominko et al., 2007 and Saravanan et al., 2009). Therefore, different synthetic methods were introduced for the preparation of nano-sized LiFePO₄ (Gong et al., 2011). For instance, hydrothermal method was used by Yang et al., (2001) to produce high purity, single crystalline LiFePO₄ nano-particles. This method, however, requires long time i.e. three days to complete the synthesis process. After that, solvothermal processes were utilized by Muraliganth et al. (2008), Murugan et al. (2008) and Saravanan et al. (2009) to produce nanostructured LiFePO₄. Some drawbacks of this method include, low precursor solubility, high cost and high reaction temperature.

Numerous studies have also been done to synthesize nano-sized LiFePO₄ with different morphologies such as nanoparticles (Delacourt et al., 2006), nanoplates (Saravanan et al., 2009) and nanowires (Lin et al., 2008 and Zhang, et al., 2013). Among the wide range of morphologies, nanowires are identified as the most promising morphology because they offer a better electrical percolation behaviour which means a higher conductivity comparing to that of other morphologies (Bruce et al., 2008).

In this project, LiFePO₄ nanowires were synthesized by using a new approach in which, the precursors of LiFePO₄ are first coated onto sago pith cellulose nanofibrils (SPCNF) aerogel. The coated SPCNF aerogel is then sintered at high temperature in a conventional furnace under N₂ atmosphere to produce highly crystalline LiFePO₄ nanowires.
1.2 Problem Statement

As the world’s third largest exporter of sago starch, Malaysia produces up to 47,000 metric tons of sago starch annually (Uthumporn et al., 2014). It is estimated that for every kilogram of sago starch extracted, a kilogram of SPW is produced (Lai et al., 2013). These wastes are normally dumped into the rivers together with the waste water. In other words, each year, 52,000 tons of SPW ends up polluting the rivers by increasing the biochemical oxygen demand (BOD) of the water. Microbiological degradation of the waste consumes oxygen dissolved in the water, leaving the water with insufficient oxygen to support higher forms of life.

One of the ways to minimize the impact of SPW is to utilize it and convert it into some value-added products such as biofuels, biomaterial, template etc. Kumaran and co-workers (1997) utilized SPW as a substrate for the production of enzyme via solid substrate fermentation. Besides that, SPW was also used as an additional carbon source in anaerobic digesters for the production of biogas (Abd-Aziz, 2002), an alternative substrate for fermentable sugars production (Linggang et al., 2012) and bioethanol production (Saravana et al., 2014). To the best of the author’s knowledge, to date, no report on the extraction of SPCNF from SPW is available.

In average, SPW contains about 23% by weight of cellulose (Linggang et al., 2012). It is believed that SPCNF could be extracted from SPW via chemical, mechanical or a combination of both methods, like what other researchers obtained from different types of lignocellulosic agricultural wastes (Jiang et al., 2013 and Chen et al., 2014). The extracted SPCNF adopt a shape similar to that of nanowires and their surface contain plenty of hydroxyl functional groups which could interact with different types of chemical compounds including metal ions via electrostatic attraction or complexation. Therefore, SPCNF has the potential to serve as a template for the synthesis of inorganic nanowires, for example LiFePO₄.
LiFePO$_4$ is an important nano-sized material for the manufacturing of rechargeable battery. It is used as cathode because of its high specific capacity (170 mAh g$^{-1}$), a relatively high redox potential (3.5V), long cycle life, and high stability (Wang et al., 2008, Wu et al., 2011). Researchers reported that, LiFePO$_4$ nanowires are more efficient as compared to that of in the form of spherical nanoparticles in conducting electricity, due to its longer mean free path (Zhu et al., 2006). Unfortunately, to date, LiFePO$_4$ only available commercially in spherical nanoparticle form because its synthesis method is easier to be industrialized for mass production (Park et al., 2009, Ban et al., 2010 and Carbana et al., 2010). Therefore, the need for the works on developing a simple and scalable method for synthesizing LiFePO$_4$ nanowires has certainly been recognized in order to solve this problem.

Hence, it is hypothesized that LiFePO$_4$ nanowires can be synthesized via a two-stage, facile synthetic method which involves the coating and calcination of LiFePO$_4$ on a SPCNF template. SPCNF surface contains plenty of hydroxyl functional groups which are able to form complex with iron (II). Lithium ion, Li$^+$ and phosphate, PO$_4^{3-}$ precursors can then be added to form LiFePO$_4$ upon calcinations.

Although the direct use of SPCNF is hypothesized to be able to assist in the formation of LiFePO$_4$ nanowires, it is highly likely that LiFePO$_4$ particles could formed as a by-product, along with the formation of the nanowires. If this happened, these particles would be challenging to be separated from the nanowires and will exist as a contaminant (Lele et al., 2014). To circumvent this particle contamination issue, it is hypothesised that converting the free-standing SPCNF into a SPCNF aerogel with large surface area would help. In aerogel form, the precursor solutions of LiFePO$_4$ could be better absorbed via capillary force on the surface. After drying, a thin layer of amorphous LiFePO$_4$ could be annealed into crystalline LiFePO$_4$ nanowires formed on the SPCNF surface and following the wire-like contour of individual SPCNF within the aerogel (Melone et al., 2013).
Therefore, this aim of this project is focused on producing LiFePO$_4$ nanowires from the precursor coated SPCNF aerogel. The precursors are expected to be coated onto the aerogel uniformly after solvent removal and be transformed into crystals at elevated temperature. Individual SPCNF in the aerogel are expected to serve as a template/platform for LiFePO$_4$ nanowires to grow upon.

1.3 Objectives

1. To synthesize and characterize SPCNF aerogel interconnected structure with web-like appearance.

2. To synthesize and characterize LiFePO$_4$ nanowires and study the effects of SPCNF aerogel’s quantity, sintering temperature and sintering duration on the quality of the LiFePO$_4$ nanowires.

1.4 Significance of the Study

The most significant contribution of this study is that LiFePO$_4$ nanowires, a very important cathode material can be obtained via a relatively safe and simple method namely, coating of LiFePO$_4$ onto the SPCNF aerogel followed by calcinations. The proposed use of aerogel template is expected to reduce the formation of particulate impurities. Additionally, this project might lead to a new application for SPCNF, thus converting this low value, environmental-polluting agricultural waste into value-added consumer products.
1.5 Scope of the Study

In this project, SPCNF was extracted from SPW using a combination of chemical and mechanical methods. The extracted SPCNF was transformed into aerogel via freeze drying. Meanwhile, LiFePO$_4$ precursors were synthesized from Iron (II) chloride, FeCl$_2$, lithium hydroxide monohydrate, LiOH.H$_2$O and phosphoric acid, H$_3$PO$_4$ using a mixture of ethylene glycol and water.

Coating of the LiFePO$_4$ precursors onto the SPCNF aerogel to produce LiFePO$_4$ nanowires were studied by varying three parameters namely, quantity of the SPCNF aerogel (0.02-0.06 g), sintering temperature (300-500 °C) and sintering duration (60-180 min). Effects of the three parameters toward the quality of the LiFePO$_4$ nanowires were evaluated using design of experiment (DOE) with the aid of a software namely, JMP 13.

Characterizations of the SPCNF aerogel and LiFePO$_4$ nanowires were done through the following techniques: lattice structure and elemental composition were analysed by Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS), surface morphology was characterized by Field-Emission Scanning Electron Microscopy, (FE-SEM). Chemical analysis was accomplished via Fourier Transform Infrared Spectroscopy (FTIR) and Powder X-ray diffraction (PXRD). Lastly, thermal stability was evaluated by using Thermo-gravimetric Analysis (TGA) and Simultaneous Thermal Analysis (STA).
REFERENCES


