Fundamental electrochemical studies on nanoarchitected olivine phosphates and vanadium pentoxide cathodes for lithium ion batteries

Cheah, Yan Ling

2013

Cheah, Y. L. (2013). Fundamental electrochemical studies on nanoarchitected olivine phosphates and vanadium pentoxide cathodes for lithium ion batteries. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/51105>

<https://doi.org/10.32657/10356/51105>

FUNDAMENTAL ELECTROCHEMICAL STUDIES ON
NANOARCHITECTURED OLIVINE PHOSPHATES AND
VANADIUM PENTOXIDE CATHODES FOR LITHIUM ION
BATTERIES

Cheah Yan Ling

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2013

Acknowledgements

It would not have been possible to write this thesis without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here.

This thesis would not have been possible without the help, support and patience of my principal supervisor, Asst. Prof. Madhavi Srinivasan. Her constant guidance and encouragement enabled the successful completion of my research for Ph. D.

I would like to acknowledge the financial, academic and technical support of the Nanyang Technological University, and its staff, particularly in the award of a Postgraduate Research Scholarship that provided the necessary financial support for this research.

I would like to thank the post-docs Dr Andreas Markus Kiebele, Dr Martti Kaempgen, Dr Yogesh Sharma, Dr Nutan Gupta, Dr Sudeshna Chaudhari, Dr Grace Wee, Dr Wong Chui Ling and Dr Vanchiappan Aravindan, for their invaluable support and advices throughout my Ph. D. studies. Not forgetting also my other labmates for providing a cheerful and supportive research environment, especially Tingji, Pei Fen, Chee Siang and Shubha, who often share my lab duties. I will always remember my Final Year Project (FYP) students Sujun, Yihong, Song Yan, Chang Kwang, Kim, Edmund and Kai Yang, with whom I underwent many learning journeys and I appreciate their patience and understanding.

I would also like to thank Dr Ali Rinaldi and Mr Rajiv Ramanujan for their help in Raman measurements, Prof Richard Webster and Dr Bahareh Khezri (School of Physical and Mathematical Sciences, NTU) in providing their assistance with inductively coupled plasma (ICP) analyses. I also acknowledge the help of Miss Chow Shiau Kee (School of Mechanical and Aerospace Engineering, NTU) for her assistance in X-ray photoelectron spectroscopy (XPS) characterisations. I am grateful to Dr Stevin Snellius Pramana for his help and guidance in transmission electron microscope (TEM) measurements, as well as meaningful discussions.

Above all, my family has given me their unequivocal support throughout, as always, for which my mere expression of thanks likewise does not suffice.

Table of contents	Page
Acknowledgements	II
Table of contents	II
List of figures	VIII
List of tables	XIX
List of equations	XIX
Abstract	XX
1. Introduction	1
1.1 Background	1
1.2 Motivation	2
1.3 Research Objectives and Scope	4
1.4 Thesis organization	7

2. Literature review	8
2.1 Cathode materials for lithium ion batteries	10
2.1.1 Framework structured polyanion cathode materials	12
2.1.1.1 Current status and issues in olivine phosphates	15
2.1.2 Layered transition metal oxides for cathode materials	17
2.1.2.1 Current status and issues in V_2O_5	20
2.2 Nanomaterials in LIB	22
2.2.1 One-dimensional (1D) nanostructures	22
2.2.2 Core-shell nanostructures	23
2.2.3 Methodology for synthesis of nanoarchitected cathode materials	25
2.2.3.1 Electrospinning	27
2.2.3.2 Urea combustion synthesis	29
2.2.3.3 Ionothermal method	30
2.3 Fundamental studies in lithium intercalation and charge storage mechanisms	31
2.4 Future challenges	33

3. Methods and materials	34
3.1 Synthesis	34
3.1.1 Hydrothermal synthesis of LiFePO_4 and LiMnPO_4	34
3.1.2 Ionothermal synthesis of LiMnPO_4 , LiCoPO_4 and LiNiPO_4	35
3.1.3 Electrospinning synthesis: LiFePO_4 , LiMnPO_4 and V_2O_5 fibers	36
3.1.4 Sol-gel synthesis of LiMnPO_4 and LiCoPO_4	41
3.1.5 Solid-state synthesis of LiMnPO_4 and LiCoPO_4	41
3.1.6 Urea combustion synthesis of V_2O_5	42
3.1.7 Chemical lithiation	44
3.2 Characterisation studies	45
3.2.1 Morphological and structural characterisation	45
3.2.2 Characterisation of organics	45
3.3 Electrochemical characterization	46
3.3.1 Cell fabrication	46
3.3.2 Electrochemical studies	47
3.3.2.1 Electrochemical Impedance Spectroscopy (EIS)	47
3.3.2.2 Lithium diffusion coefficient by Randles-Sevcik equation	48
3.3.2.3 Electrochemical thermodynamic measurement studies (ETMS)	49

4. Results	50
4.1 Nanofiber-based cathodes	51
4.1.1 Justification for electrospinning in LIB	51
4.1.2 Electrospun Olivine-Carbon nanocomposites	53
4.1.2.1 LiFePO ₄ -Carbon nanocomposites	53
4.1.2.2 Core-shell LiMnPO ₄ -carbon nanocomposites	62
4.1.3 Electrospun V ₂ O ₅ nanofibrous (VNF) cathodes	67
4.1.3.1 Effect of aluminium-insertion (Al-insertion) in VNF	78
4.1.3.2 Effect of carbon-coating on VNF	94
4.2 Nanoparticle cathodes	104
4.2.1 Olivine nanoparticle cathodes	104
4.2.1.1 LiMnPO ₄ nanoparticle cathodes	105
4.2.1.2 LiCoPO ₄ nanoparticle cathodes	110
4.2.1.3 LiNiPO ₄ nanoparticle cathodes	118
4.2.2 V ₂ O ₅ nanoparticle cathodes	121
4.2.2.1 Effect of aluminium-insertion (Al-insertion) in V ₂ O ₅ nanoparticles	136
4.3 Application of V₂O₅ powder (VUC) in full cell (vs. LTO anode)	144

5. Discussion	147
5.1 Effect of nanoarchitectures on electrochemical performance of cathodes	147
5.1.1 Effect of electrospinning morphology on electrochemical performance	147
5.1.1.1 LiFePO ₄ -C nanocomposites	147
5.1.1.2 LiMnPO ₄ core-shell nanofibers	149
5.1.1.3 V ₂ O ₅ nanofibers (VNF)	152
5.1.2 Effect of chemical / physical modifications on performance	158
5.1.2.1 Effect of Al-insertion on V ₂ O ₅ crystal structure and electrochemical performance	158
5.1.2.2 Effect of Al-insertion on V ₂ O ₅ (VUC) crystal structure and electrochemical performance	161
5.1.2.3 Effect of carbon coating on electrochemical performance of VNF	164
5.1.2.4 Effect of carbon coating on electrochemical performance of VUC	166
5.1.3 Effect of sintering temperature	168
5.1.3.1 Sol-gel synthesis of LiMnPO ₄	168
5.1.3.2 Post-ionothermal sintering of LiNiPO ₄	169
5.1.3.3 Effect of sintering temperature on electrochemical performance of urea-combustion synthesized V ₂ O ₅ (VUC)	169
5.2 Fundamental studies on mechanism of lithium intercalation	173
5.2.1 Pre-lithiation studies on LiV ₂ O ₅	174
5.2.2 Electrochemical Thermodynamic Measurement Studies (ETMS)	193

5.2.3 Lithium diffusion studies	198
6. Conclusion	207
6.1 Novel contributions from this thesis	212
6.1.1 Scientific contributions	212
6.1.2 Technological significance	213
7. Future work	214
7.1 Fundamental studies on LiFePO_4 and LiMnPO_4	214
7.2 Investigations on LiCoPO_4 and LiNiPO_4	215
7.2.1 High voltage studies	215
7.3 In-situ studies of LIBs	216
7.4 Full cell studies on V_2O_5	217
8. References	218
Appendix A List of abbreviations	248
Appendix B List of publications	251

List of figures	Page
Figure 1.1 (a) Comparison of electric vehicles and (b) Ragone plot of batteries	1
Figure 2.1 Schematic of lithium ion battery	9
Figure 2.2 Schematic of olivine phosphates and V_2O_5 with $LiCoO_2$	12
Figure 2.3 (a) Crystal structure of olivine phosphate $LiFePO_4$ with Li atoms (red spheres), PO_4 tetrahedra (blue) and FeO_6 octahedra (yellow) bonds and (b) oriented to show the [010] 1D tunnels in which Li atoms are transported	13
Figure 2.4 (a) Structure of layered orthorhombic V_2O_5 showing VO_5 square pyramids (green) sharing edges and corners and (b) distortion of layered structure after intercalation of Li^+ ions (light blue spheres)	18
Figure 2.5 Schematic of typical electrospinning setup	27
Figure 2.6 Schematic of electrospun $LiFePO_4$	28
Figure 3.1 (a) Schematic of electrospinning setup and (b) FE-SEM image of unsintered and sintered (inset) electrospun CNF	36
Figure 3.2 Schematic of core-shell spinneret	38
Figure 3.3 Schematic of Plasma-Enhanced Chemical Vapour Deposition (PECVD)	40

Figure 4.1 Field-emission scanning electron microscopy (FE-SEM) of (a) as-spun carbon nanofibers (CNF) and (b) sintered CNF	53
Figure 4.2 FE-SEM image of (a) LFP-C, (c) LFP-PAN, (e) L-CNF and corresponding TEM images of (b) LFP-C, (d) LFP-PAN and (f) L-CNF	55
Figure 4.3 TGA showing carbon and active weight percentages of respective samples	56
Figure 4.4(a) Rietveld refinement of pristine LiFePO_4 (LFP-hyd) and respective XRD patterns of LFP-C and LFP-PAN compared with LFP-hyd	57
Figure 4.5 Cyclic voltammograms at scan rate of 0.1 mV s^{-1} of the samples	58
Figure 4.6 Galvanostatic traces of first charge / discharge cycle for respective samples	59
Figure 4.7(a) Charge-discharge cycling of respective samples 0.1 C rate, and (b) extended charge discharge cycling of LFP-C and LFP-hyd.	60
Figure 4.8 Transmission electron microscopy (TEM) images of (a) LMP-C and (b) C-LMP fibers with corresponding FE-SEM images as insets	62
Figure 4.9 Cross-sectional elemental (carbon and manganese) line-scans of (a) LMP-C and (b) C-LMP fibers	62
Figure 4.10 (a) X-ray diffraction patterns and (b) TGA diagrams of C-LMP and LMP-C	63
Figure 4.11 Cyclic voltammogram of LiMnPO_4 -Carbon composite fibers	64
Figure 4.12 (a) Galvanostatic traces and (b) cycling data (showing discharge capacities) of LiMnPO_4 -Carbon composite nanofibers	65

Figure 4.13 Secondary electron images (SEI) of (a) as-spun VNF and (b) sintered VNF, and respective bright field transmission electron microscope (TEM) images of (c) and (d) with selected area diffraction (SAED) patterns (insets), (e) high resolution TEM image with indicated d -spacings and axes of (310) and (01 $\bar{1}$) planes (inset: SAED of single nanocrystallite on sintered VNF) and (f) multislice simulation of single nanocrystallite sintered at 400 °C

67

Figure 4.14 (a) Rietveld crystal structure refined X-ray diffraction pattern of sintered VNF and (b) crystal structures of V_2O_5 and $Li_xV_2O_5$ showing VO_5 octahedra and Li atoms

69

Figure 4.15 XRD pattern of VNF, VNF-powder and V_2O_5 commercial powder

70

Figure 4.16 Fourier transform infrared spectra (FTIR) of (a) as-spun and sintered VNF compared with commercial V_2O_5 powder and (b) VNF-powder and sintered VNF

70

Figure 4.17 Cyclic voltammogram (at 0.1 mV s⁻¹) of VNF showing (a) first cycle and (b) subsequent cycles and of VNF-powder showing (c) first cycle and (d) subsequent cycles

72

Figure 4.18 Galvanostatic cycles of VNF showing first and second charge and discharge cycles of VNF cells cycled between (a) 1.75 - 4.0 V at 0.1 C and (b) 2.0 – 4.0 V at 0.1 C, (c) that of VNF-powder between 1.75-4.0 V and (d) cycling of respective cells at 0.1 C rate. All voltages are reported vs. Li⁺/Li

75

Figure 4.19 Galvanostatic cycling of VNF cells (1.75-4.0 V) in various cycling rates (a) 0.1-1-0.1 C and (b) 0.1-0.2-0.5-1-1.5-0.1 C

77

Figure 4.20 Field emission secondary electron (FE-SEM) images of as-spun (a) VNF, (c) $Al_{0.5}$ VNF, (e) $Al_{1.0}$ VNF and sintered (b) VNF, (d) $Al_{0.5}$ VNF and (f) $Al_{1.0}$ VNF respectively

80

Figure 4.21 Transmission electron (TEM) images and corresponding Al, V and O (as labeled) elemental maps of (a) $\text{Al}_{0.5}\text{VNF}$ and (b) $\text{Al}_{1.0}\text{VNF}$ respectively 81

Figure 4.22 Figure 4.22 (a) X-ray diffraction (XRD) patterns of VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$, with (b) corresponding high resolution peaks, and schematic representation of (c) V_2O_5 (Shcherbinaite) crystal structure and (d) V_2O_5 lattice (not to scale) with possible positions of Al atoms, as indicated by blue spheres, and possible movement of V_2O_5 layers upon intercalation of lithium ions, as indicated by arrows 83

Figure 4.23 $\text{V}2\text{p}_{2/3}$ X-ray photoelectron spectra (XPS) of VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$ 84

Figure 4.24 Cyclic voltammograms showing first cycles of (a) VNF, (c) $\text{Al}_{0.5}\text{VNF}$, (e) and subsequent cycles of (b) VNF, (d) $\text{Al}_{0.5}\text{VNF}$ and (f) $\text{Al}_{1.0}\text{VNF}$ respectively, in which metallic lithium serves as both counter and reference electrodes in two electrode coin cell configuration at scan rate of 0.1 mV s^{-1} between 1.75-4.0 V vs. Li/Li^+ . Integer represents cycle number 85

Figure 4.25 Typical galvanostatic traces of first two charge-discharge curves of (a) VNF, (b) $\text{Al}_{0.5}\text{VNF}$ and (c) $\text{Al}_{1.0}\text{VNF}$ cells between 1.75-4.0 V vs. Li/Li^+ at 0.1 C rate in room temperature 88

Figure 4.26 Plots of specific discharge capacity vs. cycle number of VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$ cycled at (a) 0.1 C rate at room temperature and (b) 0.1 C rate at 55°C and (c) 1 C rate at room temperature 92

Figure 4.27 Field emission secondary electron (FE-SEM) images of as-prepared electrodes of (a) VNF, (c) $\text{Al}_{0.5}\text{VNF}$, (e) $\text{Al}_{1.0}\text{VNF}$ and electrochemically cycled electrodes of (b) VNF, (d) $\text{Al}_{0.5}\text{VNF}$ and (f) $\text{Al}_{1.0}\text{VNF}$ respectively 93

Figure 4.28 Field emission secondary electron (FE-SEM) images of (a) bare VNF, (b) C-VNF-15 and (c) C-VNF-30 with corresponding transmission electron microscopic (TEM) images of C-VNFs (insets)

95

Figure 4.29 (a) X-ray diffraction (XRD) patterns of bare VNF, C-VNF-15 and C-VNF-30 showing formation of V_2O_5 structure (*asterisks indicate VO_2 peak) and (b) thermogravimetric analyses (TGA) showing weight percentages of C-VNF-15 and C-VNF-30

96

Figure 4.30 Cyclic voltammograms showing first cycle of (a) bare VNF, (c) C-VNF-15, (e) C-VNF-30 and subsequent cycles of (b) bare VNF, (d) C-VNF-15 and (f) C-VNF-30 respectively, in which metallic lithium serves as both counter and reference electrodes in two electrode coin cell configuration at scan rate of 0.1 mV s^{-1} between 1.75-4.0 V vs. Li/Li^+

98

Figure 4.31 Typical galvanostatic traces of first two charge-discharge curves of (a) bare VNF, (b) C-VNF-15 and (c) C-VNF-30 cells between 1.75-4.0 V vs. Li/Li^+ at 0.1 C rate in room temperature

100

Figure 4.32 Plots of specific discharge capacity vs. cycle number of VNF, C-VNF-15 and C-VNF-30 cycled at (a) 0.1 C rate at room temperature and (b) capacity retention (according to initial discharge capacity) vs. cycle number

102

Figure 4.33 Plots of specific discharge capacity vs. cycle number of VNF and C-VNF-15 cycled at (a) 0.1 C rate at 55°C and (b) 1 C rate at room temperature

103

Figure 4.34 FESEM images of (a) hydrothermal- (LMP-hyd), (b) ionothermal- (LMP-IL) and (c) sol-gel synthesized $LiMnPO_4$ (LMP-SG)

105

Figure 4.35 XRD patterns of hydrothermal-(LMP-hyd), ionothermal- (LMP-IL) and solid-state synthesized LiMnPO_4 (LMP-SS) respectively	106
Figure 4.36 XRD patterns of sol-gel synthesized LiMnPO_4 (LMP-SG) at various temperatures	107
Figure 4.37 (a) Galvanostatic traces of LMP-IL and LMP-SS, cycling data of (b) LMP-IL, LMP-SG, LMP-hyd and LMP-SS up to 10 cycles and (c) LMP-ion and LMP-SS up to 30 cycles	108
Figure 4.38 FE-SEM images of (a) Sol-gel synthesized LiCoPO_4 LCP-SG, (b) solid-state synthesized LiCoPO_4 LCP-SS and (c) ionothermally synthesized LiCoPO_4 LCP-IL	110
Figure 4.39 XRD patterns of LiCoPO_4 synthesized by various methods	111
Figure 4.40 Cyclic voltammograms of LCP-SS in various voltage ranges	112
Figure 4.41 Cyclic voltammograms of (a) LCP-SS and (b) LCP-IL in the voltage range of 2.5- 5.5 V with and without LiBOB additive	113
Figure 4.42 Cyclic voltammograms of LCP-SG up to 10 cycles (a) without and (b) with addition of LiBOB additive	114
Figure 4.43 Cyclic voltammograms of LCP-IL up to 10 cycles (a) without and (b) with addition of LiBOB additive	115
Figure 4.44 (a) Galvanostatic discharge and (b) cycling data of LCP-SS with various concentrations of LiBOB addition to bare electrolyte	116
Figure 4.45 (a) Galvanostatic discharge and (b) cycling data of LCP-IL and LCP-SG with variations of LCP-SG	117
Figure 4.46 XRD patterns of LiNiPO_4 samples synthesized by ionothermal method	119

Figure 4.47 Cyclic voltammograms (CV) of LNP-IL-700 (a) with LiBOB additive and (b) without LiBOB additive 120

Figure 4.48 (a) Field emission secondary electron image (FE-SEM) and (b) transmission electron microscope (TEM) image with indexed selected area electron diffraction pattern (SAED) (inset) of VUC 600-1 121

Figure 4.49 (a) Rietveld refined XRD pattern of V_2O_5 prepared at 600 °C for 1 h and (b) family of XRD patterns of all samples sintered at 300, 400, 500 and 600 °C for durations of 1, 2 and 3 h respectively. 122

Figure 4.50 Rietveld refinement parameter values (a), (b), (c) Lattice parameters, and (d) crystal sizes of all samples sintered at 300, 400, 500 and 600 °C for durations of 1, 2 and 3 h respectively 123

Figure 4.51(a) Thermogravimetric analysis of as-combustion synthesized precursor and (b) Fourier-transform infrared spectra (FTIR) of samples sintered at 300, 400, 500 and 600 °C for 3 h respectively 125

Figure 4.52 Cyclic voltammograms of VUC 300-2 and VUC 600-1 showing (a) first cycle, (b) second cycle and (c) 20th cycle, in which metallic lithium serves as both counter and reference electrodes in two electrode coin cell configuration with the scan rate of 0.1 mV s⁻¹ between 1.75-4.0 V vs. Li/Li⁺ 129

Figure 4.53 Typical galvanostatic cycles showing first and second charge and discharge curves of (a) VUC 600-1 and (b) VUC 300-2 cells between 1.75-4.0 V vs. Li/Li⁺ at 0.1 C rate 131

Figure 4.54 Plot of specific discharge capacity vs. cycle number (a) VUC 600-1, 500-1, 400-3 and 300-2, (b) VUC 600-1, ball-milled VUC 600-1 and ball-milled VUC 600-1 with carbon, and (c) VUC 600-1, NUC 600-1 (non-combustion synthesized) and commercial V_2O_5 powder	132
Figure 4.55 Rate capability studies of two duplicate cells comprising VUC 600-1 sub-micron size powders at room temperature	135
Figure 4.56 XRD of Al-inserted V_2O_5 urea combustion powder (VUC)	136
Figure 4.57 XPS ($V_{2p} 3/2$) of Al-inserted V_2O_5 urea combustion powder (VUC)	137
Figure 4.58 Cyclic voltammograms of bare VUC and Al-inserted VUC showing (a) first cycle and (b) subsequent cycle	138
Figure 4.59 First and second galvanostatic charge / discharge profiles of (a) bare VUC, (b) $Al_{0.66}VUC$ and (c) $Al_{1.1}VUC$	141
Figure 4.60 Discharge capacities vs. cycle number of bare VUC and Al-inserted VUC at (a) 0.1 C rate and (b) 1 C rate	142
Figure 4.61 Cyclic voltammogram (CV) of V_2O_5 -LTO full cell	144
Figure 4.62 Typical galvanostatic charge / discharge trace of V_2O_5 -LTO full cell	145
Figure 4.63 Specific capacity vs. cycle number for V_2O_5 -LTO full cell	146

Figure 5.1 Schematic of LiFePO ₄ -Carbon nanocomposites	147
Figure 5.2 EIS of LMP-C, C-LMP and LMP-hyd	150
Figure 5.3 EIS of LMP-C, C-LMP and ball-milled variations	151
Figure 5.4 Schematic diagram showing the formation of VNF during sintering	153
Figure 5.5 Nyquist plots of VNF (a) fresh cell and after cycling and (b) Bode phase angle plot of the impedance data with equivalent circuit used for fitting the Nyquist plots. Symbols present experimental spectra and continuous lines represent fitted data using equivalent electrical circuit	154
Figure 5.6 EIS of VNF and Al-inserted VNF	159
Figure 5.7 Schematic (not-to-scale) of possible positions of inserted Al ³⁺ ions in layered structure of V ₂ O ₅ in (a) VNF and (b) VUC	162
Figure 5.8 EIS of bare VUC and Al-inserted VUC	162
Figure 5.9 Electrochemical impedance spectra (EIS) bare VNF, C-VNF-15 and C-VNF-30 with enlarged high frequency region (inset)	164
Figure 5.10 Electrochemical impedance spectra (EIS) VUC 600-1, VUC 600-1 ball-milled and VUC 600-1 ball-milled with carbon	166
Figure 5.11 EIS for VUC sintered at various temperatures	170
Figure 5.12 Equivalent circuit for EIS of VUC	170
Figure 5.13 EIS of VUC 600-1 and NUC 600-1	172
Figure 5.14 Field-emission scanning electron microscope (FESEM) images of (a) bare VUC 600-1 (V ₂ O ₅ urea combustion), (b) 0.2Li-V ₂ O ₅ , (c) 0.5Li-V ₂ O ₅ , (d) 1.0Li-V ₂ O ₅ , (e) 2.0Li-V ₂ O ₅ and (f) 3.0Li-V ₂ O ₅	175

Figure 5.15 XRD of prelithiated V_2O_5 samples	176
Figure 5.16 XPS (Li 1s) of prelithiated V_2O_5 samples	178
Figure 5.17 Cyclic voltammograms (CV) of 0.2Li- V_2O_5 showing (a) first and (b) subsequent cycles	180
Figure 5.18 Cyclic voltammograms (CV) of 0.5Li- V_2O_5 showing (a) first and (b) subsequent cycles	181
Figure 5.19 Cyclic voltammograms (CV) of 1.0Li- V_2O_5 showing (a) first and (b) subsequent cycles	182
Figure 5.20 Cyclic voltammograms (CV) of 2.0Li- V_2O_5 showing (a) first and (b) subsequent cycles	183
Figure 5.21 Cyclic voltammograms (CV) of 3.0Li- V_2O_5 showing (a) first and (b) subsequent cycles	184
Figure 5.22 First galvanostatic charge of prelithiated V_2O_5 cathodes	185
Figure 5.23 (a) First galvanostatic discharge and (b) second charge cycle of prelithiated V_2O_5 cathodes, with comparison to first charge / discharge cycles of unlithiated V_2O_5	186
Figure 5.24 Discharge capacity vs. cycle number for prelithiated V_2O_5 and V_2O_5 in voltage ranges of (a) 1.75- 4.0 V and (b) 3.0-4.0 V vs. Li/Li ⁺	188
Figure 5.25 EIS of prelithiated V_2O_5 and bare V_2O_5	190
Figure 5.26 Typical first galvanostatic discharge curve of V_2O_5 powder cathode with corresponding V_2O_5 crystal structures (a) before and (b) after Li intercalation	194

Figure 5.27 (a) First discharge cycles of VUC 600-1 and VNF with corresponding (b) entropy and (c) enthalpy traces 195

Figure 5.28 (a) First discharge cycles of VNF, Al-inserted VNF and C-VNF with corresponding (b) entropy and (c) enthalpy traces 197

Figure 5.29 Cyclic voltammograms of (a) VUC 600-1 (V_2O_5 urea combustion synthesized) and (b) V_2O_5 nanofibers (VNF) at various scan rates and (c) peak current vs. $v^{1/2}$ 199

Figure 5.30 Cyclic voltammograms of (a) VUC 300-2 (V_2O_5 urea combustion synthesized), (b) VUC 600-1 and (d) VUC 600-1 bmC (ball-milled with carbon) at various scan rates and (c) peak current vs. $v^{1/2}$ 201

Figure 5.31 Cyclic voltammograms of (a) $Al_{0.5}VNF$ and (b) $Al_{1.0}VNF$ at various scan rates and (c) peak current vs. $v^{1/2}$ 203

Figure 5.32 Cyclic voltammograms of (a) VNF, (b) C-VNF-15 and (c) C-VNF-30 at various scan rates and (d) peak current vs. $v^{1/2}$ 204

Figure 5.33 Cyclic voltammograms of (a) bare VUC, (b) $Al_{0.66}VUC$ and (c) $Al_{1.1}VUC$ at various scan rates and (d) peak current vs. $v^{1/2}$ 206

List of tables	Page
Table 2.1 Summary of common cathode materials and their properties	10
Table 2.2 Summary of electrochemical properties of Olivine Phosphates	14
Table 2.3 Various methods of synthesizing V ₂ O ₅ nanostructures and their respective properties	26
Table 4.1 Lattice parameters of LMP-SG samples	106
Table 4.2 Summary of crystal size and phase purity for LiNiPO ₄	119
Table 5.1 Lattice parameters for bare VUC and Al-inserted VUC	161
Table 5.2 Summary of EIS values for VUC prepared at different temperatures	171
Table 5.3 Summary of ICP analyses	179

List of equations

$$I_p = 2.687 \times 10^5 \text{ n}^{3/2} \nu^{1/2} D_{\text{Li}}^{1/2} A C_{\text{Li}} \quad (7)$$

$$\Delta G(x) = -FE_o(x) = \Delta H(x) - T \Delta S(x) \quad (9)$$

Abstract

Lithium-ion batteries (LIBs) are gaining increasing attention in the research field, due to the constantly increasing demand for energy. As compared to conventional batteries, rechargeable LIBs are smaller and lighter, as well as capable of providing higher energy density and longer life cycles. LIBs work on the basis of intercalation / deintercalation of lithium ions, bringing about the flow of electrons to the external circuit. Currently, commercial LIBs are used in powering portable devices such as laptops and handphones. In order to move on the large applications such as electric vehicles, lithium ion batteries with improved electrochemical performances, lower cost, reduced toxicity and good thermal properties are required.

This thesis focuses on the study of cathode materials for LIBs for high energy density energy storage devices. Higher capacity of LIB anodes ($>500 \text{ mAh g}^{-1}$), as compared to conventional cathodes ($\sim 100\text{-}200 \text{ mAh g}^{-1}$) results in a large mismatch in lithium storage properties. Herein, the study of high-voltage olivine phosphate (LiMPO_4 , where $\text{M} = \text{Fe, Mn, Co, Ni}$) and high-capacity vanadium pentoxide (V_2O_5) cathode materials were explored. Olivine phosphates LiFePO_4 and LiMnPO_4 have the advantages of non-toxicity and good thermal stability in general. However, the poor conductivity ($\sim 10^{-9} \text{ Scm}^{-1}$) of olivine phosphates limits their practical capacity. On the other hand, V_2O_5 enables high capacity by intercalation of $>2 \text{ Li}$ into its structure, but not without the consequences of irreversible capacity fade.

The electrochemical behaviours of the abovementioned cathode materials were studied via the synthesis of nanomaterials. Electrospinning was used to synthesize one-dimensional (1D) olivine phosphates-carbon composite nanofibers, leading to increased conductivity, and high aspect ratio V_2O_5 nanofibers with high surface area, enabling high

capacity values $>300 \text{ mAh g}^{-1}$. The effects of chemical / physical modifications on electrochemical behaviours of these electrospun fibers were also studied.

Alternatively, synthesis methods used to obtain nano-particles, such as ionothermal and urea combustion syntheses were employed, to enable a thorough study of the lithium intercalation mechanisms and electrochemical behavior. The study of high-voltage olivine phosphate materials LiCoPO_4 and LiNiPO_4 was carried out using alternative, high voltage electrolytes and systematic addition of electrolyte additives. Systematic studies on the urea combustion synthesis of V_2O_5 sub-micron powders were carried out, showing improved cyclic properties. Al-insertion to these V_2O_5 also proved to be beneficial to high temperature electrochemical performance.

In general, properties of the cathode materials were characterised using field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared red (FTIR) spectroscopy and thermogravimetric analyses (TGA), among other characterization techniques. In addition, electrochemical properties of the cathode materials were studied using galvanostatic cycling, cyclic voltammetry and electrochemical impedance spectroscopy. Lithium diffusion studies and electrochemical thermodynamic measurement spectroscopy (ETMS) were done to gain new understandings on the lithium intercalation properties of olivine phosphate and vanadium pentoxide cathode materials. Furthermore, phase transitions of V_2O_5 upon Li intercalation were studied using chemical prelithiation, enabling a new understanding on the Li intercalation into V_2O_5 , and finally, the application of V_2O_5 cathode material in a full cell was presented.

1. Introduction

1.1 Background

Energy is pervasive in nature and for centuries, it has been generated mainly by the burning of fossil fuels, which is a non-renewable resource. In the present world, there is increased awareness of the negative effects of such energy production, such as the inevitable exhaustion of fuels and global warming. Consequentially, the demand for renewable energy resources is constantly increasing, in a bid against time to replace the use of fossil fuels and progress towards clean energy[1, 2]. Renewable resources such as solar, wind (turbine) and tidal energy tend to be intermittent and variable in nature. Hence, reliable energy storage and conversion systems are required to provide portability of such stored chemical energy with high conversion efficiency.

a Modes of operation	battery capacity needed, kWh	Energy density, Wh/kg	Weight of battery, Kg	Speed, kilometres per hour	Distance on one charge, kilometres
Hybrid	<3	40-50 (Ni-MH)	60 (Ni-MH)	100+	15
Plug in Hybrid	5.6-18	90-100 (Li-ion)	60-200 (Li-ion)	100+	10-60
Full EV	35-54	90-100 (Li-ion)	450 (Li-ion)	>100	150-200

Figure 1.1 (a) Comparison of electric vehicles and (b) Ragone plot of batteries[2]

Rechargeable lithium ion batteries (LIBs), in comparison to the traditional lead acid and nickel-cadmium batteries, are smaller, lighter, provide higher voltage (4V) and energy density and can be recharged for up to 1200 cycles. Current LIBs are generally used in portable devices such as handphones, PDAs and laptops. As the research world pushes towards the development of clean energy, LIBs are prospective candidates that provides higher power and energy density than its predecessors (nickel-metal hydride and lead-acid batteries, Figure 1.1b), for large-scale applications such as hybrid electric vehicles (HEVs), as seen in Figure 1.1a. In addition, issues related to safety and thermal stability have to be taken into consideration.

1.2 Motivation

Despite the widespread use of LIB today, future increased usage of HEVs and reliance on renewable sources of energy will require large-scale lithium ion batteries with extremely long life cycles (>5000 cycles), high safety and thermal stability, reliability, low cost, much higher energy and power density. In general terms, the energy density is used as a measure for good performance in LIBs, and in turn the energy density is affected by the working voltage and the specific capacity.

Conventional lithium cobalt oxide (LiCoO_2) cathodes[3-5] possess specific capacity of 135 mAh g^{-1} , which is much lower than that of the anode materials like graphite. In order to maximize the energy storage potential between the cathode and the anode, the mass of the cathode is usually doubled. Due to the high cost of LiCoO_2 , the overall cost of lithium ion batteries is markedly increased. In addition, LiCoO_2 have safety issues related to thermal stability, overcharging and toxicity. This makes lithium ion batteries dangerous if misused. Hence LiCoO_2 LIB cathodes are not desirable for

future large scale applications. Therefore, a need arises for high capacity, low cost, safe and more stable lithium-intercalating electrode materials.

Most importantly, typical graphite anodes have practical capacity $>300 \text{ mAh g}^{-1}$ and silicon anodes have even higher capacity $\sim 2000 \text{ mAh g}^{-1}$ [6]. Currently, a drastically larger mass in the cathode is required to offset the total capacity of the anode material, in order to achieve the efficiency in LIB. Hence, there is now an urgency to develop high capacity cathode materials in order to optimize the utilization of the storage properties of the lithium ion battery.

In order to be suitable for large-scale applications of LIB, higher energy density is also required. Current LIB cathode materials only provide energy density $\sim 1000 \text{ Wh kg}^{-1}$ while future applications, require LIB to have energy density $>1500 \text{ Wh kg}^{-1}$. Energy density is proportionately affected by working voltage and specific capacity. Thus, a LIB containing a cathode with higher working voltage and / or higher specific capacity will lead to an increase in overall energy density. Often, cathode materials can achieve higher capacity via the intercalation of >1 mole of Li per mole of active material[7, 8], but subsequent instability of the structure leads to poor cyclic efficiencies. On the other hand, issues related to high voltage materials include dissolution of compounds, as well as electrolyte instability / decomposition. Such side reactions are unwanted as they often lead to large irreversible capacity loss and decrease the life-span of LIBs. In-depth studies regarding such high energy density cathode materials would definitely be required to develop future high-voltage cathode materials for applications in LIBs.

Along with the future development of lithium-sulphur and lithium air batteries[3-5, 9, 10], such high-capacity, high energy and power density cathode materials which are cost-effective or widely available, safe, non-toxic, environmentally-friendly and chemically-robust with long cycle life, are needed to achieve good electrochemical

properties and applications in large-scale devices. Hence, the thesis will focus on the key challenge highlighted above: (1) development of alternative, high energy-density, safe and low cost LIB cathode materials and (2) to gain an understanding on the impact of nanomaterials on the lithium intercalation and charge storage properties of cathode materials for LIBs.

1.3 Research Objectives and Scope

The objectives of this thesis are to

(1) Investigate the effect of morphology on the electrochemical behavior of cathode materials

One of the main objectives of this thesis is to design new cathode nanoarchitecture based on olivine phosphates (LiMPO_4 , where $M = \text{Fe, Mn, Co, Ni}$) and vanadium pentoxide (V_2O_5). Firstly, olivine phosphates have good thermal stability in general, making them suitable candidates for cathode materials in large-scale applications. The higher theoretical capacity values of $\sim 170\text{--}190 \text{ mAh g}^{-1}$ over LiCoO_2 are further advantages. In addition, lithium cobalt phosphate (LiCoPO_4) and lithium nickel phosphate (LiNiPO_4) have potential as high-voltage[10] (5 V) cathode materials. As for V_2O_5 , the multiple oxidation states of vanadium enables the intercalation of more than one Li per V_2O_5 , leading to a high achievable capacity of up to $\sim 300 \text{ mAh g}^{-1}$.

To study the effect of nanoscale one dimensional (1D) and nanoparticle morphology on these cathode materials, they were synthesized using various novel techniques such as electrospinning, ionothermal and urea combustion methodologies. The impact of different nano-morphologies obtained using these synthesis methods was studied thoroughly using various characterization techniques such as field emission

scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Also the electrochemical performance and properties of these cathode materials was characterized with galvanostatic and cyclic voltammetry studies, as well as electrochemical impedance spectroscopy (EIS).

(2) Study the effects of chemical / physical modifications on nanoarchitected cathodes

As previously mentioned, olivine phosphates and V_2O_5 have promising attributes as cathode material applications in LIBs. However, the low conductivity of these olivine phosphate materials ($\sim 10^{-9} \text{ S cm}^{-1}$) has greatly reduced their practical working capacity values. Also, the possible degradation of organic electrolytes and dissolution of cathode materials at high voltages ($>4.5 \text{ V vs. Li/Li}^+$) is indeed a pertinent issue, which leads to drastic capacity fading. On the other hand, the layered structure of V_2O_5 undergoes distortion to accommodate the intercalation of the Li^+ ions, in turn contributing to the severe capacity fade during subsequent electrochemical cycling.

In order to overcome the aforementioned issues, in-situ addition of carbon during the synthesis of olivine phosphate nano-materials in lithium iron phosphate (LiFePO_4) and lithium manganese phosphate (LiMnPO_4) was done to obtain olivine phosphate-carbon nanocomposites. It was hypothesized that the formation of nanostructures enables intimate contact of these poorly-conducting cathode materials with the conductive carbon species, enabling improvement in achievable capacity via the increase in conductivity. Practical applications of high-voltage cathode materials LiCoPO_4 and LiNiPO_4 was studied via the systematic addition of additives to the electrolytes, to prevent breakdown of electrolytes and reduce dissolution of active materials at high voltages. The limitation of irreversible distortion of the V_2O_5 layered structure was attempted via the insertion of metallic ions, enabling support within the structure, during further lithium intercalation.

The effect of physical carbon coatings on the lithium intercalation properties of V_2O_5 nanomaterials would also be studied. In addition to the abovementioned characterization techniques, techniques to characterize the presence of carbon, such as thermogravimetric analysis (TGA), and insertion of metallic ions, such as X-ray photoelectron spectroscopy (XPS) and inductively-coupled plasma (ICP) analyses, would be carried out. The impact of these modifications would also be studied in detail.

(3) Fundamental studies on charge storage mechanisms in these nanoarchitected cathodes

In this era of nanotechnology, nanomaterials or materials synthesized in various nanoarchitectures have found widespread applications in biomaterials, transistors and also energy applications, including lithium ion batteries. At the same time, while creating high energy density LIBs, the lifespan of these energy storage devices also need to be sustained in order to be applied to future applications. As such, scientists have explored the use of nanotechnology in synthesizing active materials for LIB. In such nanomaterials, the rate of reaction is increased more than tenfold or hundred fold as compared to micron-sized or bulk materials. At the same time, the reaction mechanisms can drastically differ, due to the large surface-area-to-bulk ratio. It is then evident that using nanosized particles / nanoarchitectures in battery materials will lead to differences in the main working principle behind LIBs: lithium intercalation.

This work is aimed to enable better understanding of the olivine phosphates and V_2O_5 cathode materials via the synthesis of nanoarchitectures through various methodologies. Systematic studies involving comparisons of EIS was conducted. In addition, the lithium diffusion coefficients calculated using the Randles-Sevcik equation and a novel in-situ thermodynamics study, known as the electrochemical thermodynamics

measurement study (ETMS), of the intercalation of lithium ions into V_2O_5 cathodes would be conducted. The latter technique enables study of phase changes via the variation in enthalpy and entropy values. Finally, the chemical pre-lithiation of V_2O_5 via butyllithium (BuLi) would be done to enable systematic correlation of the electrochemical processes. With these objectives in mind, it is hoped that new insights related to the charge storage mechanisms affected by morphology and chemical / physical modifications of V_2O_5 can be achieved.

1.4 Thesis organization

The thesis is organized as follows. Chapter 2 briefly introduces the mechanism of lithium ion batteries and a brief literature review is done on cathode materials for lithium ion batteries, including the effects of nanotechnology and fundamental studies conducted in the literature. Chapter 3 describes the various techniques employed in this thesis including material synthesis, structural and electrochemical. Chapter 4 details the experimental results followed by discussion in Chapter 5. Conclusions are then presented in Chapter 6 and recommendations for future studies in Chapter 7.

2. Literature review

Primary LIBs were first commercialised in 1970s[2] and since then, research has focused on developing rechargeable LIBs, leading to the appearance of Li-TiS₂, Li-MoS₂ and Li-Li_xMnO₂ systems. However, problems related to safety and short lifetime prevented the commercialization of the abovementioned systems. Yazami (1983)[11] and Goodenough (1983)[12] led groundbreaking research in graphite (Li_xC₆) as anode and lithium cobalt oxide (LiCoO₂) as cathode materials respectively, during the 1980s and this eventually led to the commercialization of the first LIBs by Sony Corporation in 1991. Today, the graphite-LiCoO₂ LIB system is used to power most electronic devices such as the cellphones, laptops and digital cameras.

As compared to the other secondary battery systems, such as lead acid and Nickel-cadmium batteries, the lithium ion battery LIB has at least twice the working voltage (~3.7V) and also high gravimetric energy density[13]. Due to the high voltage and presence of Li⁺ ions, the LIB cannot function using an aqueous electrolyte, thus organic solvents like ethylene carbonate (EC), diethyl carbonate (DEC), propylene carbonate (PC) and dimethyl carbonate (DMC) with large potential windows are usually used. Besides higher voltage, LIBs do not suffer from the memory effect, as opposed to nickel-cadmium (Ni-Cd) batteries.

The most common form of LIBs existing today consists of a LiCoO₂ cathode, a graphite anode and an organic lithium-conducting electrolyte as shown in Figure 2.1. LIBs function mainly by intercalation and deintercalation of Li⁺ ions. During charging, lithium ions (Li⁺) are deintercalated from the cathode and are conducted through the electrolyte to form Li metal at the anode. During discharging, Li metal at the anode splits into Li⁺ ions and electrons, releasing Li⁺ ions back to the electrolyte. The Li⁺ ions are then intercalated back into the cathode. Charging and discharging of the battery occur

reversibly through the intercalation and deintercalation processes. These reactions are summarized in the two equations below.

Figure 2.1 Schematic of lithium ion battery[9]

As the lithium ion battery relies heavily on the insertion and deinsertion of Li^+ ions into and from the electrodes, these materials need to have excellent selectivity for Li^+ ions. This forms the basis of selection of electrode materials for applications in lithium ion batteries.

As seen in Equation 1 above, LiCoO_2 only enables deintercalation of 0.5 Li per LiCoO_2 , giving rise to a theoretical specific capacity of 135 mAh g^{-1} . On the other hand, graphitic anode is able to intercalate 1 mole of Li per mole of graphite, leading to theoretical capacity of 300 mAh g^{-1} . The mis-match in specific capacity of cathodes and anodes leads to an increase in the mass of the cathode in order to achieve higher efficiency in batteries. As a result, the overall energy density of the commercial LIB is

compromised. Evidently, a cathode with higher energy density is required for future applications in LIBs, and energy density is affected by the operating voltage and specific capacity of the active material.

2.1 Cathode materials for lithium ion batteries

Cathode material	Working Voltage (V vs. Li/Li ⁺)	Theoretical capacity (for 1 mol Li per mol of active material)	Working capacity	Cycleability	Toxicity	Thermal stability	References
LiCoO₂	3.7	270	135		yes	poor	[8, 14, 15]
LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂	3.8	278	170		low	good	[4, 16]
LiMn₂O₄	4	150	130		no	good	[14, 15]
LiFePO₄	3.45	170	160	good	no	excellent	[14, 17-21]
LiMnPO₄	4.1	170	120	poor	no	good	[21-26]
LiCoPO₄	4.8	170	120	poor	yes	poor	[27-30]
LiNiPO₄	5.1	170	60	n/a	n/a	excellent	[30, 31]
V₂O₅	3	147	320 (~2.2 Li per V ₂ O ₅)	poor	yes	excellent	[7, 8, 32-40]
LiV₃O₈	3	90	270 (~3 Li per V ₂ O ₅)	good	yes	good	[3, 4, 41, 42]
Li₂FeSiO₄	2.8	160	140	good	no	n/a	[14, 21, 43]
LiVPO₄F	4.2	160	156		low	excellent	[44, 45]
Li₃V₂(PO₄)₃	4	197	132	good	low	excellent	[46-50]

Table 2.1 Summary of common cathode materials and their properties

In LIBs, the main cathode materials researched today are the layered lithium metal oxides such as LiCoO₂, layered integral materials such as Li₂MnO₃ and LiMnO₂[2] and olivine phosphates (LiMPO₄, where M=Co, Fe, Mn, Ni). All these materials become electrochemically active via lithium intercalation / deintercalation into and out of their respective layered / framework structures[1]. LiCoO₂, as the classic cathode material has working voltage of 3.6-4 V and high theoretical capacity of ~274 mAh g⁻¹, but only half of this value is achieved practically. It also faces problems of Co dissolution. Also,

problems related to safety plague the future development of LiCoO_2 as cathode materials for LIBs. This is because, during charging, the formation of the delithiated cathode leads to evolution of oxygen, which could lead to the possible explosion of the LIB.

Current studies on cathodes have thus progressed to safer options such as the olivine phosphates, which have higher capacity and also higher working voltage than LiCoO_2 , and also V_2O_5 , which has a layered structure that can enable insertion of more than 1 Li per V_2O_5 , leading to overall higher capacity.

Prior to the extensive studies carried out in olivine LiFePO_4 [10, 51-53] today, layered and spinel oxide cathodes were the most widely studied. In LiCoO_2 and LiNiO_2 [3, 54, 55], it is difficult to stabilize the higher oxidation states of the transition metal ions during the electrochemical process. LiCoO_2 cathode materials have a theoretical capacity of 135 mAh g^{-1} , equivalent to intercalation and deintercalation of 0.5 Li atoms per mole of LiCoO_2 during charge / discharge process. Furthermore, LiCoO_2 is highly expensive and toxic. On the other hand, properties of good structural stability are found in the spinel material LiMn_2O_4 [4, 5, 56] but there exists the problem of Mn^{2+} ions leaching into the electrolyte from the cathode lattice. Hence, such materials are less viable for practical applications on a large scale.

Following current research trends, alternative cathode materials have been suggested, as shown in Figure 2.2, including framework structured cathode materials olivine phosphates[10, 51-53] like LiFePO_4 (theoretical capacity 170 mAh g^{-1}) and LiMnPO_4 (theoretical capacity 171 mAh g^{-1}), which have the advantage of good safety, low cost and environmental friendliness and transition metal oxides with layered structure like V_2O_5 [7, 32, 38, 57]. However, the drawback of these materials is their low conductivity, which lowers the potential of the performance of these cathode materials in

lithium ion batteries. Thus, research is ongoing to improve the conductivity, and in turn, the specific capacity and energy density of these materials.

Figure 2.2 Schematic of olivine phosphates and V_2O_5 with $LiCoO_2$

2.1.1 Framework structured polyanion cathode materials

Of late, polyanion-based materials[14] in the form of $(AO_4)^{b-}$ ($A = S, P, Si$) have been explored as possible alternative cathode materials. It is believed that the inductive effect from phosphate $(PO_4)^{3-}$ and sulphate $(SO_4)^{2-}$ ions increases redox energies compared to oxides like $LiCoO_2$ and leads to the formation of a more stable structure. The strong covalent A-O bonds increases the working potential of such cathode materials and typically, lithium metal phosphate compounds containing the FeO_6 octahedra have potentials in the range $\sim 3-3.5$ V vs. Li/Li^+ [52]. As such, olivine phosphate materials, which have a framework structure as shown below, are one of the many types of such compounds for cathode materials.

Olivine phosphates[10, 58, 59], with the chemical formula LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$) and 3D framework structure shown in Figure 2.3, have been claimed to be able to reversibly intercalate and deintercalate lithium ions. They have high selectivity[60] for Li^+ ions, which make them suitable for application in lithium ion batteries. Of these, LiFePO_4 has the best electrochemical performance so far and is beginning to make a practical mark. This is partly due to the reason that iron-based compounds are more naturally abundant, making them low in cost and environmentally friendly, as compared to other compounds like layered oxides (LiCoO_2 , LiNiO_2).

Figure 2.3 (a) Crystal structure of olivine phosphate LiFePO_4 with Li atoms (red spheres), PO_4 tetrahedra (blue) and FeO_6 octahedra (yellow) bonds and (b) oriented to show the [010] 1D tunnels in which Li atoms are transported

Olivine phosphate LiFePO_4 has the advantages of long cycle life, high energy and power density, making it a suitable candidate for large scale lithium-ion batteries. Its theoretical specific capacity is reasonably high at 170 mAh g^{-1} , where one lithium ion can be inserted and deinserted reversibly per iron atom. It has a flat intercalation voltage at

3.5 V *vs.* Li/Li⁺ and has good thermal stability in the fully charged state. Recent research showed that the synthesis of LiFePO₄ nanostructures[3, 17, 20, 61-64] led to an increase in surface area, shorter mass and charge diffusion lengths and more freedom for volume change within the crystal structure, thus improving its tenacity to charge / discharge cycles and improving the overall cyclability.

LiMPO ₄ (M=Fe, Mn, Co, Ni)	Intercalation Voltage (V) <i>vs.</i> Li/Li ⁺	Theoretical Capacity (mAh g ⁻¹)	Energy density (Wh kg ⁻¹)	Diffusivity (cm ² S ⁻¹)
LiFePO₄	3.5	170	590	10 ⁻⁷
LiMnPO₄	4.1	171	700	10 ⁻⁸
LiCoPO₄	4.8	167	800	10 ⁻⁹
LiNiPO₄	5.1	167	850	10 ⁻⁵

Table 2.2 Summary of electrochemical properties of Olivine Phosphates[65]

On the other hand, LiMnPO₄[26, 60, 65, 66] has higher intercalation voltage of 4.1 V *vs.* Li/Li⁺, which makes it difficult to incorporate into the lithium ion batteries used today, which makes use of 1M LiPF₆ EC/DEC organic electrolyte. The higher voltage causes a breakdown of the electrolyte compounds and prevents further electrochemical reactions, this in turn contributes to poorer reversibility of lithium intercalation / deintercalation reactions. Although it has poorer conductivity and greater lattice mismatch with lithium ions than in LiFePO₄, it is believed that LiMnPO₄ could have better, or equally good, electrochemical performance, with a theoretical capacity of 171 mAh g⁻¹, higher energy density and intercalation voltage of 4.5 V *vs.* Li/Li⁺.

As for LiCoPO₄[28, 29, 67] and LiNiPO₄[10, 30, 31], they have intercalation voltages of 4.8 V and 5.1 V *vs.* Li/Li⁺ (Table 2.2) respectively and both theoretical capacities of approximately 167 mAh g⁻¹. These compounds will require significant

advances in organic electrolytes to be applied in lithium ion batteries, apart from the possible higher cost required to obtain these materials. Despite this, they are promising cathode materials due to their much higher energy densities, which will be able to provide for the energy demands of future large-scale electronics. Preliminary observations show LiCoPO_4 to be thermally-stable with specific capacity of $70 - 100 \text{ mAh g}^{-1}$, while LiNiPO_4 has specific capacity of 60 mAh g^{-1} .

2.1.1.1 Current status and issues in olivine phosphates

The greatest drawback of LiFePO_4 and other olivine phosphates is the lack of electronically-conducting species[17], leading to overall poor electronic conductivity. For example, LiFePO_4 has only a conductivity of $10^{-9} \text{ S cm}^{-1}$, while the other olivine phosphates fair far worse.

It has been noted[14, 68] that the diffusion of Li in LiFePO_4 structure occurs preferentially in the 1D tunnel along the b-axis, in which the LiO_6 octahedra are edge-shared parallel to this direction. As a result, electrons cannot easily transport through the material and the electronic conductivity of LiFePO_4 is thus limited.

Attempts have been made to enhance its electron conductivity by coating with carbon (usually by means of pyrolysis of co-synthesized organic compounds)[17, 69], preparing composites with activated carbon[70] and carbon nanotubes (MWNT)[20, 61], doping with metal ions[71-73] and also reducing the particle size[4, 74-76]. By doing so, specific capacity values as high as 160 mAh g^{-1} have been achieved[61, 62, 70, 75, 77]. Creating carbon nanocomposites with olivine phosphate materials, like embedding the olivine phosphate particles in a conductive matrix[3, 20], and carbon coatings[62, 70], can enhance the electronic conductivity and stabilize the SEI (solid electrolyte interface) films, improving the performance of the cathode by increasing the reversibility of

intercalation / deintercalation of Li^+ ions. Carbon coatings have also been done using various carbon-containing precursors like glucose[62, 74, 75] and citric acid[76], improving the conductivity of LiFePO_4 from $10^{-11} \text{ S cm}^{-1}$ to $10^{-5} - 10^{-6} \text{ S cm}^{-1}$, but such conductivity is still not high enough to fulfill the requirements for a high power lithium ion battery. Carbon nanotubes[20, 61] were added to the precursor solution of LiFePO_4 , improving discharge capacity and rate capability. This addition also caused a slight decrease in crystallite size and charge-transfer resistance, leading to an overall improved electrochemical performance. However, thick carbon coating reduces the volumetric energy density, and also affects the cyclic reliability of the olivine phosphates adversely. In order to render these olivine phosphates suitable for widespread application in lithium ion battery technology, one must maximize the conductivity and minimize the carbon content.

Besides carbon coatings, metallic coatings like iron phosphides Fe_2P and FeP [70, 78], protective aluminium fluoride (AlF_3)[79] coatings and conductive transition metal oxide coatings like ruthenium oxide (RuO_2)[80] have been used on LiFePO_4 , giving improved electrochemical behavior, with steady cycling performance and high capacity values maintained at high cycling rates. More recently, Kavan *et al.* (2007, 2008, 2009)[81-84] used molecular wiring to improve the conductivity of LiFePO_4 and LiMnPO_4 , which in turn improved their electrochemical properties.

Other than LiFePO_4 , LiMnPO_4 [8, 24] has also gained a lot of interest due to its higher potential of the $\text{Mn}^{3+} / \text{Mn}^{4+}$ redox couple at 4.1 V vs. Li/Li^+ . The main drawback of the LiMnPO_4 cathode material is its poor conductivity due to the Jahn-Teller distortion in the d -orbital. LiMnPO_4 experiences large polarization during charging, and cannot be charged at normal C rates (ie. 0.1 C). In general, the crystallinity affects the polarization in electrode materials and usually low temperature routes[85] are used to synthesize LiMnPO_4 nanostructures to prevent grain growth and agglomeration. Attempts to

improve the electrochemical performance of LiMnPO_4 include synthesizing nanoflakes via a polyol method[26], carbon coatings[75, 86] and also doping with metallic ions such as Zn[87, 88], Fe[89] and Co[90, 91]. It has been mentioned in the literature that reducing the particle size of LiMnPO_4 via ball-milling[25, 92, 93] and adding larger amounts of carbon (up to 40 wt. %) during the electrode fabrication process could improve the electrochemical performance.

Besides LiMnPO_4 and LiFePO_4 , research in LiCoPO_4 [28, 29] is commencing with initial specific capacity values of 113 mAh g^{-1} . Little research has been published in literature regarding the application of LiNiPO_4 [30, 31, 58] in lithium ion batteries. Gangulibabu *et al.* (2009)[58] synthesized LiCoPO_4 and LiNiPO_4 via sol-gel methods and carried out cyclic voltammetry and electrochemical impedance studies. The higher working voltages of LiCoPO_4 and LiNiPO_4 require new research into electrolytes, by addition of additives such as lithium bis (oxalato) borate (LiBOB)[94, 95] and also alternative electrolytes such as ionic liquids[96-98]. The current instability of conventional LiPF_6 in EC:DEC electrolytes at $>4.5 \text{ V vs. Li/Li}^+$ impedes the current progress of LiCoPO_4 and LiNiPO_4 towards practical application in LIB. Much is to be studied regarding this aspect of the olivine phosphate cathode materials.

2.1.2 Layered transition metal oxides for cathode materials

Vanadium-based layered oxides with tunable oxidation states (V^{5+} , V^{4+} and V^{3+}) such as VO_2 , V_6O_{13} and V_2O_5 are potential cathode materials for rechargeable lithium batteries[99, 100]. Among these vanadium pentoxide (V_2O_5) is an attractive candidate for cathodes in Li-ion batteries as they exhibit high theoretical capacities ($\sim 400 \text{ mAh g}^{-1}$) due to their capability to intercalate nearly 3 Li^+ ions per mole of active material[100]. Also, vanadium oxides crystallize in a variety of 1D nanoarchitectures[7, 32, 54, 100, 101],

such as nanorods[102], nanotubes[37] and nanobelts[40, 103], which are well-suited for lithium intercalation.

Figure 2.4 (a) Structure of layered orthorhombic V₂O₅ showing VO₅ square pyramids (green) sharing edges and corners and (b) distortion of layered structure after intercalation of Li⁺ ions (light blue spheres)[34]

Vanadium pentoxide (V₂O₅) has a layered structure (Figure 2.4a) consisting of layers of VO₅ square pyramids that share edges and corners. The layered structure[8, 38-40] is built up of VO₅ square pyramids sharing edges and corners, which is convenient for intercalation and deintercalation of Li⁺ ions. The V₂O₅ structure accommodates Li⁺ ions into its structure via phase transformations as elucidated in the following equation with increasing distortion of the layers (Figure 2.4b).

During the first electrochemical discharge cycle to 1.75 V vs. Li/Li⁺, lithium intercalation to the V₂O₅ structure occurs, leading to the formation of Li_xV₂O₅ (Equation 3), via the multistep reduction of V⁵⁺ in V₂O₅ and simultaneous accommodation of Li⁺ ions into the V₂O₅ structure[7, 37]. Firstly, the reduction of V⁵⁺ to V⁴⁺ leads to the formation of ε-Li_xV₂O₅, as indicated in equation (4). Then, partial reduction of V⁴⁺ to V³⁺ occurs, leading to the formation of a mixed phase comprising of δ- and γ-Li_xV₂O₅, as shown in equations (5) and (6). Upon cycling below 2.0 V vs. Li/Li⁺, the γ-Li_xV₂O₅ phase is irreversibly formed. This reduction process of the vanadium ion enables the accommodation of more than 2 Li per V₂O₅[7]. It is mentioned in the literature that V₂O₅ can reversibly intercalate Li up to x=1, maintaining its original layered structure. Further intercalation to 2 Li per V₂O₅ leads to the formation of the γ-Li_xV₂O₅ phase. Finally, at intercalation of ~3 mole of Li per mole of V₂O₅, the ω-Li₃V₂O₅ phase forms and stabilizes in the rock-salt structure.

As such, several works have been done to study these phase transformations by ex-situ method of prelithiation of V₂O₅. Whittingham (1977)[104], Garcia *et al.* (1999)[105] and Pecquenard *et al.* (1995)[106] carried out prelithiation of V₂O₅ using Butyl lithium solution while Murphy *et al.* (1979)[107] prelithiated V₂O₅ using lithium iodide (LiI) in acetonitrile. Garcia *et al.* (1999)[105] prepared chemically-lithiated V₂O₅ in various concentrations and showed that the intercalation of lithium into V₂O₅ was only reversible to a certain extent, while Pecquenard *et al.*(1995)[106] mentioned that the phase transformation of δ→γ Li_xV₂O₅ was irreversible, where x increases from <1 to >1. On the other hand Eguchi *et al.* (2007)[108] prepared LiV₂O₅ compounds using H₂O₂ and lithium and vanadium alkoxides, it was noted that the Li_{2.2}V₂O₅ phase had the best lithium intercalation / deintercalation properties in terms of cycleability. Finally Mai *et al.*

(2010)[36] noted that the prelithiation of nanostructured electrode materials led to increased cycling stability in general.

2.1.2.1 Current status and issues in V_2O_5

V_2O_5 has high initial specific capacity, but cyclic retention proves to be a problem. The rapid degradation in cyclic performance is a sign of the structure breakdown as the vanadium species undergo other redox reactions[109-112] to form α , ϵ , δ , ω and γ - $Li_xV_2O_5$ during the intercalation process, as proven in several studies via cyclic voltammetry. Also, V_2O_5 is poorly conducting[38, 113, 114].

Sol-gel[103] and hydrothermal[32, 39, 40, 100] methods are commonly used to synthesize vanadium oxides. Zhai *et al.* (2010)[100] synthesized nanowires, via a hydrothermal method, which had an initial capacity of 350 mAh g^{-1} and faded to 170 mAh g^{-1} after 20 cycles. The V_2O_5 nanowires, despite the 1D nanoarchitecture, which is supposed to be ideal for electrochemical applications, have poor cyclic retention.

In order to improve the cyclic properties and rate capabilities of V_2O_5 , polymeric precursors like polyethylene glycol (PEG)[40] and polyvinylpyrrolidone (PVP)[39] have been added in the syntheses. Koltypin *et al.* (2007)[109] has mentioned that the presence of a carbon coating on V_2O_5 nanoparticles can prevent the formation of surface film and unwanted reaction with the electrolyte, giving rise to better electrochemical performance.

Electronic conductivity of V_2O_5 has been improved via surface modifications by conductive coatings or making composites with either carbon[57, 109] or conductive additives for example polyaniline (PANI)[115], polypyrrole (Ppy)[116], and poly(vinylpyrrolidinone) (PVP)[39]. The concept of making composite not only improves the conductivity and also provides necessary stability during electrochemical cycling.

Conducting polymer nanocomposites with V_2O_5 enabled increase in the electrical conductivity to 10^4 times that of the pristine V_2O_5 electrode material. The specific capacity obtained for V_2O_5 -Ppy composite was 310 mAh g^{-1} as compared to 236 mAh g^{-1} in pristine V_2O_5 nanoparticles. Ponzio *et al.* (2007)[38] stabilized V_2O_5 nanofibers by addition of Pani in a reverse micelle method, giving a stable capacity of 300 mAh g^{-1} .

Another approach is to dope V_2O_5 with metallic ions to reduce the phase transitions. Giorgetti *et al.* (2007)[117] mentioned that such doping enabled the formation of $[MO_6]$ octahedra within the V_2O_5 layers, thus stabilizing the structure during lithium intercalation / deintercalation. So far, doping by nickel (Ni)[118], aluminium (Al)[112, 119], silver (Ag)[101, 120, 121], chromium (Cr)[122, 123] and copper (Cu)[111, 117, 124-126] has been carried out by various groups. The work by Parent *et al.* (1999)[118] suggests that nickel may be added to V_2O_5 for higher rate capability. Al^{3+} doped V_2O_5 [112] showed almost no sign of capacity fading, maintaining the capacity at about 170 mAh g^{-1} . Ag-doping enhanced the electronic conductivity of V_2O_5 dramatically from 0.08 S cm^{-1} to 0.5 S cm^{-1} [101], by causing a large increase in the lithium diffusion coefficient. A similar effect was observed in Cr-doped V_2O_5 [122, 123]. Chu and Qin (2002)[120] conducted a systematic study of silver-doping on V_2O_5 , showing that $Ag_{0.5}V_2O_5$ had the good capacity retention at a stable capacity of 270 mAh g^{-1} . Finally, Cu-doped V_2O_5 [111, 124] was able to maintain a stable capacity of 160 mAh g^{-1} . Besides improving the electrochemical performance of V_2O_5 , these doping studies allowed a better understanding of the phase transformations that occur during lithium intercalation.

2.2 Nanomaterials in LIB

Recent research has focused on nanomaterials[4] as they often offer improved mechanical, electrical and optical properties, combining properties of bulk and surface properties. Due to the increased surface-area-to-volume ratio in nanostructured materials, there is the possibility of improved energy storage capacities and charge / discharge kinetics, as well as improved cyclic stability. These improved properties can be attributed to the increased surface area for Faradaic reaction, reduced distances for ionic and electronic diffusion and added freedom for volume change during the Li intercalation / deintercalation process.

On the other hand, nanomaterials also bring about new challenges in the field of LIBs. For example, dissolution of active material species (such as cobalt (Co) dissolution in LiCoO_2) and also reaction of the cathode materials with the electrolyte can occur. In addition, nanoparticles have a tendency to agglomerate and this decreases the overall efficiency by decreased surface area resulting in reduced electrochemical activity. Other challenges arise from unknown reactions and increased rate and extent of reactions, which can lead to a possible new chapter(s) in scientific research.

2.2.1 One-dimensional (1D) nanostructures

For the applications in LIB, 1D nanostructures[127] are believed to provide a direct pathway for efficient charge transport and thus lead to improved rate capabilities. Often, active materials are grown onto carbon nanotubes or nanofibers[20, 61, 128, 129] to improve the intermittent contact of less-conducting species to more-conductive ones to improve the electronic conductivity. The electrospinning method (elaborated later) is also a method used in recent years to produce random, highly interconnected nanofibrous networks.

Hosono *et al.* (2010)[20] successfully electrospun LiFePO_4 nanowires with carbon nanotubes and also LiFePO_4 -PAN[130, 131] composites were synthesized using the electrospinning method. Von Hagen *et al.* (2012)[132] also reported the application of electrospun free-standing LiMnPO_4 sheets in LIBs.

On the other hand, it has been mentioned that V_2O_5 generally crystallises in 1D nanostructure and this is easily synthesized via hydrothermal methods. Ren *et al.* (2009)[103] synthesized V_2O_5 nanobelts using a hydrothermal method with the aid of H_2O_2 , while Pitchai *et al.* (2008)[37] synthesized V_2O_5 nanostrips using the polyol method. In both cases, higher initial capacity was achieved, as compared to commercially available V_2O_5 . However, it was noted that the cyclability of the V_2O_5 nanostrips was reduced due to the phase transformations of V_2O_5 during Li intercalation / deintercalation. Ban *et al.* (2009)[7] and Mai *et al.*(2010)[35] also synthesized single-crystalline and polycrystalline V_2O_5 nanostructures respectively using the electrospinning method. Ban *et al.* obtained high initial discharge capacity $\sim 360 \text{ mAh g}^{-1}$ as compared to bulk V_2O_5 , along with high retention of 67% of initial capacity after 25 charge / discharge cycles.

2.2.2 Core-shell nanostructures

Among the various nanoarchitectures, researchers have used core-shell nanostructures to improve the electrochemical properties of active materials for applications in lithium ion batteries. It is believed that such core-shell nanostructures enable active and inactive materials to complement each other to improve overall performance. Also, the inherent hollows in the core-shell structure create larger surface area and decrease in diffusion path lengths for lithium ions, leading to better rate capabilities[133, 134]. For example, core-shell structures typically contain an

electrochemically active core and the shell acts as a conductive pathway or protective layer to strengthen the performance of the core material.

Core-shell nanostructures are prospective solutions to the new cathode materials such as olivine phosphates, which have relatively poor electronic transportation properties, leading to high irreversible capacity in many cases[133]. For example, by using carbon, which has high electronic conductivity and other benefits of ease of synthesis and low cost, as the shell for less-conducting active materials, the electrochemical performance is often greatly enhanced. Moreover, such carbon shells can act as HF scavengers which are released from the organic electrolytes during electrochemical charging / discharging. Other than improving the conductivity, a protective shell structure can also prevent dissolution of active material species in the electrolyte, thereby increasing the overall reversibility and lifetime of the LIB.

Relatively simple and common methods of synthesis such as sol-gel, hydrothermal or solvothermal, chemical vapour deposition, microwave-assisted methods and spray pyrolysis can be used to create core-shell nanostructures. For example, olivine phosphate LiFePO_4 can be coated with carbon using mesocarbon microbead (MCMB), graphite and polymeric precursors such as polyaniline.

Other than nanoparticles, 1D nanostructures such as nanofibers can also be synthesized with a core-shell configuration. A core-shell 1D nanostructure can combine both the advantages of core-shell structures and also 1D nanostructures. Zhang *et al.* (2010)[135] synthesized LiFePO_4 -Carbon nanofibers by electrospinning method and achieved stable capacity over 50 galvanostatic charge / discharge cycles. Also, Sathiya *et al.* (2011)[136] and Hu *et al.* (2009)[137] also synthesized V_2O_5 -coated carbon nanotubes (CNT), improving the conductivity and capacity by enabling easy electronic access to active material via the conductive pathways provided by the CNT networks.

2.2.3 Methodology for synthesis of nanoarchitected cathode materials

In general, sol-gel[58, 138], hydrothermal and solvothermal[1, 63, 85] methods are used for the synthesis of cathode nano-materials. In contrast, solid-state methods are used to synthesize active electrode materials for lithium ion batteries, with large micron-ranged particles. The polyol method has also been employed to synthesize nanoplates of LiMnPO_4 [26] and LiFePO_4 [139]. The polyol method proved to be effective initially for LiMnPO_4 (an initial specific capacity of 160 mAh g^{-1}), giving the first evidence of promising cathode performance in LiMnPO_4 .

Nanoarchitectures of V_2O_5 have also been synthesized by various methods including sol-gel[103, 113], and electrodeposition[140, 141]. Studies have shown that nanostructured V_2O_5 exhibits better electrochemical performance as compared to bulk V_2O_5 owing to their small particle size, microstructure / morphology that shorten Li-diffusion pathways[142]. Table 2.3 below shows a summary of various methods of synthesis for V_2O_5 nanostructures, as well as their corresponding electrochemical performances.

Nanostructure	Synthesis method	Initial discharge capacity (mAh g ⁻¹) at 0.1 C	Capacity at nth cycle (mAh g ⁻¹) at 0.1 C	Crystal size (nm)	Diameter (nm)	BET surface area (m ² g ⁻¹)	Ref.
Nanofibers	Electrospinning	375	347 (20 th)	15.5	350	97	[143]
Nanofibers	Electrospinning	316	220 (20 th)	70-80	500-1200	NA	[34]
Micro-spheres	Hydrolysis	437	245 (20 th)	NA	NA	31.2	[144]
Nanorod	Thermal decomposition	266	240 (30 th)	48	NA	NA	[102]
Nanowires	Electrospinning	390	201 (50 th)	50	200-250	NA	[35]
Nanocompo-site (PANI)	Hydrothermal	239	209 (30 th)	10-40	NA	NA	[115]
Thin film	E-beam irradiation	343	NA	NA	NA	NA	[141]
Nanowires	Hydrothermal	351	NA	NA	80-120	NA	[100]
Nanorods	Annealing	260	260 (50 th)	7-35	NA	NA	[145]
Nanofibers	Electrospinning	360	240 (25 th)	NA	40-70	NA	[7]
Submicron belts	Sol-gel	346	240 (20 th)	NA	NA	NA	[103]
Nanoscale single crystal	Electrospinning	120	NA	NA	250	NA	[32]
Nanostrips	Polyol	300	80 (20 th)	NA	NA	NA	[37]
Nanorods	Melt quenching	385	230 (50 th)	NA	10-50	NA	[146]
Micro-spheres	Solution method	319	160 (45 th)	NA	NA	NA	[126]
Nanowires	Hydrothermal	327	NA	NA	NA	NA	[110]

Table 2.3 Various methods of synthesizing V₂O₅ nanostructures and their respective properties[33]

2.2.3.1 Electrospinning

Figure 2.5 Schematic of typical electrospinning setup[147]

Electrospinning[133, 142, 148, 149] is a simple, one-step method which enables the synthesis of porous nanofibers from a polymeric precursor solution, which is usually spun from a syringe connected to a metallic needle. Usually, a polymeric solution is injected from a small nozzle under the influence of an electric field in the order of 20 to 30 kV. The accumulation of electrostatic charges on the surface of a liquid droplet induces the formation of a jet, or a cone-like spray, which becomes stretched to give the final nanofibers. Following the electrospinning process usually involves a series of drying and sintering processes at elevated temperatures. Depending on the viscosity of the solution, various magnitudes of electric field and feed rate can affect the thickness and formation of nanofibers[150].

With the current push towards nanostructures in materials for lithium ion batteries, electrospinning provides an ideal solution in the form of 1D nanoarchitectures (with larger aspect ratios than nanorods, nanotubes and nanobelts)[148]. As mentioned before, the 1D nanoarchitecture, is vital to achieve improved rate capability and cyclic retention in active materials for lithium ion batteries[149, 151].

Electrospinning is a versatile method[127] which allows the easy control of parameters, such as flow rate, viscosity, precursor concentration and applied potential, to obtain the desired thickness and length of the fibers. In addition, the electrospun fibers form a random, porous network, which is beneficial in electrochemical applications as it shortens the diffusion length for conductive ions between the electrolyte and active material. It is also possible to obtain aligned fibers via the electrospinning technique by making slight modifications to the setup[152, 153]. Moreover, electrospinning allows the co-spinning of two chemically different fibers[142, 154], as well as the option of aligned or hollow fibers.

Already, several spinel oxides like LiCoO_2 [151, 155-157], LiNiO_2 [158] and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [154, 159-161] have been successfully electrospun in recent years. Electrospinning of metal oxide fibers[142] like V_2O_5 and Nb_2O_5 have also been attempted, with good electrochemical performance. Ban *et al.* (2008, 2009)[7, 32] have successfully electrospun V_2O_5 fibers with PMMA as the polymeric precursor. After subjecting the fibers the V_2O_5 nanofibers to hydrothermal treatment to introduce hydronium ions (H_3O^+) into the layered structure of V_2O_5 , an initial capacity of 350 mAh g^{-1} was obtained.

Figure 2.6 Schematic of electrospun LiFePO_4 [20]

As mentioned in the previous section, LiFePO_4 was successfully made from the electrospinning technique[20]. In this study, the nanowires obtained had a conductive carbon nanotube core structure, which was covered with the LiFePO_4 -carbon composite outer shell (Figure 2.6). It was claimed that the uniformly dispersed carbon content of the LiFePO_4 nanowire played an important role in forming an electron conduction pathway. Also, the oxidation of Fe^{2+} was prevented by the presence of carbon. Through the above study, it is also noted that carbon nanotubes may be added to the precursor solution for electrospinning[20, 162], thus increasing the conductivity of the electrospun cathode material. In addition, electrospinning of conducting polymer polyaniline[163] and carbon nanofibers[127, 164, 165] have also been reported. These materials have high surface area and are suitable for applications in lithium ion batteries.

2.2.3.2 Urea combustion synthesis

Combustion synthesis is a low temperature, relatively simple, cost effective and convenient method to obtain the materials with high yield. Urea combustion is one of the more common methods and it involves exothermic reaction between urea (fuel) and nitrates (oxidizer) which drives the chemical synthesis[166]. Due to the self-propagating effect of this exothermic reaction, it enables the reaction to occur spontaneously at relatively lower temperatures leading to the formation of metal oxides thereby liberating nitrogen, hydrogen and oxygen gases[167].

The urea combustion method has been used to synthesize oxides for applications in lithium ion batteries, such as LiCoO_2 [167, 168], LiMn_2O_4 [169, 170], LiV_3O_8 [171], and spinel cobaltites[166, 172] like FeCo_2O_4 , MgCo_2O_4 and ZnFe_2O_4 , while a citric acid assisted combustion method was used to synthesize nanoparticulate $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ [173]. It is mentioned that these materials are formed in the sub-micron range and

have good crystallinity, in addition to increased specific capacity compared to bulk materials and good cycling properties.

2.2.3.3 Ionothermal method

More recently, ionothermal method has been used to synthesize nano-sized particles. It is mentioned to be an economical method due to the small amount of ionic liquid used in the synthesis and in some cases, it is reported that the ionic liquid used can be recovered and reused in subsequent syntheses.

LiFePO_4 and LiMnPO_4 nanoparticles have been obtained using the ionothermal method[23, 174, 175]. It is mentioned that the ionic liquids offer Lewis-neutrality and moderate solvating properties, leading to better control over the reaction kinetics via the selection of ionic liquids. Also, using the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) ionic liquid during the synthesis leads to formation of nanoparticles with sizes <500 nm and controlled formation of morphology. 150 mA h g^{-1} specific capacity was obtained for LiFePO_4 while 35 mA h g^{-1} reversible capacity was obtained in pure LiMnPO_4 and the carbon coated LiMnPO_4 gave rise to 95 mA h g^{-1} capacity.

2.3 Fundamental studies in lithium intercalation and charge storage mechanisms

In the fabrication process of LIB, the sensitivity of the Li-conducting electrolyte to ambient atmosphere requires the Li-ion cell to be sealed during the electrochemical charge / discharge process. Thus this makes it difficult for researchers to determine the chemical processes caused by such electrochemical processes. A number of studies involve simulation techniques, in-situ techniques and also ex-situ analyses of the electrodes. It is believed that the Li intercalation process occurs by a combination of charge-transfer and diffusion-controlled processes. Hence, a variety of in-situ techniques including methods like electrochemical impedance studies, galvanostatic intermittent titration technique (GITT), potentiostatic intermittent titration technique (PITT), lithium diffusion studies and also entropy thermodynamic measurement studies (ETMS) are used to study the different processes.

GITT was used by Pitchai *et al.* (2008)[37] to determine the diffusion coefficient of V_2O_5 nanostrips. Both GITT and PITT techniques have been used by Bramnik *et al.* (2007)[27] and Muraliganth and Manthiram (2010)[176] to study the intercalation potentials and polarizations in olivine phosphate materials. The PITT method is used to determine phase changes during the charging / discharging process while the GITT is more commonly used to determine the equilibrium voltages at different stages of deintercalation (charge).

Electrochemical impedance studies (EIS) are one of the most common methods used to explain the electrochemical processes, while the determination of the lithium diffusion coefficient using the Randles-Sevcik equation is sometimes applied in certain LIB studies. Finally, ETMS has been carried out mainly on graphitic anodes.

By fitting the EIS with an appropriate equivalent circuit, it is possible to gain insights to the effects of nanoarchitectures, conductivity *etc.* For example, Bakenov and

Taniguchi (2010)[22] elucidated the effect of different conductive carbons on the charge-transfer properties of LiMnPO_4 using EIS, while Oh *et al.* (2010)[177] compared the differences between different amounts of carbon on LiMnPO_4 . Rui *et al.* (2010)[46] and Muraliganth and Manthiram (2010)[176] also compared EIS with GITT techniques to elucidate the effects on lithium diffusion and redox potentials respectively.

Zhan *et al.* (2010)[112] used the Randles-Sevcik equation to elucidate the effect of Al-dopants on lithium diffusion rates in the V_2O_5 structure. This equation describes the effect of scan rate on the peak current in cyclic voltammetry. The diffusion coefficient of Li is then determined by the gradient of the plot of the peak current against the square root of the scan rate, as elucidated in the equation below.

$$I_p = 2.687 \times 10^5 n^{3/2} \nu^{1/2} D_{\text{Li}}^{1/2} A C_{\text{Li}} \quad (7)$$

Where I_p is peak current, n is the number of electrons per reactive species, ν is the scan rate, D_{Li} is the diffusion rate of Li^+ , A is the electrode area and C_{Li} is the concentration of Li^+ in electrolyte[112].

Lithium intercalation compounds undergo phase transitions during electrochemical charging / discharging and affect battery performance in terms of cycle life and specific capacity, among others[178]. The in-situ thermodynamic studies during electrochemical charge / discharge can enable insights to the phase transformations during the Li intercalation / deintercalation process. It is also discussed that particle size may affect the thermodynamics of Li intercalation compounds such as olivine phosphates, leading to possible amorphization of the active material. In the work of Yazami *et al.* (2006)[179], in-situ enthalpy and entropy values were recorded during the lithium intercalation of graphitic coke. Through this method, the process of graphitization during the open circuit voltage was studied and also the effect of graphitization on lithium intercalation was further elucidated.

2.4 Future challenges

Despite the abovementioned efforts and studies, cathode materials still remain as the limiting factor in the performance of lithium ion batteries. The search for a high energy density cathode material continues, along with the reduction of cost of raw materials and at the same time, maintaining the safety and thermal stability.

Firstly, by development of cathode materials with higher capacity (such as V_2O_5), it is possible to reduce the active cathode mass, to offset the high capacity of current anode materials. This in turn leads to lowered costs and also increased overall energy density of the lithium-ion cell. Development of cathode material with relatively good cycleability is also important to ensure long cycle life. Synthesis of nanostructures, doping and carbon coatings are some ways to improve the electrochemical properties of cathode materials.

Also, cathode materials with intrinsically higher working voltages, like olivine phosphates) can ensure high energy density. However, issues related to electrolyte decomposition and active material dissolution must be taken into account and thoroughly studied. Various analytical methods may be used to provide insights to the mechanisms related to lithium intercalation in cathode materials and other side reactions, if any, in order to enable future development of lithium ion batteries with long cycle life, higher energy density and good safety.

3. Methods and materials

3.1 Synthesis

In this section, methods of synthesis of various materials studied in this thesis are described in detail.

3.1.1 Hydrothermal synthesis of LiFePO_4 and LiMnPO_4

Hydrothermal methods are commonly used to synthesize olivine phosphate. In the hydrothermal synthesis of olivine lithium iron phosphate (LiFePO_4), the precursor solution was formed by mixing lithium hydroxide monohydrate (SigmaUltra, Sigma-Aldrich), iron(II) sulphate heptahydrate (reagent grade, Scharlau) and phosphoric acid (85 % H_3PO_4 , MalincKrodt) in the molar ratio of 3:1:1 and 0.315 ml of hydrazine (35wt. % in water, Sigma-Aldrich) in 15 ml solution of distilled water. 0.02 g of ascorbic acid (Sigma-Aldrich) was added to the solution to prevent premature oxidation of the Fe(II) salt. The solution was stirred thoroughly until a homogeneous solution was obtained and then transferred to a 23 ml Teflon-lined autoclave, where reaction was carried out in the oven at 220 °C for 5 hours. A similar method was used to synthesize LiMnPO_4 , replacing FeSO_4 with manganese (II) sulphate (MnSO_4 , >99%, Sigma-Aldrich), and the hydrothermal reaction was carried out at 220 °C for 48 hours to form LiMnPO_4 . The synthesis products are denoted as LFP-hyd and LMP-hyd for LiFePO_4 and LiMnPO_4 respectively.

3.1.2 Ionothermal synthesis of LiMnPO_4 , LiCoPO_4 and LiNiPO_4

The ionothermal method is a novel method used to synthesize olivine phosphate materials. So far, only ionothermal syntheses of LiFePO_4 and LiMnPO_4 have been reported in the literature[23, 174].

Ionothermal synthesis of LiMnPO_4 is similar to that reported in the literature[23]. Lithium acetate (99.9% metals basis, Alfa Aesar), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, Merck) and manganese (II) acetate tetrahydrate (99+%, Aldrich) were used in the molar ratio of 1:1:1 at 2 mmol concentration. It is mentioned[23] that the concentrations of the reactants affect the purity and the particle size of the final product. Lithium acetate and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ were dissolved in 5 ml of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI, >98%, Aldrich) while manganese (II) acetate was dissolved in 10 ml of ethylene glycol (Merck). The two solutions were mixed thoroughly before being stirred together. 0.1 g of sucrose (99.5%, BioXtra, Sigma) was added to the precursor before being sealed in a 23ml Teflon-lined autoclave. The autoclave was allowed to heat up to 250 °C in the oven at approximately 5 °C min⁻¹ heating rate and was held at this temperature for 48 hours. The reaction was allowed to cool naturally to room temperature before the products were washed thoroughly by centrifugation, twice by ethanol, thrice by distilled water and finally by ethanol again. The washed samples were dried in a vacuum oven at 80 °C overnight and the final product is denoted as LMP-IL.

For ionothermal synthesis of LiCoPO_4 , the same chemicals and proportion was used as described above, replacing manganese (II) acetate with cobalt (II) acetate tetrahydrate (Sigma-Aldrich) and without the addition of sucrose. The ionothermal reaction was held at 250 °C for 72 hours to enable formation of LiCoPO_4 and the final product is denoted as LCP-IL.

To obtain lithium nickel phosphate (LiNiPO_4), the same precursors are used as those mentioned for LiCoPO_4 , replacing cobalt (II) acetate with nickel (II) acetate tetrahydrate (98%, Aldrich), and reacting for three days at 250°C . To enable the complete formation of nickel (II) acetate, the product obtained from ionothermal synthesis was sintered at a range of temperatures from 700 - 850°C for 5 hours. Ionothermal synthesized LiNiPO_4 is denoted as LNP-IL.

3.1.3 Synthesis by Electrospinning: LiFePO_4 , LiMnPO_4 and V_2O_5 fibers

Electrospinning[148, 164] is a versatile method to produce random networks of nanofibrous structures with large aspect ratio. The application of a high-voltage (in kV range) to the precursor solution at the needle tip breaks the surface tension, leading to instantaneous evaporation of the solvent resulting in fiber formation. Resulting 1D nanofibers with possibly high surface areas make electrospinning a popular method to synthesize cathode materials.

Figure 3.1 (a) Schematic of electrospinning setup and (b) FE-SEM image of unsintered and sintered (inset) electrospun CNF[147]

Carbon nanofibers (CNF, Figure 3.1b) were electrospun from a precursor solution of 0.5 g polyacrylonitrile (PAN, Mw 150, 000, Aldrich) dissolved in 8ml of anhydrous N,N dimethyl formamide (DMF, 99.8%, Sigma-Aldrich) under heating at 80°C . The precursor solution was loaded onto a syringe attached with a 0.40 mm

thick disposable needle (Biomed Diagnostics Medical, USA), and ejected with a flow rate of 3 ml h^{-1} , in a setup represented schematically in Figure 3.1a. A positive potential of 15 kV was applied between the needle tip and an aluminium foil collector with a distance of 10 cm to obtain nanofiber net.

Firstly a slow heating rate of $1 \text{ }^{\circ}\text{C min}^{-1}$ was used and the temperature was held at $280 \text{ }^{\circ}\text{C}$ to stabilize the physical structure of the CNF, then a $2 \text{ }^{\circ}\text{C min}^{-1}$ ramping rate was used to increase the temperature to $800 \text{ }^{\circ}\text{C}$, which was held for 15 mins to thermally activate the CNF. Sintered CNF retains its fibrous structure after sintering (Figure 3.1b inset).

Three different olivine-carbon composite samples were synthesized (*viz.*, LFP-PAN, LFP-C and L-CNF). As-synthesized LiFePO_4 powder from the above precursor solution was mixed in the precursor carbon solution (PAN and *n,n* dimethyl formamide) for carbon nanofibers via ultrasonication and electrospun into a nanofiber net as described above, which was carbonized to obtain LFP-PAN sample. LiFePO_4 -CNF composite (LFP-C) was prepared by addition of as-formed pristine electrospun carbon nanofibers (CNF) to the above olivine precursor solution and hydrothermal heating at $220 \text{ }^{\circ}\text{C}$ for 5 hours before the product was filtered, washed with distilled water and dried. For comparison, L-CNF sample was prepared by simple mechanical mixing of CNF and LiFePO_4 powders synthesized by above-mentioned routes.

To electrospin lithium manganese phosphate (LiMnPO_4), a core-shell structure was applied to improve the intermittent contact of the LiMnPO_4 nanoparticles with the nanofibrous carbon structure. The CNF precursor solution was prepared as described above. As the addition of several precursors can affect the solubility in the solvent, lithium dihydrogen phosphate was used as both lithium and phosphate precursor. LiMnPO_4 precursor solution was prepared by dissolving 0.8 g lithium dihydrogen phosphate (LiH_2PO_4 , 97%, Alfa Aesar) and 1.34 g manganese (II) nitrate tetrahydrate

($\text{Mn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$, >97%, Sigma-Aldrich) in 5ml of DMF. To ensure the formation of LiMnPO_4 fibers, a separate solution of 0.6 g PAN dissolved in 15 ml DMF was prepared. The latter two solutions were then mixed together and stirred overnight to achieve a homogeneous solution.

Using a custom-made core-shell spinneret (Figure 3.2) attached to an electrospinning setup (Nanon), LiMnPO_4 core vs. Carbon shell fibers (LMP-C) and Carbon core vs. LiMnPO_4 shell fibers (C-LMP) were obtained. A flow rate of 2 ml h^{-1} was used for the core and 1 ml h^{-1} was used for the shell. A needle-to-collector distance of 15 cm and voltage of 30 kV was used. The as-spun fibers were collected on aluminium foil wrapped on a rotating drum and sintered in Argon with an initial slow ramping rate of 1°C and held at 280°C for 1 hour before sintering at 850°C for 5 h, using a heating rate of 2°C min^{-1} , to form LiMnPO_4 -carbon core-shell nanocomposite fibers.

Figure 3.2 Schematic of core-shell spinneret

V_2O_5 nanofibers (VNF) were synthesized as follows. 1.0 g polyvinylpyrrolidinone (PVP, M_w 360,000, Fluka) was dissolved in 6 ml of absolute ethanol (Merck). In a separate solution, 0.848 g of vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$, 98%, Sigma-Aldrich, 2.65 g) was dissolved in a mixture of 2 ml absolute ethanol and 2 ml acetic acid. These

two solutions were stirred for 30 mins before electrospinning. The well-mixed precursor solution was loaded in syringe attached with a 0.60 mm thick disposable needle and 2 ml h⁻¹ flow rate was used. 18.0 kV voltage was then applied to the needle tip to electrospin the fibers and they were collected on aluminium foil placed at a distance of 10 cm from the needle. The as-spun VNF was then sintered at 400 °C for 15 mins at a heating and cooling rate of 2 °C min⁻¹ to maintain the fibrous structure of the VNF. For comparison, VNF precursor was sintered under the same conditions without electrospinning and denoted as VNF-powder.

Aluminium-inserted (Al-inserted) VNF was synthesized using similar precursors, with the addition of aluminium nitrate (Al(NO₃)₃, Riedel de Haën, >98%). 0.6 g PVP was dissolved in 6 ml of absolute ethanol and 0.848 g of vanadyl acetylacetonate, was dissolved in a separate solution of 1 ml acetic acid and 3 ml absolute ethanol. 0.012 g ml⁻¹ and 0.03 g ml⁻¹ of aluminium nitrate (Al(NO₃)₃, Riedel de Haën, >98%) was added to the second solution to obtain Al_{0.5}VNF and Al_{1.0}VNF phases respectively. The distance between needle (same as for VNF) and Al collector was kept a distance of 10 cm with flow rate of 1.5 ml h⁻¹. As-spun fibers were then heat-treated at 400 °C for 15 min in air with a heating and cooling rate of 2 °C min⁻¹ to yield the resultant phase.

Figure 3.3 Schematic of Plasma-Enhanced Chemical Vapor Deposition (PECVD)[180]

To obtain carbon-coated VNF (C-VNF), the sintered VNF were coated with amorphous carbon by plasma-enhanced chemical vapor deposition (PECVD) using acetylene (C_2H_2) as precursor for carbon at 500 °C as shown schematically in Figure 3.3. PECVD process was performed on a commercial vacuum system (Plasma Electronics, CVD-PECVD DOMINO) working with radio-frequency excitation (13.56 MHz). 80 sccm of acetylene (C_2H_2) were introduced into the reaction chamber through a mass flow controller (MKS MFC 1179) controlled by a software interface during the reaction and the reactor pressure was kept constant at 14 Pa. C_2H_2 was used as unique precursor source without any additional carrier gas and was decomposed directly on the VNFs deposited which were loaded in a ceramic boat placed on the heatable RF electrode. The temperature was set to 500 °C and the plasma power to 50 W (resulting in a bias of 214-218 V). The VNF were coated with carbon using this setup for two different durations namely, 15 and 30 min and hereafter denoted as C-VNF-15 and C-VNF-30, respectively.

3.1.4 Sol-gel synthesis of LiMnPO_4 and LiCoPO_4

Citric-assisted (CAM) sol-gel method[58] is commonly used to synthesize active electrode nanomaterials for LIBs. Herein, olivine phosphates LiMnPO_4 and LiCoPO_4 are synthesized using CAM sol-gel method, with slight variation from methods previously reported in literature.

1:1:1:0.1 molar ratio of lithium acetate (99.9% metals basis, Alfa Aesar), diammonium hydrogen phosphate $((\text{NH}_4)_2\text{HPO}_4$, Merck), manganese (II) acetate tetrahydrate (99+%, Aldrich) or cobalt (II) acetate tetrahydrate (Sigma-Aldrich), and citric acid monohydrate (>99.5%, Sigma-Aldrich) were dissolved in 20 ml distilled water. Lithium acetate was used in slight excess to ensure formation of the end compounds. The solution was mixed and stirred with heating at 120 °C for several hours to form a gel. Subsequently the gel was decomposed at 200 °C and the product was sintered in air at 400 °C for 3 hours to remove the excess carbon from the decomposition of citric acid. To obtain LiMnPO_4 , the pre-sintered product was calcined under Argon atmosphere at a range of temperatures from 550 °C to 850 °C for 5 hours. For LiCoPO_4 , the pre-sintered product was sintered at 850 °C for 10 hours in air. Sol-gel synthesized LiMnPO_4 and LiCoPO_4 are denoted as LMP-SG and LCP-SG respectively.

3.1.5 Solid-state synthesis of LiMnPO_4 and LiCoPO_4

The solid-state synthesis method is usually one of the first methods of synthesis used to synthesize electroactive compounds for applications in LIB. However, the larger particle size obtained is usually considered undesirable as current research focuses on nanomaterials. Nevertheless, the larger particle size seems to benefit the electrochemical performance of LiCoPO_4 due to reduced extent of Co dissolution in the electrolyte.

To synthesize LiMnPO_4 , stoichiometric amounts of Li_2CO_3 , MnO and $\text{NH}_4\text{H}_2\text{PO}_4$ were ball-milled for 1 hour using a high energy ball mill (Spex 8000D) and decomposed at $400\text{ }^\circ\text{C}$ for 3 h to decompose the ammonium moieties. Then, the resultant materials were mixed and pressed into a pellet before firing at $850\text{ }^\circ\text{C}$ for 6 h in Ar atmosphere. The sintered pellets were then ground in an analytical mill (Cole-Parmer) for use in preparation as cathode materials, denoted as LMP-SS.

Lithium carbonate (Li_2CO_3 , Merck), cobalt (II) nitrate hexahydrate (98+%, Sigma-Aldrich) and $(\text{NH}_4)_2\text{HPO}_4$ were mixed together (as above) in molar ratio of 1:1:1 for the synthesis of LiCoPO_4 . The well-mixed precursor was sintered in air at $400\text{ }^\circ\text{C}$ for 3 hours, and it was sintered further in $900\text{ }^\circ\text{C}$ for 10 hours in air. The sintered pellets were then ground in an analytical mill for use in preparation as cathode materials, denoted as LCP-SS.

3.1.6 Urea combustion synthesis of V_2O_5

Urea combustion is a low temperature, relatively simple, cost effective and convenient method to obtain the materials with high yield. It involves exothermic reaction between urea (fuel) and nitrates (oxidizer) which drives the chemical synthesis[166]. Due to the self-propagating effect of this exothermic reaction, it enables the reaction to occur spontaneously at relatively lower temperatures leading to the formation of metal oxides thereby liberating nitrogen, hydrogen and oxygen gases.

2.65 g of vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$, 98%, Sigma-Aldrich) was dissolved in 5 ml of nitric acid (69%, Honeywell) by heating at $60\text{ }^\circ\text{C}$ with continuous stirring resulting in a blue coloured solution to which 1.8 g of urea (Panreac) was added until dissolution occurred. This mixture was heated at $300\text{ }^\circ\text{C}$ for 20 min to enable self-propagating combustion reaction. The obtained powder comprising the mixture of ~55

wt.% V_2O_5 and ~ 46 wt.% VO_2 in the crystalline phase (as confirmed by Rietveld refinement via Topas V3 software), as well as ~ 20 wt.% amorphous carbon. Hence, a subsequent heat treatment is required to achieve highly crystalline and single phase V_2O_5 particles. The powder obtained from the combustion was sintered at various temperatures (300–600 °C) for different durations ranging from 1–3 h in air to obtain single-phase V_2O_5 . For comparison, V_2O_5 was also prepared by direct heating of 2.65 g of $\text{VO}(\text{acac})_2$ at 600 °C for 1 h without any combustion process (NUC). In addition, heat-treated (600 °C sintered for 1 h) powder was ball-milled for further size reduction using high energy ball-mill (Spex, 8000D) for 1 h with and without carbon. For ball milling with carbon, active material to carbon ratio of 3:1 was maintained and no more carbon was included during the fabrication of the electrode. From here on, the obtained products are denoted as the following example VUC 300-1, where VUC denotes V_2O_5 urea combustion, ‘300’ denotes 300 °C used as sintering temperature and ‘1’ as sintering duration of 1 hour.

To improve the electrochemical properties of V_2O_5 , doping[112] with metallic ions such as aluminium can be carried out. Al-inserted VUC was obtained by dissolving 1.0 g of the as-combustion synthesized compound in 0.3 M oxalic acid solution and adding of 0.38 and 0.94 g respectively of $\text{Al}(\text{NO}_3)_3$ to obtain $\text{Al}_{0.66}\text{V}_2\text{O}_5$ and $\text{Al}_{1.1}\text{V}_2\text{O}_5$ respectively. The blue solution was stirred for 5-6 hours at 80 °C before being dried overnight at 80 °C. The obtained powder was then sintered at 400 °C for 6 hours to obtain the final product. For comparison, the as-combustion synthesized powder was also sintered under similar conditions, without addition of $\text{Al}(\text{NO}_3)_3$.

3.1.7 Chemical lithiation

Due to the variable oxidation states of vanadium in V_2O_5 , researchers have acknowledged that the V_2O_5 structure undergoes distortion to accommodate the intercalation of Li^+ ions into its layered structure. As such, several works have been done to study these phase transformations by prelithiation of V_2O_5 by ex-situ method. Whittingham (1977)[104], Garcia *et al.* (1999)[105] and Pecquenard *et al.* (1995)[106] carried out prelithiation of V_2O_5 using butyl lithium solution while Murphy *et al.* (1979)[107] prelithiated V_2O_5 using lithium iodide (LiI) in acetonitrile. Mai *et al.* (2010)[36] also noted that the prelithiation of nanostructured electrode materials led to increased cycling stability in general.

In this thesis, ex-situ prelithiation of urea-combustion synthesized V_2O_5 is done to study the corresponding phase transformations and its effects on electrochemical behavior. VUC 600-1, urea-combustion synthesized V_2O_5 obtained by sintering at 600 °C for 1 hour in air, was used for the chemical lithiation. 1.0 g of VUC 600-1 was dispersed in 20 ml n-hexane (99 %) and stoichiometric proportions of n-butyllithium (1.6 M in hexane, Aldrich) were added[105]. Due to the reactive nature of BuLi, the entire reaction was conducted in an Argon-filled glovebox.

With reference to the above equation, the mixtures were stirred for two days to obtain $x < 1$ and for one week to get for $x \geq 1$ composition. The lithiated powders were then obtained via filtration and washed with hexane and dried in the glovebox. The lithiated samples are denoted as 0.2Li- V_2O_5 , 0.5Li- V_2O_5 , 1.0Li- V_2O_5 , 2.0Li- V_2O_5 and 3.0Li- V_2O_5 , in accordance to the stoichiometric proportions of BuLi added.

3.2 Characterisation Studies

3.2.1 Morphological and structural characterisation

Morphological features of all samples were studied using field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F) with an accelerating voltage of 5 kV and a transmission electron microscope (TEM, JEOL 2100F) in high resolution mode operating at 200 kV attached with elemental mapping. Multislice simulation was performed using JEMS (Version 3.3111 U2008, P. Stadelmann, CIME-EPFL, Switzerland) for comparison with the high resolution image. Where required, scanning electron microscope (SEM, JEOL-JSM 5310) attached with energy dispersive spectroscopy (EDS) was used. Structural properties were examined using Bruker X-ray diffractometer using Cu-K α radiation between 10 to 80 ° 2-theta (2θ), with a step size of 0.02 °. The obtained X-ray diffraction (XRD) patterns were analyzed by Rietveld crystal structure refinement[181, 182] using Topas V3 (Bruker-AXS) software using fundamental parameters approach[183]. X-ray photoelectron spectroscopy (XPS) was performed with an Axis Ultra (Kratos) spectrometer with monochromatic Al-K α excitation and analysed using CasaXPS software (Version 2.3.15). Inductively-coupled plasma (ICP, Agilent 7700) analyses were carried out on acid-digested samples.

3.2.2 Characterisation of organics

Fourier transform infrared spectroscopy (FTIR), where required, were recorded on pellets of the materials mixed with KBr using a Perkin Elmer Spectrum GX FTIR in the range of 4000 to 400 cm⁻¹ (step size 2 cm⁻¹). Thermo-gravimetric analyses (TGA) for carbon-composites and as-combustion synthesized V₂O₅ precursor were recorded using Perkin Elmer Q500 with the scan rate of 5 °C min⁻¹ from room temperature to 800 °C under 60% air + 40% nitrogen atmosphere. Brunauer-Emmet-Teller (BET) surface area studies were also conducted using Nova 3200e surface area and porosity analyser.

3.3 Electrochemical characterisation

3.3.1 Cell fabrication

Composite cathodes were formulated by mixing active material, binder (Kynar 2801), and conductive additive (Super P Li carbon, Timcal) in the weight ratio 60:20:20, respectively, using 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich) as solvent for binder to form slurry. The resulting viscous slurry was subsequently coated over aluminium (Al) foil using a doctor blade technique. Electrode coated Al foils were dried in a vacuum oven for several hours to remove the solvent molecules and pressed in between the twin rollers to provide necessary adherence towards Al current collector. The dried electrodes were punched out with 16 mm diameter blanks and same area of counter electrode lithium foil (~0.59 mm thick, Hohsen Corporation, Japan) was used for the fabrication of test cells. The lithium insertion properties of all materials were evaluated in half-cell configuration using two-electrode CR 2016 coin cell assembly. Where the full-cell configuration was used, graphite powder (~325 mesh, 99.9995% purity, Sigma-Aldrich) or lithium titanate spinel (nanopowder, Sigma-Aldrich) coated on copper foil were used as the anodes. The coin-cells were assembled under Argon filled glove box (MBraun) and the electrodes were separated by Celgard 2400 separator. For cells in which high temperature testing was required, glass fiber (Whatman) separators were used. The 1 M lithium hexafluorophosphate (LiPF_6) in EC: DEC (1:1 w/w, Danvec) binary mixture was used as electrolyte solution. For LiCoPO_4 and LiNiPO_4 -based half-cells, where higher voltage was required, LF 40 SelectilyteTM (1 M Lithium tris(pentafluoroethyl)trifluorophosphate (LiFAP) in EC : DEC 1:1 w/w, Merck) and Lithium bis(oxalato) borate (LiBOB , Chemetall) was used as electrolyte additive.

3.3.2 Electrochemical studies

Galvanostatic discharge-charge profiles of test cells were conducted between 1.75-4.0 V vs. Li/Li⁺ at ambient and elevated temperature (55 °C) conditions, using battery testing systems (Neware) at constant current mode. Cyclic voltammetric (CV) traces and electrochemical impedance spectroscopic (EIS) studies were conducted using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat.

In the fabrication process of LIB, the sensitivity of the Li-conducting electrolyte to ambient atmosphere requires the Li-ion cell to be sealed during the electrochemical charge / discharge process. Thus this makes it difficult for researchers to determine the chemical processes caused by such electrochemical processes. A number of studies involve simulation techniques, in-situ techniques and also ex-situ analyses of the electrodes. It is believed that the Li intercalation process occurs by a combination of charge-transfer and diffusion-controlled processes. Here, several electrochemically-related analytical techniques were used to elucidate the electrochemical reactions and are described further in the following sub-sections.

3.3.2.1 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance studies (EIS) are one of the most common methods used to elucidate the electrochemical processes and understand the kinetics of the electrochemical Li intercalation / deintercalation processes. In general, EIS enables qualitative comparisons of charge-transfer and diffusion-controlled reactions before and after electrochemical charging / discharging, as well as among different materials.

In the typical EIS of a LIB, the semicircle observed in the high frequency region is due to the formation of solid electrolyte interphase (SEI) layer and surface film capacitance, while the middle-to-low frequency region refers to the charge transfer (CT)

and interfacial capacitance across the electrode/electrolyte interface. The inclined vertical line in low frequency regions refers to the lithium-diffusion-related kinetics[184, 185], and is usually denoted as the Warburg element in the equivalent circuit.

By fitting the EIS with an appropriate equivalent circuit, it is possible to gain insights to the effects of nanoarchitectures, conductivity *etc.* For example, Bakenov and Taniguchi (2010)[22] elucidated the effect of different conductive carbons on the charge-transfer properties of LiMnPO₄ using EIS, while Oh *et al.* (2010)[177] compared the differences between different amounts of carbon on LiMnPO₄. Rui *et al.* (2010)[46] and Muraliganth and Manthiram (2010)[176] also compared EIS with GITT techniques to elucidate the effects on lithium diffusion and redox potentials respectively.

In this thesis, EIS studies were carried out on equilibrated cells before cycling, by applying a.c. amplitude of 10 mV over the frequency range 100 kHz to 5 mHz at open circuit potential, at room temperature. The Nyquist plots Z'' vs. Z' were derived and analysed using Zplot and Zview software (Version 2.2, Scribner Associates Inc., USA).

3.3.2.2 Lithium diffusion coefficient by Randles-Sevcik equation

The Randles-Sevcik equation describes the effect of scan rate on the peak current in cyclic voltammetry. The diffusion coefficient of Li is then determined by the gradient of the plot of the peak current against the square root of the scan rate, as elucidated in the equation below.

$$I_p = 2.687 \times 10^5 \text{ n}^{3/2} \nu^{1/2} D_{Li}^{1/2} A C_{Li} \quad (7)$$

Where I_p is peak current, n is the number of electrons per reactive species, ν is the scan rate, D_{Li} is the diffusion rate of Li⁺, A is area of electrode and C_{Li} is the concentration of

Li^+ in electrolyte. Zhan *et al.* (2010)[112] used this method to elucidate the effect of Al-dopants on lithium diffusion rates in the V_2O_5 structure.

To obtain the D_{Li} values, V_2O_5 -based half-cells were cycled in potentiostatic mode (CV) at scan rates of 0.1, 0.2, 0.5, 1 and 2 mV s^{-1} . The peak currents of the main oxidation peaks were used for the calculations.

3.3.2.3 Electrochemical thermodynamic measurement studies (ETMS)

Electrochemical thermodynamic measurement studies are in-situ thermodynamic studies during electrochemical charge / discharge can enable insights to the phase transformations during the Li intercalation / deintercalation process. According to the works of Reynier and Yazami *et al.* (2006)[179, 186, 187], the Gibbs free energy ΔG can be related to the open circuit voltage (OCV) E_o , as expressed in the following equation,

$$\Delta G(x) = -FE_o(x) = \Delta H(x) - T \Delta S(x) \quad (9)$$

where F is the Faraday constant and T the absolute temperature. The temperature dependence of the OCV can be used to determine the entropy ΔS and enthalpy ΔH of the equilibrated half-cells.

Electrochemical thermodynamic measurements (ETMS) were measured in a two-electrode configuration (vs. Li/Li^+) using an electrochemical thermodynamic measurement system (ETMS, BA 1000, KVI Pte Ltd). The OCV of the half-cells at temperatures of 25 °C, 20 °C, 15 °C, and 10 °C were recorded and calculated automatically to give the entropy and enthalpy values at corresponding states of charge.

4. Results

This chapter details the results of various experiments undertaken in this thesis. Firstly, the application of the electrospinning technique on the synthesis of cathode materials for LIBs was explored. The various combinations of carbon composites with poorly-conducting olivine phosphate LiFePO_4 are explored and this work contributed to the idea of the formation of core-shell nanostructures in electrospun LiMnPO_4 , in an effort to improve intermittent contact with conducting species. Besides high-voltage cathode materials, the desire for high energy density materials also led the exploration of high capacity V_2O_5 , which undergoes multistep redox reactions to accommodate $\sim 2\text{-}3$ Li per V_2O_5 . The applicability of nanoparticles is also studied via the various methods of syntheses and also extensive electrochemical studies.

Hydrothermal, ionothermal, sol-gel, solid-state, urea combustion synthesis methods are presented and their effects of the electrochemical performance as cathode materials are elucidated. In addition, charge-transfer and diffusion-controlled mechanisms, which is a good indicator of the properties of various cathode materials, enable new insights into the in-situ environment of the LIB. A correlation of the charge storage and transport mechanism of cathode materials with morphology, surface area, and interfacial properties affected by process parameters, electrode and electrolyte treatments had been carried out through various materials and electrochemical characterization techniques. Pre-lithiation, entropy and lithium diffusion studies also enable correlation of the multistep phase changes within the V_2O_5 cathode materials.

4.1 Nanofiber-based cathodes

4.1.1 Justification for electrospinning in LIB

Olivine LiFePO_4 is a promising cathode material[52, 53, 55] owing to its low cost, low toxicity and safety. Although it possesses high theoretical capacity (170 mAh g^{-1}), its practical achievable capacity is less than 120 mAh g^{-1} , owing to low electronic conductivity (10^{-9} - $10^{-10} \text{ S cm}^{-1}$) and low ionic diffusivity, which in turn prevents its large-scale application in electric vehicles (EVs) and hybrid electric vehicles (HEVs). The poor rate capability of LiFePO_4 cathodes is an impediment to their applicability in lithium-ion batteries unless modifications are made to improve their low electronic conductivity and the slow lithium ion diffusion across the $\text{LiFePO}_4/\text{FePO}_4$ interface. Various approaches, such as conductive carbon coatings[17, 188], co-synthesis with carbon precursors[70, 74], decreasing particle size[18], cation doping[71, 89, 189], and carbon nanotubes (CNT) addition[61, 77] have been studied to improve LiFePO_4 conductivity.

Vanadium-based layered oxides with tunable oxidation states (V^{5+} , V^{4+} and V^{3+}) such as VO_2 , V_6O_{13} and V_2O_5 are potential cathode materials for rechargeable lithium batteries[190]. Among these vanadium pentoxide (V_2O_5) is an attractive candidate for cathodes in Li-ion batteries as they exhibit high theoretical capacities ($\sim 400 \text{ mAh g}^{-1}$) due to their capability to intercalate nearly 3 Li^+ ions per mole of active material ($\text{V}_2\text{O}_5 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{V}_2\text{O}_5$).

On the other hand, performance of conventional bulk V_2O_5 powder cathodes is limited by slow lithium diffusion rate ($\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) in the lattice, structural instability with lithium intercalation/de-intercalation and low electronic conductivity (10^{-2} - $10^{-3} \text{ S cm}^{-1}$), leading to inferior battery performance such as low initial capacity, rapid capacity fading and poor rate capability. In order to improve the electrochemical performance of V_2O_5 , there has been an increased interest in fabricating nanoarchitectures of V_2O_5 .

Studies have shown that nanostructured V_2O_5 exhibits better electrochemical performance as compared to bulk V_2O_5 owing to their small particle size, microstructure / morphology that shorten Li- diffusion pathways[142].

Electrospinning is a method of production of nanofibers from polymeric liquids via application of an electrostatic field. This involves use of high accelerating voltage to overcome surface tension of polymeric precursor solution resulting in a ejecting of a continuous jet, producing nanofibers on the collector upon evaporation of solvent[127, 148, 149]. Diameter and length of fibers can be controlled by varying parameters such as the flow-rate, accelerating voltage and also the needle-to-collector plate distance[5, 164, 191]. Electrospinning is a promising method for electrode material synthesis as the resulting nanofiber mats have a large aspect ratio that would facilitate lithium-ion transport due to small electronic resistance and short diffusion pathways, hence enabling higher rate lithium-ion storage capability, faster charge-discharge kinetics, and better cyclic stability.

4.1.2 Electrospun Olivine-Carbon nanocomposites

4.1.2.1 LiFePO_4 -Carbon nanocomposites

The physical and electrochemical properties of LiFePO_4 -carbon nanocomposites are compared in this section. Hydrothermally-synthesized LiFePO_4 (LFP-hyd) is mixed with carbon nanofiber precursor in various combinations, as described in section 3.1.3. In the following paragraphs, LFP-C denotes co-synthesized LiFePO_4 -carbon composite, in which LiFePO_4 nanoparticles are hydrothermally grown onto electrospun carbon nanofibers, while LFP-PAN comprises of co-electrospun LiFePO_4 mixed in carbon nanofiber precursor solution. L-CNF, a physical mixture of LiFePO_4 nanoparticles and carbon nanofibers, is also presented as comparison.

Figure 4.1 Field-emission scanning electron microscopy (FE-SEM) of (a) as-spun carbon nanofibers (CNF) and (b) sintered CNF[147]

Under the FE-SEM, morphology of pristine electrospun carbon nanofibers (CNF, Figure 4.1b) showed that the average diameter of the unsintered fibers is about 500 nm, which remained unchanged upon sintering. Subsequent hydrothermal synthesis carried out on CNF soaked in olivine precursor solution to obtain LFP-C resulted in a homogeneous distribution of LiFePO_4 particles growing onto these carbon fibers (Figure 4.2a). TEM image of LFP-C (Figure 4.2b) also shows the

presence of LiFePO_4 particles distributed along the length of the carbon nanofiber. However, in the physically-mixed sample (L-CNF) of LiFePO_4 with CNF (Figure 4.2e), the LiFePO_4 particles are not homogeneously distributed and there is very little contact surface between the olivine particles and carbon nanofibers. On the other hand, the LiFePO_4 particles were embedded inside the carbon fibers in the LFP-PAN sample (Figure 4.2c & d), as seen from the SEM and TEM images.

The morphological difference between the LFP-PAN and LFP-C can be attributed to their respective synthesis method. In the LFP-PAN sample, the LiFePO_4 particles were added to the PAN precursor, the particles are thus covered by the CNF which formed around the particles during electrospinning, whereas in the LFP-C sample, the CNF was added to the LiFePO_4 precursor solution resulting in the growth of the olivine particles on the CNF (inset schematic, Figure 4.2a-b). The tenacity of these two samples was evident from the TEM sample preparation, as the LiFePO_4 crystallites were still attached onto the carbon fibers after ultrasonication.

Figure 4.2 FE-SEM images of (a) LFP-C, (c) LFP-PAN, (e) L-CNF and corresponding TEM images of (b) LFP-C, (d) LFP-PAN and (f) L-CNF[147]

From the TGA, average weight percentages of pristine LiFePO_4 , and active material in the LFP-C and LFP-PAN composites were derived. LFP-hyd contains ~100% active material while LFP-C contained ~14 wt. % of active material (Li-Fe-P-O), with ~86 wt. % carbon, and LFP-PAN contained ~61 wt. % of active Li-Fe-P-O phase respectively.

Figure 4.3 TGA showing carbon and active weight percentages of respective samples

XRD patterns of all the samples are shown in Figure 4.4, indicated that the main crystalline phase in the composites is LiFePO_4 (Tryphylite, $Pnma$, $a = 10.304(7) \text{ \AA}$, $b = 6.005(7) \text{ \AA}$, $c = 4.710(8) \text{ \AA}$). Rietveld refinement was carried out on all three diffraction patterns and hydrothermally synthesized powder showed single-phase formation of LiFePO_4 . Rietveld phase analysis of the XRD pattern of LFP-C XRD showed 95 wt. % of LiFePO_4 phase, with 5 wt. % of a mixture of iron phosphides (FeP_2 , FeP_4) and iron oxide (Fe_2O_3), while LFP-PAN had 100 wt. % LiFePO_4 in its crystalline phase. In general, the peaks in XRD patterns of LiFePO_4 -carbon composites (LFP-C and LFP-PAN) were broad due to the presence of large

amounts of carbon. In LFP-C, a broad hump at can be observed at around 20° 2θ because of the higher amount of carbon present in this sample as compared to LFP-PAN. This observation is in agreement with the TGA results.

Figure 4.4(a) Rietveld refinement of pristine LiFePO_4 (LFP-hyd) and (b) respective XRD patterns of LFP-C and LFP-PAN compared with LFP-hyd[147]

BET (Brunauer-Emmett-Teller) surface area for LFP-C was in the range of $10\text{-}20\text{ m}^2\text{ g}^{-1}$ and the average pore diameter was about $300\text{ \AA}$, similar to that of pristine CNF. In contrast, LFP-PAN had lower surface area ($\sim 2\text{ m}^2\text{ g}^{-1}$), and the lower average pore diameter ($\sim 180\text{ \AA}$). It can be expected that LFP-C would have higher initial specific capacity, due to the larger surface area, and larger porosity of LFP-C could also mean that the carbon-nanofibrous structure can absorb more electrolyte, hence increasing the

surface area of contact between the electrolyte and the active electrode material LiFePO_4 . Electronic conductivity of pristine hydrothermally-synthesized LiFePO_4 (LFP-hyd), measured by a four-point probe method, was $5.0 \times 10^{-9} \text{ S cm}^{-1}$ which is in agreement with the reported literature values. The electronic conductivity of the LFP-C and LFP-PAN samples increased to 0.01 and $1.7 \times 10^{-4} \text{ S cm}^{-1}$ respectively, which can be attributed to the presence of conducting carbon nanofibers, which have electronic conductivity $\sim 1 \text{ S cm}^{-1}$, in these composites.

Figure 4.5 Cyclic voltammograms at scan rate of 0.1 mV s^{-1} of the samples[147]

Cyclic voltammogram (CV) of LFP-C, showed symmetrical peaks when cycling in the range of 2.0 to 4.5 V vs. Li/Li^+ , indicating reversible Li-intercalation/deintercalation (Figure 4.5) during charge / discharge. LFP-hyd exhibited an oxidation peak at 3.7 V vs. Li/Li^+ and a reduction peak at 3.25 V vs. Li/Li^+ . The potential difference between the two peaks is 0.45 V. As compared to LFP-hyd, the potential difference in oxidation-reduction peaks in LFP-C is much smaller (0.1 V), with the oxidation peak occurring at 3.5 V vs. Li/Li^+ and reduction peak at 3.4 V vs.

Li/Li^+ demonstrating that the reversibility and reactivity of LFP-C are enhanced due to improvement of electronic conductivity. This is also seen in L-CNF, where the oxidation peak is at 3.55 V vs. Li/Li^+ and reduction peak is at 3.3 V vs. Li/Li^+ with a potential difference of 0.25 V. This is an indication of better reversibility of intercalation / deintercalation of lithium ions into the LiFePO_4 structure, by the addition of CNF, either by the synthesis route or physically-mixing. In comparison, cyclic voltammograms of LFP-PAN did not show prominent redox peaks corresponding to LiFePO_4 lithium intercalation-deintercalation. Also, the redox peaks for LFP-PAN appear at ~ 3.2 V and ~ 3.7 V respectively, are further apart.

Figure 4.6 Galvanostatic traces of first charge / discharge cycle for respective samples

In the first galvanostatic charge / discharge cycles at 0.1 C rate (17 mA g^{-1}), it is observed that the LFP-hyd has a flat intercalation voltage at ~ 3.4 V vs. Li/Li^+ and initial specific discharge capacity of $\sim 130 \text{ mAh g}^{-1}$. It can also be observed LFP-C and L-CNF also have similar discharge plateaus at ~ 3.4 V. However, it is observed that for

L-CNF, a much shorter plateau is formed and as a result, there is some irreversible capacity loss in the first charge / discharge cycle. The initial discharge capacities for LFP-C and L-CNF are $\sim 160 \text{ mAh g}^{-1}$ (close to theoretical capacity) and $\sim 140 \text{ mAh g}^{-1}$, respectively. Finally it is observed that LFP-PAN undergoes large polarisation during galvanostatic charge / discharge, with an intercalation voltage starting at $\sim 3.3 \text{ V}$ and deintercalation voltage of $\sim 3.5 \text{ V}$, along with heavily sloping plateaus. The low initial capacity $\sim 105 \text{ mAh g}^{-1}$ of LFP-PAN sample may be attributed to the polarisation.

Figure 4.7(a) Charge-discharge cycling of respective samples 0.1 C rate, and (b) extended charge discharge cycling of LFP-C and LFP-hyd[147]

Upon further cycling, charge-discharge cycling data of LFP-C (Figure 4.7a) show $>80\%$ retention of initial capacity ($\sim 130 \text{ mAh g}^{-1}$) after 20 cycles. It can be observed that LFP-hyd had the best stability, maintaining almost 100 % cyclic efficiency throughout 50 cycles. Although L-CNF showed higher initial capacity as compared to LFP-hyd, the capacity fading was rapid with capacity dropping down to 120 mAh g^{-1} after 20 cycles. The higher initial specific capacity and cyclic retention behavior of LFP-C, as compared to L-CNF, indicates that the advantage intimate

chemical contact of the olivine LiFePO_4 nanoparticles (LFP-C) could improve the electrochemical properties more than that of physically-attached nanoparticles (L-CNF). LFP-PAN showed the lowest initial specific capacity ($\sim 105 \text{ mAh g}^{-1}$) as compared to other samples and exhibited poor cycling stability with the capacity dropping to 40 mAh g^{-1} within 10 cycles. Such electrochemical behaviour could be due to reduced reversibility of Li^+ intercalation / deintercalation as observed in the CV.

4.1.2.2 Core-shell LiMnPO_4 -carbon nanocomposites

The superior electrochemical performance of the LiFePO_4 -Carbon composite fibers (LFP-C) as compared to LFP-hyd and physical L-CNF mixtures lays the foundation for this concept of core-shell LiMnPO_4 -carbon composite fibers. In the core-shell electrospinning method, it was expected to combine the advantageous properties of higher electronic conductivity, improved intimate olivine particle-carbon fiber contact, as well as higher surface area, to enable the application of LiMnPO_4 in LIBs. In comparison to LiFePO_4 , LiMnPO_4 has inherently much poorer conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) and lithium intercalation / deintercalation in such a compound is further impeded by the disorder of the crystal structure caused by the d-orbital, known as the Jahn-Teller effect[23, 26, 192].

Electrospun core-shell LiMnPO_4 -carbon composite fibers were synthesized using a core-shell spinneret. After sintering, it can be nanofibers in the range of 500-800 nm can be observed under the FE-SEM and TEM as shown in Figure 4.8. The light and dark areas of contrast show the formation of LiMnPO_4 and carbon layers, as elucidated further in Figure 4.9. It is also observed in Figure 4.8a the fiber has a smoother surface (carbon shell, LMP-C) as compared to that in Figure 4.8b (LiMnPO_4 shell, C-LMP).

Figure 4.8 Transmission electron microscopy (TEM) images of (a) LMP-C and (b) C-LMP fibers with corresponding FE-SEM images as insets

Figure 4.9 Cross-sectional elemental (carbon and manganese) line-scans of (a) LMP-C and (b) C-LMP fibers

Figure 4.9 shows the cross-sectional C and Mn elemental linescans for the corresponding fibers as shown in Figure 4.8. In LiMnPO_4 -core carbon-shell fibers (LMP-C, Figure 4.8a & 9a), it is observed that there is higher carbon content extending to the sides of the fiber, which indicate the formation of a carbon shell on LiMnPO_4 . Correspondingly, for the carbon-core LiMnPO_4 -shell fibers (C-LMP, Figure 4.8b & 4.9b), the line-scans show higher content of Mn, as compared to carbon, at the sides of the fiber, which indicates the formation of LiMnPO_4 shell.

Figure 4.10 (a) X-ray diffraction patterns and (b) TGA diagrams of C-LMP and LMP-C

To determine the phase purity of the LiMnPO₄-carbon composite fibers, X-ray diffraction patterns were analysed by the Rietveld refinement method, showing 100% LiMnPO₄ formation in the crystalline phase. All peaks could be indexed to the Lithiophilite *Pnmb* phase of LiMnPO₄. From the refinement, lattice parameters as evaluated in the LiMnPO₄ phase in C-LMP are $a = 6.0974(3) \text{ \AA}$, $b = 10.4409(5) \text{ \AA}$, $c = 4.7383(3) \text{ \AA}$ and crystal size = 24.8(1) nm, while for LMP-C, the lattice parameters are $a = 6.1192(2) \text{ \AA}$, $b = 10.4760(3) \text{ \AA}$, $c = 4.7565(2) \text{ \AA}$, and crystal size = 47.9 (2) nm. The large amount of carbon present in the fibers led to the sloping background of the XRD patterns, while no extra peaks related to carbon were detected. Analysis via TGA method showed the presence of ~28 wt. % and ~30 wt. % of carbon in C-LMP and LMP-C fibers respectively.

Figure 4.11 Cyclic voltammogram of LiMnPO₄-Carbon composite fibers

To elucidate the Li intercalation / deintercalation occurring during electrochemical charging / discharging, the half-cells based on LMP-C and C-LMP fibers were cycled in the range of 2.4-4.5 V vs. Li/Li⁺ and the cyclic voltammogram (CV) traces are presented in Figure 4.11. The CV of LMP-C shows two prominent oxidation (anodic) peaks at ~3.7 and ~4.05 V respectively, while only one cathodic (reduction) peak occurs at ~4.2 V. These redox peaks could refer to the Mn²⁺/Mn³⁺ redox couple[189]. In C-LMP, the overall current density of the CV is reduced, as compared to that of LMP-C. Also, the redox peaks are not as prominent as compared to that of LMP-C. The oxidation peaks occur at ~3.5 and ~4.25 V, while one reduction peak occurs at ~4.0 V respectively. The appearance of two oxidation peaks and one reduction peak for both samples could indicate some irreversibility in the Mn²⁺/ Mn³⁺ redox during the Li intercalation / deintercalation processes. In comparison to C-LMP, LMP-C has higher current density, which could in turn lead to higher initial specific capacity than that of C-LMP. It is

possible that the conductive carbon-fiber-shell of LMP-C leads to an increase in surface conductivity. Moreover, the porous nature of the carbon shell could lead to increase in uptake of lithium-conducting electrolyte via absorption, and thus places the LiMnPO_4 active material in intimate contact with the electrolyte, reducing the ionic diffusion path length of the lithium ions. On the contrary, for C-LMP, the conductive carbon network is enclosed within the electrospun LiMnPO_4 -shell, this could possibly reduce the uptake of electrolyte by the electrode. Although the LiMnPO_4 layer is in direct contact with the electrolyte, the poor conductivity of LiMnPO_4 drastically hinders the electrochemical performance in C-LMP.

Figure 4.12 (a) Galvanostatic traces and (b) cycling data (showing discharge capacities) of LiMnPO_4 -Carbon composite nanofibers

Galvanostatic charge / discharge cycling (Figure 4.12a) of LMP-C and C-LMP half-cells showed the formation of a sloping plateau ~ 4.2 V, in agreement with the CV data. Comparatively, the plateau in that of C-LMP was not as flat as that observed in LMP-C, indicating that Li intercalation was occurring less in the former compound. Initial specific capacity values obtained for LMP-C and C-LMP were low, at ~ 7 mAh g^{-1} and ~ 8 mAh g^{-1} respectively, even though the low C-rate of 0.02 C (~ 3 mA g^{-1}) was used.

In the literature[23, 154], it is mentioned that pristine LiMnPO_4 has initial capacity of $\sim 40 \text{ mAh g}^{-1}$.

Upon further cycling to 10 cycles, it is interesting to note that the specific capacity increases slowly up to $\sim 10 \text{ mAh g}^{-1}$ for both LMP-C and C-LMP. The increase in capacity could indicate that it takes more time for the nanofibrous structure to intercalate / deintercalate Li^+ ions into and from its structure. Thus, to reduce this effect, the fibers were ball-milled and tested galvanostatically as half-cells. The ball-milled fibers showed $>100 \%$ increase in initial capacity, reaching $\sim 22 \text{ mAh g}^{-1}$ in the first cycle for ball-milled LMP-C and $\sim 30 \text{ mAh g}^{-1}$ ($>200 \%$ increase) for ball-milled C-LMP. Also, the time taken to reach equilibrium (in terms of Li intercalation / deintercalation) was reduced in the ball-milled fibers, as the increase in capacity was limited only to the first two galvanostatic cycles. The maximum capacity achieved in the ball-milled fibers were noted as $\sim 24 \text{ mAh g}^{-1}$ and $\sim 43 \text{ mAh g}^{-1}$ for LMP-C and C-LMP respectively.

In this section, it can be observed that the even distribution of active material with carbon matrix (via electrospinning methods) enables improved contact of poorly-conducting active materials with the electrolyte and conductive matrix, which leads to improved electrochemical performance. In LMP-C, the carbon shell acts as a conductive matrix and also formation of an electroactive layer (along with the electrolyte) on the LiMnPO_4 -core, enabling larger amount of lithium intercalation / deintercalation. Whereas for C-LMP, the non-conductive LiMnPO_4 layer partially blocks the conductive carbon core, thus hindering the lithium intercalation / deintercalation process. Further processing by ball-milling increases the overall capacity, however, it is then observed that the conductive coating on LMP-C then loses its effectiveness due to loss of the fibrous structure. On the other hand, the conductive carbon core of C-LMP becomes exposed in the ball-milling process and ultimately leads to larger increase in specific capacity, which can be attributed to the highly increased contact with the active material LiMnPO_4 .

4.1.3 Electrospun V_2O_5 nanofibrous (VNF) cathodes

Vanadium pentoxide (V_2O_5) is a promising candidate choice as cathode material for LIBs due to its ability to intercalate >1 Li per V_2O_5 , giving rise to capacity >300 mAh g^{-1} . Here, V_2O_5 has been synthesized in a 1D nanostructure via electrospinning method, in attempt to improve the electrochemical properties of V_2O_5 .

Figure 4.13 Secondary electron images (SEI) of (a) as-spun VNF and (b) sintered VNF, and respective bright field transmission electron microscope (TEM) images of (c) and (d) with selected area diffraction (SAED) patterns (insets), (e) high resolution TEM image with indicated d -spacings and axes of (310) and (01 $\bar{1}$) planes (inset: SAED of single nanocrystallite on sintered VNF) and (f) multislice simulation of single nanocrystallite sintered at 400 °C[34]

Scanning electron micrographs (Figure 4.13a) show nanofibers of as-spun VNF that are 20-60 μm long, 500-1200 nm in diameter with aspect ratio > 50 . Subsequent sintering of these fibers at 400 $^{\circ}\text{C}$ (2 $^{\circ}\text{C min}^{-1}$) led to crystallization of V_2O_5 nanocrystallites (~ 70 -80 nm) and removal of polymer precursor, resulting in a porous nano-particulate interconnected fibrous morphology (Figure 4.13b). It is observed that sintered VNF have reduced diameter in the range of 400-800 nm. The thermal decomposition of PVP polymer of the fibers resulted in meager shrinkage of the fibers.

Bright-field TEM images, together with the selected area diffraction (SAED), (Figure 4.13c, d) of the VNF clearly show a transition from smooth, amorphous as-spun nanofibers to porous polycrystalline nanofibers after sintering. Sintered VNF are composed of uniformly sized fibers with porous structure, which exhibits polycrystallinity in random orientation with an average crystallite size ~ 70 -80 nm. The selected area electron diffraction (SAED) of the sintered VNF (Figure 4.13d inset) shows the random orientation of nanocrystals, consistent with the XRD data of VNF (Figure 4.14a), which does not show any preferred orientation. The diffraction rings can be indexed to the (200), (101), (110) and (111) planes of the Shcherbinaite V_2O_5 phase.

High resolution image (Figure 4.13e) and SAED of a single VNF nanocrystal (Figure 4.13e inset) oriented along [133] zone axis are obtained and resembles the structure obtained from the simulation (Figure 4.13f). The d_{hkl} , calculated from SAED pattern, agree reasonably with the XRD data of VNF sintered at 400 $^{\circ}\text{C}$. By comparison with the multislice simulation, no defect is observed in the high resolution image, and the thickness of the crystal is estimated to be $\sim 10(2)$ nm.

Powder X-ray diffraction pattern (XRD) of sintered VNF (Figure 4.14a) collected to elucidate its crystal structure shows the formation of single phase orthorhombic V_2O_5 corresponding to the layered Shcherbinaite structure ($Pmn2_1$) in VNF (Figure 4.14b). Rietveld crystal structure analysis using TOPAS software evaluated lattice parameters $a =$

11.5214(1) Å, $b = 4.3738(6)$ Å, $c = 3.5667(4)$ Å and crystallite size of ~ 78 nm from Scherrer equation.

Figure 4.14 (a) Rietveld crystal structure refined X-ray diffraction pattern of sintered VNF and (b) crystal structures of V_2O_5 and $Li_xV_2O_5$ showing VO_5 octahedra and Li atoms[34]

For further comparison, the precursor for VNF was simply heat treated under the same conditions without electrospinning, giving rise to the formation of V_2O_5 powders. As seen from Figure 4.15, the VNF-powder and VNF have similar reflections, as well as

matching to that of commercial V_2O_5 powder, indicating that single-phase V_2O_5 was formed in the VNF-powder sample.

Figure 4.15 XRD pattern of VNF, VNF-powder and V_2O_5 commercial powder

Figure 4.16 Fourier transform infrared spectra (FTIR) of (a) as-spun and sintered VNF compared with commercial V_2O_5 powder[34] and (b) VNF-powder and sintered VNF

FTIR spectra of as-spun and sintered VNF were also studied (Figure 4.16a). Several additional peaks due to the organics are observed in the spectra of the as-spun VNF as comparison to the sintered VNF. The FTIR bands observed at 3485 and 1642 cm⁻¹ for as-spun VNF correspond to O-H stretching and bending modes[114, 120], which are correlated to the organic solvents ethanol and acetic acid. The peaks at 2946 and 1282 cm⁻¹ are due to C-H stretching and bending modes observed due to the presence of PVP in as-spun VNF[141]. The band at 990 cm⁻¹ is related to the V=O stretching vibrations[114]. Vibrational modes of O-H and C-H from PVP are absent in the sintered VNF IR spectra, indicating the complete degradation of PVP during the sintering step of VNF. For the spectra of sintered VNF, the peaks around 1026 and 834 cm⁻¹ correspond to the V=O stretching vibration and asymmetric stretching of the V-O-V bond respectively. The 637 and 476 cm⁻¹ peaks in the spectra for sintered VNF correspond to the symmetric stretching of the V-O-V bond[7, 101], which is observed as a broad peak ~567 cm⁻¹ for the V₂O₅ powder. Liu *et al.* (2006)[193] mentioned the presence of the abovementioned peaks in V₂O₅ nanotubes sintered at 400 and 500 °C.

The FTIR spectra (Figure 4.16b) of the VNF-powder show a sharp peak present at 1026 cm⁻¹, as well as broad peaks at 1615 and 834 cm⁻¹. Peaks at 1026 cm⁻¹ are indicative of the presence of V-O bonds, whereas the peak at 1615 cm⁻¹ could indicate incomplete decomposition of the VNF precursor. Peaks at 637 and 476 cm⁻¹ are also absent from the spectra of VNF-powder, which are indicative of the symmetric stretching of the V-O-V bond. This could mean that the formation of V₂O₅ is to a smaller extent in VNF-powder as compared to VNF.

Cyclic voltammograms (CV) of VNF cells were collected in the range of 1.75 to 4.0 V vs. Li/Li⁺ at a rate of 0.1 mV s⁻¹ to study the phase transformation that occurs during lithium intercalation/de-intercalation (cycling) into V₂O₅.

During the 1st cycle (Figure 4.17a), several oxidation/reduction peaks are observed, corresponding to the intercalation/de-intercalation processes of Li^+ in the VNF. The reduction (cathodic) peaks are observed at 3.16, 2.22, 2.11 and 1.95 V, while one main oxidation current peak is observed at 2.70 V vs. Li/Li^+ . The presence of these peaks indicates that the reduction of V^{5+} in V_2O_5 takes place as a multistep process within the voltage range 1.75 to 4.0 V. The reduction peak at 3.16 V indicates the reduction of V^{5+} to V^{4+} , leading to the formation of $\epsilon\text{-Li}_x\text{V}_2\text{O}_5$, as indicated in equation (4) below. At the reduction peaks of 2.22 and 2.11 V, partial reduction of V^{4+} to V^{3+} occurs, leading to the formation of a mixed phase of $\delta\text{-}$ and $\gamma\text{-Li}_x\text{V}_2\text{O}_5$, as shown in equations (5) and (6). Upon cycling below 2.0 V vs. Li/Li^+ , the $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase (Figure 4.17b) is irreversibly formed, as shown by the reduction peak at 1.95 V. This reduction process of the vanadium ion enables the accommodation of more than 2 Li per V_2O_5 . Some reverse reactions take place as indicated by the oxidation peak at 2.70 V.

Figure 4.17 Cyclic voltammogram (at 0.1 mV s^{-1}) of VNF showing (a) first cycle and (b) subsequent cycles[34] and of VNF-powder showing (c) first cycle and (d) subsequent cycles

During subsequent cycles (Figure 4.17b), only one main oxidation/reduction pair of peaks is present. The reduction peak shifted to 2.27 V, while oxidation peak remained at around 2.68 V. These peaks are intact upon further cycling, indicating the reversibility of oxidation/reduction reactions.

In the CV of VNF-powder, cathodic (reduction) peaks can be observed at ~2.18 V and ~1.87 V in the first cycle. Also, one large anodic (oxidation) peak is also present at ~2.71 V. In comparison to VNF, the reduction peak at ~3.16 V, related to $\text{V}^{5+} \rightarrow \text{V}^{4+}$ transformation, is much smaller for VNF-powder, and also, the formation of the ~2.18 V peak could be related to the merging of two peaks observed in VNF, namely ~2.22 and ~2.11 V. This indicates that less phase transformations could be occurring during the first discharge of the VNF-powder sample. In the subsequent cycles, the formation of one pair of redox peaks, namely at ~2.54 V (reduction) and ~2.69 V (oxidation), is similar to that of VNF, indicating reversibility of Li intercalation / deintercalation in subsequent cycles. The smaller current density in all the redox peaks of VNF-powder could be an indication that the interconnected network of 1D nanostructures in VNF leads to overall increased electroactive surface area, as well as increased electrochemical efficiency, as opposed to bulk materials in the case of VNF-powder. Hence, the overall current density of the CV is reduced in VNF-powder, as compared to that of VNF, possibly indicating lower overall specific capacity.

VNF coin cells were cycled between 1.75 and 4.0 V vs. Li/Li^+ at a rate of 0.1 C (or 35 mA g^{-1}). The first discharge (Figure 4.18a) shows multiple plateaus, similar to the data in the work of Ban *et al.* (2009)[7] and Mai *et al.* (2010)[35]. Due to the absence of impurities in VNF, additional plateaus at 2.8 and 2.5 V, attributed to the V_xO_2 impurities

by Mai *et al.*, are not observed. The first discharge plateau occurs at 3.18 V *vs.* Li/Li⁺, this can be correlated to the reduction peak occurring at 3.16 V, indicating the reduction of V⁵⁺ to V⁴⁺ to enable the intercalation of Li into the layered structure of V₂O₅. As a result, a mixture of $\alpha+\epsilon$ -Li_xV₂O₅ phases are formed as indicated in equation (6)[39, 145, 194]. The structures of these phases do not differ much from the layered structure of V₂O₅, as shown in Figure 4.14b. Upon further discharge, two stable plateaus at 2.27 and 2.07 V are observed, which is related to the reduction peaks in the CV at 2.22 V and 2.11 V. The plateau at 2.27 V is an indication of the formation of δ -Li_xV₂O₅, as V⁴⁺ is partially reduced to V³⁺, forming the mixed phase of δ - and γ -Li_xV₂O₅. In contrast to α , ϵ and δ phases, the γ -phase has distorted layers of VO₅ octahedra. (Figure 4.14b) At the 2.07 V plateau, it is believed that formation of δ - Li_xV₂O₅ to γ -Li_xV₂O₅ has occurred. Further discharge to 1.75 V causes the irreversible formation of γ -Li_xV₂O₅, reducing the cyclic retention capabilities of the VNF. This is consistent with the reduction peak at 1.95 V as seen in the CV.

In subsequent charge-discharge cycles (Figure 4.18a) for VNF, the plateaus are not prominent, indicating the Li⁺ intercalation/de-intercalation processes occurred reversibly in the mixed phases of Li_xV₂O₅ formed after the first discharge. Specific capacity of 300 mAh g⁻¹ can be obtained from the first discharge and increased to 316 mAh g⁻¹ in the second discharge cycle. The cyclic retention was 70% after 20 cycles and 50% after 50 cycles. The columbic efficiency of the VNF cell is maintained at nearly 100% for all the cycles.

Figure 4.18 Galvanostatic cycles of VNF showing first and second charge and discharge cycles of VNF cells cycled between (a) 1.75 - 4.0 V at 0.1 C and (b) 2.0 – 4.0 V at 0.1 C, (c) that of VNF-powder between 1.75-4.0 V and (d) cycling of respective cells at 0.1 C rate. All voltages are reported vs. Li/Li⁺[34]

The VNF cell was also cycled at 0.1 C rate in a cathodic voltage range of 2.0–4.0 V vs. Li/Li⁺ (Figure 4.18b). Similar to the first charge-discharge cycle in Figure 4.18a, there was the presence of three prominent plateaus at 3.20, 2.27 and 2.07 V respectively, however, at the last plateau (2.07 V), the phase transformation is reduced, as discharging is not carried out below 2.0 V vs. Li/Li⁺. The fourth discharge plateau due to discharging below 2.0 V is also not present. In comparing the second discharge cycles in Figure 4.18a and b, it is observed that the second discharge cycle in Figure 4.18b still had the presence of multiple plateaus, as compared to that in Figure 4.18a, which had no plateaus. This is an indication that irreversible phase transformation of δ -Li_xV₂O₅ to γ -Li_xV₂O₅ is reduced by using a cathodic voltage range. This leads to an improved cyclic retention of the VNF

cells, as compared to the lithium cell cycled from 1.75 to 4.0 V (Figure 4.18d). It is possible that the cyclic retention of VNF is improved by preventing the formation of the γ - $\text{Li}_x\text{V}_2\text{O}_5$ phase, which has a distorted crystal structure (Figure 4.14b). This data is in agreement with that mentioned by Mai *et al.*(2010)[35], in which an irreversible phase transition occurred at 1.9 V. Specific capacity of 230 mAh g^{-1} is achieved in the first discharge cycle, which is increased to 310 mAh g^{-1} in the second discharge cycle. Due to the reduction in extent of irreversible phase transformations, the cyclic retention of the cell cycled within the range 2.0 to 4.0 V was 74% after 50 cycles. This cell shows a large improvement, as compared that of the cell cycled within the full range of 1.75 to 4.0 V, for which the cyclic retention is 50% after cycling for 50 cycles at 0.1 C rate.

In contrast, the VNF-powder cell was cycled in the full voltage range of 1.75-4.0 V vs. Li/Li^+ (Figure 4.18c). Firstly, the VNF-powder cell had lower OCV (~ 2.6 V vs. Li/Li^+) than the VNF cells. Due to the lower OCV, the plateau occurring above 3 V could not be observed, instead, two main plateaus are observed at 2.3 and 2.0 V respectively. This indicates that less phase transformation is occurring in the VNF-powder cell. As a consequence, the initial capacity is much lower at ~ 170 mAh g^{-1} . Subsequent cycling of the cell shows that no prominent plateaus are formed, indicating that no other phase transformations occur in the first cycle. It can be observed that the VNF-powder cell gives overall lower capacity of ~ 115 mAh g^{-1} after 50 galvanostatic cycles. As mentioned earlier in Section 2.2.1, the 1D nanostructure (which is present in VNF) provides a shorter lithium diffusion pathway, and thus higher capacity, as opposed to the bulk structure of VNF-powder. Moreover, the presence of organic impurities in the structure of VNF-powder can possibly decrease the energy density of the cell.

Figure 4.19 Galvanostatic cycling of VNF cells (1.75-4.0 V) in various cycling rates (a) 0.1-1-0.1 C and (b) 0.1-0.2-0.5-1-1.5-0.1 C[34]

Cycling of the VNF cells at varying constant C-rates was carried out (Figure 4.19) between 1.75 to 4.0 V. Changes in C-rate (ie. current density) resulted in stepwise dependence of the specific capacity on cycle number. The capacity decreases slowly at 0.1 C for prolonged cycling but reduced significantly when the C-rate is increased to 1 C (Figure 4.19a). While the capacity is reduced at higher C-rates, the cyclic retention is still maintained. Upon increasing the cycling rate from 0.1 to 1 C, the specific capacity decreases from 200 to 160 mAh g⁻¹, but the cyclic retention is maintained at 70% after cycling for 20 cycles at 1 C rate. When the cycling rate is returned to 0.1 C, the capacity is recovered, increasing from 110 to 160 mAh g⁻¹.

In another VNF cell (Figure 4.19b), different current rates, namely 0.1, 0.2, 0.5, 1 and 1.5 C were applied to ensure the capacity retention. As the C-rate is increased from 0.1 to 0.2 C, the decrease in specific capacity is small (from 179 to 168 mAh g⁻¹). Further increase of the C-rate to 0.5 C only reduced the capacity from 126 mAh g⁻¹ (after 10 cycles at 0.2 C rate) to 110 mAh g⁻¹. After cycling for 10 cycles at 0.5 C rate, the cell was cycled at 1 C rate, in which 88% of the capacity was retained. When the C rate was increased from 1 to 1.5 C, the specific capacity did not decrease much, retaining 96% of

the capacity. Upon returning the cell to cycling at 0.1 C rate, the capacity recovers to 110 mAh g⁻¹ and is subsequently maintained at 130 mAh g⁻¹ for at least the next 10 cycles. It can be concluded that the VNF cells show good rate capabilities as the capacity retention is maintained despite cycling at higher C rates.

The electrospun, interconnected nanofibrous structure of VNF, obtained by electrospinning, enabled efficient removal of polymer precursor during the short sintering duration of 15 min. In contrast, the bulk structure of VNF-powder still contained the polymeric impurities after the sintering step, as observed by FTIR analysis. The beneficial effect of the 1D nanostructure on the electrochemical performance VNF, as a cathode material for lithium ion batteries is observed by higher initial capacity than that of VNF-powder. This is in agreement with the discussion[7, 37, 40, 149] that the 1D nanostructured materials have higher efficiency in terms of charge and ionic conductivity, as compared to bulk materials.

4.1.3.1 Effect of aluminium-insertion (Al-insertion) in VNF

V₂O₅ offers several advantages such as low cost and ability to intercalate a variety of metallic ions. At the same time, problems such as severe capacity fading and poor rate capability inhibit its practical LIB application. Poor Li-diffusion kinetics, structural instability with Li-intercalation/de-intercalation and inherent electronic conductivity ($\sim 10^{-2} - \sim 10^{-3}$ S cm⁻¹) of V₂O₅ are main causes of the aforementioned issues[195, 196]. Inclusion of transition metal cations like Al³⁺ and Ag⁺ into V₂O₅ layers leads to the formation of [MO₆] octahedral units that enhance the structural stability during Li-intercalation/de-intercalation[117]. Thus Al-insertion into V₂O₅ nanofibers was attempted to improve the cyclic retention properties of such 1D nanostructures.

In the following paragraphs, the properties and electrochemical behaviours of V₂O₅ nanofibers (VNF) without Al insertion is compared with Al-inserted VNF in

increasing Al concentration, namely $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$. The derived formula is further explained via the elemental analyses.

Figure 4.20 represents the surface morphological features of as-spun and sintered VNFs with and without Al insertion. From Figure 4.20a, c, and e, the formation of smooth morphology with long aspect ratios and mainly with fiber diameters ranging from 500-800 nm for VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$, respectively can be observed. Incorporation of $\text{Al}(\text{NO}_3)_3$ in to the VNF precursor leads to a slight decrease in viscosity of the solution, which results in a lower flow rate (1.5 ml h^{-1}) during the electrospinning process compared to native VNF fibers (2 ml h^{-1}). As a result, it gives rise to larger size distribution of fibers in the Al-VNFs with reduced thickness ($\sim 100\text{-}200 \text{ nm}$) as can be seen from the Figures 4.20c and e. Sintering at 400°C for 15 min in air results in the formation of porous fibers for pure V_2O_5 and the obtained morphology is similar to bare VNF (Figure 4.20b)[34]. Nevertheless, polycrystalline fibers are obtained in the case of Al-VNF (Figures 4.20d, f and 4.21a, b).

Figure 4.20 Field emission secondary electron (FE-SEM) images of as-spun (a) VNF, (c) $\text{Al}_{0.5}\text{VNF}$, (e) $\text{Al}_{1.0}\text{VNF}$ and sintered (b) VNF, (d) $\text{Al}_{0.5}\text{VNF}$ and (f) $\text{Al}_{1.0}\text{VNF}$ respectively[197]

Figure 4.21 Transmission electron (TEM) images and corresponding Al, V and O (as labeled) elemental maps of (a) $\text{Al}_{0.5}\text{VNF}$ and (b) $\text{Al}_{1.0}\text{VNF}$ respectively[197]

Transmission electron microscopy (TEM) also revealed the presence of porous fibers, irrespective of Al insertion (Figure 4.21). The presence of such porous structure is expected to enable the facile insertion/extraction of Li-ions and thereby providing better electrochemical properties, especially at high current rates. Elemental analysis (energy dispersive X-ray spectroscopy, attached to FE-SEM) was carried out to estimate the amount of Al^{3+} present in the V_2O_5 layers of two samples synthesized resulted in Al:V molar ratios of 1:4 and 1:2, respectively. Hereafter, the former and latter compositions are denoted as $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$, respectively. Mapping is one of the efficient techniques to study the distribution of elements in the specified area. Figure 4.21 shows the elemental mapping (energy dispersive X-ray spectroscopy) of Al-VNF with two different compositions and it was recorded during TEM analysis. It is evident that, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$ showed the even distribution of Al^{3+} throughout the area mapped according to the concentration of the inserted element.

The XRD patterns of Al-inserted and native VNFs were collected and presented in Figure 4.22a. Rietveld refinements were carried out for all the three samples (VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$) using TOPAS software. The observed reflections for VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$ clearly indicate the formation of pure phase structure without any impurity traces or preferred orientation. The crystalline peaks were indexed according to the layered Shcherbinaite structure with $Pmn2_1$ space group. The lattice parameter values of VNF are calculated and found to be $a = 11.521$ (4) Å, $b = 4.374$ (8) Å, $c = 3.567$ (4) Å. Variations in the lattice parameter values are noted for inclusion of Al; $\text{Al}_{0.5}\text{VNF}$ is $a = 11.531$ (2) Å, $b = 4.384$ (8) Å and $c = 3.571$ (5) Å; and $\text{Al}_{1.0}\text{VNF}$ $a = 11.551$ (6) Å, $b = 4.401$ (3) Å and $c = 3.581$ (2) Å. The observed values are consistent with the literature values (JCPDS 89-2482 $a = 11.5202$ (3) Å, $b = 4.3783$ (1) Å and $c = 3.5704$ (1) Å). The inclusion of Al^{3+} ions leads to increased strain in the crystal structure, leading to broadening of the

XRD peaks (Figure 4.22b), and clearly indicates influence of Al^{3+} ion towards the structural properties of V_2O_5 .

Figure 4.22 (a) X-ray diffraction (XRD) patterns of VNF , $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$, with (b) corresponding high resolution peaks, and schematic representation of (c) V_2O_5 (Shcherbinaite) crystal structure and (d) V_2O_5 lattice (not to scale) with possible positions of Al atoms, as indicated by blue spheres, and possible movement of V_2O_5 layers upon intercalation of lithium ions, as indicated by arrows[197]

Figure 4.23 V2p_{3/2} X-ray photoelectron spectra (XPS) of VNF, Al_{0.5}VNF and Al_{1.0}VNF[197]

X-ray photo electron spectra (XPS) of VNF, Al_{0.5}VNF and Al_{1.0}VNF samples with energy level of V 2p_{3/2} were recorded and given in Figure 4.23. In the native VNF, the peak observed at 517.6 eV corresponds to the V⁵⁺ oxidation state of V₂O₅[112, 198]. Introduction of Al³⁺ into the V₂O₅ lattice leads to the shifting of binding energy to lower energy levels and evident from the energy level spectra of V 2p_{3/2}. The binding energy 516.0 - 516.1 eV indicates the presence of V⁴⁺ ions and the observed values are similar to VO₂ phase, in which vanadium is in 4+ state[112, 198]. In the case of Al_{1.0}VNF, a small shoulder at 514.0 eV is noted which indicates the presence of mixed valence state of vanadium (V³⁺ and V⁴⁺)[112]. Al_{0.5}VNF possibly contains the mixed valence states of V⁵⁺ and V⁴⁺, which is necessary to balance the net charge in the crystal structure of V₂O₅ matrix due to the accommodation of Al³⁺ ions. At the same time, the crystal structure of V₂O₅ is still intact and evident from the XRD reflections obtained above. The molar ratio of Al:V are in good agreement with elemental analysis described above and formula for Al_{0.5}VNF can be written as Al_{0.5}(V⁵⁺_{0.5} V⁴⁺_{1.5})O₅. Similarly for Al_{1.0}VNF, the larger

amount of Al^{3+} inserted leads to the formation of V^{4+} and V^{3+} ions in place of V^{5+} . In combination with the elemental analysis, the molecular formula is derived to be $\text{Al}_{1.0}(\text{V}^{4+}_{1.0}\text{V}^{3+}_{1.0})\text{O}_5$.

Figure 4.24 Cyclic voltammograms showing first cycles of (a) VNF, (c) $\text{Al}_{0.5}\text{VNF}$, (e) and subsequent cycles of (b) VNF, (d) $\text{Al}_{0.5}\text{VNF}$ and (f) $\text{Al}_{1.0}\text{VNF}$ respectively, in which metallic lithium serves as both counter and reference electrodes in two electrode coin cell configuration at scan rate of 0.1 mV s^{-1} between 1.75-4.0 V vs. Li/Li^+ . Integer represents cycle number[197]

Electrochemical properties of the Al-inserted and native VNF were evaluated by means of both galvanostatic and potentiostatic modes in half-cell (Li/VNF) configurations. Generally, insertion of Li-ions into V_2O_5 layers results the transformation of V_2O_5 in to $Li_xV_2O_5$ phase. Thus results the distortion in layered structure due to the occupancy of Li^+ ions into the spaces between the layers of VO_5 octahedral unit. Slow scan (scan rate 0.1 mV s^{-1}) cyclic voltammograms (CV) of Li/VNF, Li/ $Al_{0.5}$ VNF and Li/ $Al_{1.0}$ VNF cells are collected in the range between 1.75-4.0 V *vs.* Li/Li⁺ to understand the phase transformation during Li-intercalation/de-intercalation and presented in Figure 4.24. The following equation describes the overall Li-intercalation mechanism in V_2O_5 matrix,

The test cells were first discharged to intercalate the Li-ions in to V_2O_5 lattice. In the 1st cycle (Figure 4.24a, c, e), several oxidation/reduction peaks are observed for the Al-inserted and native VNF corresponding to the intercalation/de-intercalation processes of Li-ions in V_2O_5 . For VNF and $Al_{0.5}$ VNF, the reduction (cathodic) peaks are observed at ~ 3.37 , ~ 3.16 , ~ 2.22 , and ~ 1.90 V *vs.* Li/Li⁺. In addition $Al_{0.5}$ VNF has a smaller reduction peak at ~ 3.16 V *vs.* Li/Li⁺ when compared to native VNF, and in addition smaller peaks are also observed at ~ 2.71 and ~ 2.54 V *vs.* Li/Li⁺. On the other hand, vanishing of reduction peaks at ~ 3.37 and ~ 3.16 V are noted for $Al_{1.0}$ VNF phase when compared to native VNF and $Al_{0.5}$ VNF phases. Appearance of remaining reduction peaks are noted at ~ 2.66 , ~ 2.22 and ~ 1.9 V *vs.* Li/Li⁺ in both cases. VNF and $Al_{0.5}$ VNF showed a broad oxidation (anodic) peak at ~ 2.70 V *vs.* Li/Li⁺ and showing variation in area under the curve, whereas two sharp oxidation peaks are observed for $Al_{1.0}$ VNF at ~ 2.28 and ~ 2.83 V *vs.* Li/Li⁺. Current densities of the Al-inserted Al-VNFs also appear to be less than that of native VNF, which could be attributed to the presence of Al^{3+} ions occupied between the layers. Wei *et al.* (2007, 2008)[111, 125] also noted the similar kind of reduction in

current densities while introducing metal-ion on V_2O_5 lattice. The appearances of cathodic peaks are indicative of the multistep reduction of V^{5+} in V_2O_5 within the voltage range 1.75 to 4.0 V vs. Li/Li^+ . The cathodic peaks at ~ 3.37 and ~ 3.16 V vs. Li/Li^+ indicates the reduction of V^{5+} to V^{4+} , leads to the formation of ϵ - $Li_xV_2O_5$ phase, which is observed only for VNF and $Al_{0.5}VNF$ phases. The absence of V^{5+} in $Al_{1.0}VNF$ is well reflected in CV measurements and it is in good agreement with XPS data. The other cathodic peaks ~ 2.22 and ~ 1.90 V vs. Li/Li^+ belongs to partial reduction of V^{4+} to V^{3+} and this reduction reveal the formation of δ - and γ - $Li_xV_2O_5$ mixed phases. Presence of additional reduction peak at ~ 2.71 V vs. Li/Li^+ for $Al_{0.5}VNF$ and ~ 2.66 V vs. Li/Li^+ for $Al_{1.0}VNF$ could be attributed to the increased instances of reduction of V^{4+} . Cycling below 2.0 V vs. Li/Li^+ leads to the formation of irreversible γ - $Li_xV_2O_5$ phase which is confirmed by the appearance of reduction peak at ~ 1.90 V vs. Li/Li^+ and it is noted for all three VNFs tested[34].

Subsequent electrochemical cycling in potentiostatic modes are given in Figure 4.24b, d & f. The observed traces in the successive cycles are entirely different from the first cycle for the case of native VNF and $Al_{0.5}VNF$ phases. In VNF, the reduction peak is shifted from ~ 2.28 to ~ 2.31 V vs. Li/Li^+ for consecutive cycles, whereas oxidation peak remains at ~ 2.68 V vs. Li/Li^+ . On the other hand, in $Al_{0.5}VNF$ the oxidation and reduction peaks remains at same potentials. Similar to VNF, it is possible that $Al_{0.5}VNF$ underwent similar phase changes as observed in V_2O_5 , although to a smaller extent. Due to the smaller amount of insertion of Al^{3+} to the V_2O_5 layers, the crystal structure of $Al_{0.5}VNF$ can be assumed to be similar to that of VNF. Hence, substantial structural distortion could still occur during the first electrochemical discharge cycle. Contrary to above, $Al_{1.0}VNF$ displayed the reduction at ~ 2.65 V ($V^{4+} \rightarrow V^{3+}$) and two oxidation peaks at ~ 2.27 and ~ 2.84 V vs. Li/Li^+ , respectively. The observed redox potentials are same as that of in the first cycle with intense peaks, which is due to the influence of Al^{3+} insertion. It is evident

that, presence of Al^{3+} ions between the layers, especially in the case for $\text{Al}_{1.0}\text{VNF}$, supports the V_2O_5 crystal structure and reduces distortion of the layered structure, effectively improving the structural properties during electrochemical Li-insertion/extraction and retaining the crystal structure of V_2O_5 . However, in all three samples there is no deviation of shape noted from 2nd cycle onwards, which indicates the excellent reversibility of the V_2O_5 fibers during lithium intercalation and de-intercalation. Further, it is noted that for VNF and $\text{Al}_{0.5}\text{VNF}$, the net area under the curve tends to decrease, which is indicative of capacity fade during cycling. Nevertheless, very small amount of reduction in the net charge under the curve is noted for $\text{Al}_{1.0}\text{VNF}$. Hence, an improved cycleability is expected for the $\text{Al}_{1.0}\text{VNF}$ irrespective of the capacity.

Figure 4.25 Typical galvanostatic traces of first two charge-discharge curves of (a) VNF, (b) $\text{Al}_{0.5}\text{VNF}$ and (c) $\text{Al}_{1.0}\text{VNF}$ cells between 1.75-4.0 V vs. Li/Li^+ at 0.1 C rate in room temperature[197]

Galvanostatic cycling profiles of Li/VNF, Al_{0.5}VNF and Al_{1.0}VNF coin cells cycled between 1.75– 4.0 V *vs.* Li/Li⁺ at 0.1 C rate (1 C is assumed to be 350 mA g⁻¹) in room temperature is shown in Figure 4.25. As expected, all the three samples showed multiple plateaus during first discharge, which is consistent with the CV analysis and representative phase transitions occurring during Li-intercalation/de-intercalation. The first discharge plateau at ~3.18 V *vs.* Li/Li⁺ is attributed to the reduction of V⁵⁺ to V⁴⁺ to enable the intercalation of Li-ions into layered V₂O₅. It is interesting to notice the vanishing of obvious plateau at ~3.18 V *vs.* Li/Li⁺ upon introduction of Al³⁺ ions in to the V₂O₅ matrix. For Al_{0.5}VNF, it is observed that the plateau at ~3.18 V *vs.* Li/Li⁺ is shortened when compared to native VNF which is attributed to the reduction of remaining V⁵⁺ in to V⁴⁺. There is no such obvious plateau is observed for the Al_{1.0}VNF due to the unavailability of V⁵⁺ ions. Upon further reduction, two prominent plateaus at ~2.28 and ~2.08 V *vs.* Li/Li⁺ are observed for all the three cases with small shift in the range. The plateau at ~2.24 V is an indication of the formation of δ-Li_xV₂O₅ phase and V⁴⁺ is partially reduced to V³⁺ forming δ- and γ-Li_xV₂O₅ mixed phases. The plateau ~2.08 V *vs.* Li/Li⁺ is believed to be the transformation of δ- Li_xV₂O₅ to γ-Li_xV₂O₅ phase. Further discharge into 1.75 V *vs.* Li/Li⁺ causes the irreversible formation of γ-Li_xV₂O₅ phase, and this is in good agreement with CV traces obtained above. Further, the plateau ~2.3 V is also shortened and this leads to the lower initial discharge capacity of ~250 mAh g⁻¹ (~1.7 moles of lithium). However, in Al_{1.0}VNF phase distinct plateau at ~3.12 V *vs.* Li/Li⁺ is not observed. Instead, observation of a broad plateau at ~2.67 V and a shortened plateau at ~2.3 V *vs.* Li/Li⁺ indicates the reduction of V⁴⁺ to V³⁺, consistent with the CV data obtained above. The plateau observed at ~2.0 V *vs.* Li/Li⁺ in Al_{1.0}VNF is also not as sharp as observed in the case of VNF and Al_{0.5}VNF. In the second charge-discharge cycle, there are no plateaus observed for VNF and Al_{0.5}VNF, whereas shortened plateaus are observed ~2.7 V and ~2.76 V *vs.* Li/Li⁺ in the discharge and charge curves

respectively for $\text{Al}_{1.0}\text{VNF}$, corresponding to the improved structural stability of $\text{Al}_{1.0}\text{VNF}$ phase rendered by Al^{3+} insertion. This is an indication that an irreversible phase transformation of V_2O_5 to $\text{Li}_x\text{V}_2\text{O}_5$ occurred during the first discharge for VNF and $\text{Al}_{0.5}\text{VNF}$, but there is some reversibility of the phase transformation occurring in the more heavily-inserted $\text{Al}_{1.0}\text{VNF}$ phase which is in good agreement with the observations in CV trace. In all three samples, first charge capacity is slightly higher than discharge capacity and the observed excess capacity is obtained from the interfacial storage across the electrolyte/electrode interface. Except for the initial cycle, all the three materials exhibited columbic efficiency over 99% in subsequent cycles, which indicates excellent reversibility during galvanostatic cycling.

As mentioned earlier, all VNF cells were cycled galvanostatically between 1.75 to 4.0 V vs. Li/Li^+ at 0.1 C rate (35 mA g^{-1}) at room temperature and presented in Figure 4.26a. VNF delivered an initial discharge capacity of 316 mAh g^{-1} (~ 2.2 moles of lithium) and retained only 43% of initial capacity upon cycling to 50 cycles. $\text{Al}_{0.5}\text{VNF}$ starts off with initial capacity of $\sim 250 \text{ mAh g}^{-1}$, which is equivalent to ~ 1.7 moles of lithium and retains 63% of initial capacity after 50 cycles. The lower initial capacity could be due to the reduced transformation of V^{5+} to V^{4+} . As for $\text{Al}_{1.0}\text{VNF}$, it also displayed higher initial discharge capacity of $\sim 350 \text{ mAh g}^{-1}$ and maintained $\sim 85\%$ of cyclic retention within 20 cycles. The higher initial capacity is possibly due to the increased space between the V_2O_5 layers (Figure 4.22c), enabling initial intercalation of larger amount of Li^+ ions. In addition, similar to the observations in the CV, the presence of larger amount of Al^{3+} ions in the V_2O_5 layered structure of $\text{Al}_{1.0}\text{VNF}$ enabled better support, and hence stability, of the layered V_2O_5 structure during lithium intercalation / deintercalation, which is vital and beneficial to the cyclic retention properties of the Al-inserted VNF.

It is attractive to test the stability and electrochemical performance of LIBs at high temperatures, which is important for practical applications, where portable devices may heat up during charging / discharging. The addition of other ions[47, 199-201] to electrode materials had been shown to improve the high temperature electrochemical performance. Thus, to study the influence of Al^{3+} insertion towards the electrochemical properties of VNF at elevated temperature conditions (55 °C) with same current rate (0.1 C), galvanostatic charge-discharge studies were conducted and corresponding cycling profiles are illustrated in Figure 4.26b. The native VNF fibers delivered the discharge capacity of ~ 285 (~ 2 moles lithium) and $\sim 120 \text{ mAh g}^{-1}$ (~ 0.8 moles lithium) for first and 50th cycle, respectively with $\sim 40\%$ capacity retention. Incorporation of Al^{3+} , $\text{Al}_{0.5}\text{VNF}$ showed the initial discharge capacity of $\sim 360 \text{ mAh g}^{-1}$ (~ 2.4 moles lithium) with improved capacity retention of over 50% after 50 cycles. For $\text{Al}_{1.0}\text{VNF}$, the insertion of Al^{3+} is beneficial for achieving highest discharge capacity of $\sim 350 \text{ mAh g}^{-1}$ (~ 2.4 moles lithium) with capacity retention of $\sim 66\%$ after 50 cycles. Also, it is interesting to note that the $\text{Al}_{1.0}\text{VNF}$ has the highest initial capacity at 0.1 C rate for both room temperature as well as elevated temperature (55 °C) cycling. Also, the obtained result clearly shows the influence of Al^{3+} ions towards thermal stability of V_2O_5 at elevated temperature conditions. Unfortunately, there are no reports available on the high temperature performance of V_2O_5 to compare the obtained results.

High-rate performance is one of the pre-requisite for cathode materials and in order to establish the effect of Al^{3+} insertion, the test cells were cycled at 1 C (350 mA g^{-1}) in room temperature conditions and corresponding cycling profiles are given in Figure 4.26c. The cell comprising VNF showed the lower initial discharge capacity of $\sim 114 \text{ mAh g}^{-1}$ (~ 0.8 moles lithium) when compared to $\sim 320 \text{ mAh g}^{-1}$ at 0.1 C rate. However, the capacity retention is improved to 60 % after 50 cycles. The $\text{Al}_{0.5}\text{VNF}$ cell exhibited the capacity of 240 mAh g^{-1} which is almost same capacity at low current rates (~ 250

mAh g⁻¹), however improvement in the capacity retention is noted after 50 cycles (~60%). As for Al_{1.0}VNF, the larger amount of Al-inclusion led to the slightly less initial capacity of ~208 mAh g⁻¹ when compared to low rates (~250 mAh g⁻¹ at 0.1 C rate), but enhanced capacity retention of ~70% is noted after 50 cycles. Zhan *et al.*(2010)[112, 119] reported the synthesis of Al-inserted V₂O₅ nanopowder (Al_{0.2}V₂O₅) and delivered the initial discharge capacity of ~190 mAh g⁻¹ at ~0.1 C rate with ~76% capacity retention after 50 cycles. When increasing the current rate to 0.2 C, the cell displayed a discharge capacity of ~140 mAh g⁻¹ with cyclic retention of ~57% after 50 cycles. In the present work, increasing the concentration of Al³⁺ ions in the VNF matrix contributed to higher cycling stability and capacity retention at higher C-rates. Furthermore, the porous morphology of the fibers contributed the advantage of higher initial capacity and improved capacity retention when compared to Al-inserted nanopowders, as discussed in later sections.

Figure 4.26 Plots of specific discharge capacity vs. cycle number of VNF, Al_{0.5}VNF and Al_{1.0}VNF cycled at (a) 0.1 C rate at room temperature and (b) 0.1 C rate at 55 °C and (c) 1 C rate at room temperature[197]

Figure 4.27 Field emission secondary electron (FE-SEM) images of as-prepared electrodes of (a) VNF, (c) Al_{0.5}VNF, (e) Al_{1.0}VNF and electrochemically cycled electrodes of (b) VNF, (d) Al_{0.5}VNF and (f) Al_{1.0}VNF respectively[197]

Ex-situ FE-SEM analysis was carried out after electrochemical cycling to ensure the retention of fibrous morphology after the cycling. Hence, the cycled test cells were opened in an Argon-filled glovebox and electrodes were carefully taken and washed with DEC and subsequently dried. For comparison, fresh test electrodes were also subjected to

FE-SEM investigations and obtained images are presented in Figure 4.27. From Figure 4.27a, it can be seen that, as-prepared VNF electrode shows the presence of nanofibers (indicated by arrow) morphology before cycling and there is no fibrous morphology is retained after cycling (Figure 4.27b). Nanofibrous morphology is observed in as-prepared electrodes of Al-VNF (arrowed, Figures 4.27c & e). In contrast to native VNF, the fibers are still intact (arrowed, Figures 4.27d & f) after the electrochemical cycling. The improved tenacity of the Al-VNF could contribute to the improved electrochemical properties, especially capacity retention during high rate testing, when compared to native VNF.

4.1.3.2 Effect of carbon-coating on VNF

Electronic conductivity of V_2O_5 has been improved via surface modifications by conductive coatings or making composites with either carbon[57, 202] or conductive additives for example polyaniline (PANI)[38, 115], polypyrrole (Ppy)[113], poly(vinylpyrrolidinone) (PVP)[39] and poly(ethylene oxide) (PEO)[40, 203]. The underlying concept of making composites is not only to improve the conductivity but also to provide necessary stability during electrochemical cycling[39]. In addition, the morphology of V_2O_5 nanostructures and herein preferably 1D nanostructures, has shown to play a vital role in to achieving high capacity[196]. Carbon coating was employed here to improve the electronic conductivity of VNF using plasma enhanced chemical vapour deposition method (PECVD). A main advantage of using PECVD technique was that morphological features of the μm -long sintered 1D V_2O_5 nanofibers were retained during the gas phase process. Additionally, it enabled a homogeneous coating with desired thickness of carbon layer and no work up step was needed unlike in time consuming conventional wet-chemical coating procedures[204].

Figure 4.28 Field emission secondary electron (FE-SEM) images of (a) bare VNF, (b) C-VNF-15 and (c) C-VNF-30 with corresponding transmission electron microscopic (TEM) images of C-VNFs (insets)[180]

Figure 4.28 represents the FE-SEM pictures of VNF and C-VNF synthesized by electrospinning technique. After the calcination process, bare VNF were subjected to carbon coating by PECVD. PECVD is a non-destructive technique to produce a thin layer of carbon over the VNF, more specifically on V_2O_5 nanocrystals. In addition, this PECVD technique enables the retention of fibrous morphology as evidenced from the FE-SEM pictures (Figures 4.28b and c). To ensure the formation of carbon layer, a TEM study was conducted and presented as inset in Figure 4.30b and c. It can be seen from the TEM images that C-VNFs show variation in thicknesses of the carbon-layers due to the difference in duration inside the plasma. The C-VNF-15 (inset Figure 4.28b) showed a heterogeneous carbon coating over the V_2O_5 nanocrystals which indicates the duration is not sufficient to enable homogeneous coating. Hence, coating duration is increased to 30 min (C-VNF-30) to achieve homogenous carbon layer with thickness of ~ 5 nm over V_2O_5 nanocrystals as evidenced from Figure 4.28c inset.

Figure 4.29 (a) X-ray diffraction (XRD) patterns of bare VNF, C-VNF-15 and C-VNF-30 showing formation of V₂O₅ structure (*asterisks indicate VO₂ peak) and (b) thermogravimetric analyses (TGA) showing weight percentages of C-VNF-15 and C-VNF-30[180]

Structural properties of bare and carbon-coated VNFs were analyzed by XRD and presented in Figure 4.29a. Rietveld refinements were carried out for all the three samples (VNF, C-VNF-15 and C-VNF-30) using TOPAS software. The observed reflections for VNF can be indexed according to layered Shcherbinaite structure ($a=11.5181(6)$ Å, $b=4.3804(3)$ Å, $c=3.5671(2)$ Å and crystallite size = 98.2(2) nm) with $Pmn2_1$ space group. The observed patterns clearly indicate the formation of single phase V₂O₅. However, in C-VNF-15 and C-VNF-30, there are reflections showing trace amount of impurity peaks at $\sim 28^\circ$, which corresponds to the formation of VO₂ phase. The presence of VO₂ impurity

phase is due to the carbothermal reduction of V_2O_5 (V^{5+} to V^{4+}) during carbon coating procedure by PECVD. During the carbon coating procedure, the precursor C_2H_2 is decomposed ($C_2H_2 + V_2O_5 \rightarrow 2C + (V_2O_5, VO_2) + H_2O$) and formed as carbon on the surface under inert atmosphere, leading to the formation of VO_2 impurity. Evidently, increasing the plasma duration from 15 to 30 min. leads to an increase in intensity of the peak ($2\theta = 28^\circ$) related to VO_2 phase. Rietveld refinement has been used to estimate the amount of VO_2 formed during carbon coating and found to be ~ 4.5 and ~ 7.5 wt.% for C-VNF-15 and C-VNF-30, respectively. In addition, no extra peaks related to carbon are detected in the XRD observations, which correspond to the formation of amorphous carbon layer over the V_2O_5 nanocrystals.

In order to estimate amount of carbon present in C-VNF-15 and C-VNF-30, TGA was carried out in 60% air + 40% nitrogen atmosphere and presented in Figure 4.29b. Observed weight loss (%) during TGA studies are directly related to the amount of carbon present in the compound. C-VNF-15 and C-VNF-30 showed the weight loss of ~ 1.4 and ~ 4.2 wt.%, respectively. The TGA results suggested that increasing coating duration provided higher amount of carbon content, which is consistent with increase in the intensity of VO_2 phase noted in XRD observations.

Li-insertion properties of electrospun bare and carbon-coated VNFs were evaluated by means of both galvanostatic and potentiostatic modes in half-cell (Li/VNF or C-VNF) assembly. Generally, Li-insertion into V_2O_5 lattice resulted in phase transition from V_2O_5 to $Li_xV_2O_5$. To investigate the phase transformations observed during electrochemical Li-intercalation/de-intercalation, cyclic voltammograms (CV) were recorded at slow scan rate of 0.1 mV s^{-1} between 1.75-4.0 V vs. Li/Li^+ and shown in Figure 4.30. All the test cells fabricated exhibited the open circuit voltage (OCV) ~ 3 V vs. Li/Li^+ and were subsequently discharged to insert Li.

Figure 4.30 Cyclic voltammograms showing first cycle of (a) bare VNF, (c) C-VNF-15, (e) C-VNF-30 and subsequent cycles of (b) bare VNF, (d) C-VNF-15 and (f) C-VNF-30 respectively, in which metallic lithium serves as both counter and reference electrodes in two electrode coin cell configuration at scan rate of 0.1 mV s^{-1} between 1.75-4.0 V *vs.* Li/Li⁺[180]

Figure 4.30 shows the typical CV traces of VNF recorded in the slow scan rate. The half-cells exhibited several oxidation/reduction peaks during cathodic and anodic scan, which clearly evident from Figure 4.30a, c & e which corresponds to the intercalation/de-intercalation processes of Li-ions in V₂O₅ lattice[34]. In bare VNF, main

reduction (cathodic) peaks are noted at ~ 3.15 , ~ 2.20 , ~ 1.99 and ~ 1.90 V vs. Li/Li^+ , whereas only one broad oxidation (anodic) peak is observed ~ 2.66 V vs. Li/Li^+ . Similarly, in the case of C-VNF-15 and C-VNF-30, reduction peaks are observed at ~ 2.24 , ~ 1.99 and ~ 1.90 V vs. Li/Li^+ , and a broad oxidation peak at ~ 2.66 V vs. Li/Li^+ . Cathodic peak observed at ~ 3.15 V vs. Li/Li^+ in bare VNF is not present for both C-VNFs. The appearance of such cathodic peak is indicative of the multistep reduction process of V^{5+} in V_2O_5 and this leads to the formation of $\epsilon\text{-Li}_x\text{V}_2\text{O}_5$ phase. The CV traces of the C-VNFs do not show any peak at ~ 3.15 V, it is possible that some of the V^{5+} could be reduced during the PECVD process to V^{4+} , as observed from the presence of VO_2 in the XRD. The absence of V^{5+} possibly relates to the less amount of phase transformation related to the electrochemical reduction of V^{5+} to V^{4+} . Other cathodic peaks ~ 2.20 and ~ 1.90 V vs. Li/Li^+ , as observed in all VNFs belong to partial reduction of V^{4+} to V^{3+} and this reduction process is associated with the formation of δ - and $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ mixed phases. Appearances of additional reduction peak at ~ 1.99 V vs. Li/Li^+ in C-VNFs could be attributed to the increased instances of reduction of V^{4+} . Cycling below 2.0 V vs. Li/Li^+ leads to the formation of irreversible $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase which is confirmed by the appearance of reduction peak at ~ 1.90 V vs. Li/Li^+ and noted for all three VNFs tested.

CV studies were continued up to 10 cycles and selected cycles (2, 5 and 10) are presented in Figure 4.30b, d & f. The observed traces in the successive cycles only showed one pair of broad reduction and oxidation peaks, which indicates that the phase transformations occur reversibly in the $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase formed at the end of the first discharge. In the bare VNF, the main reduction peak occurred at ~ 2.30 V vs. Li/Li^+ for consecutive cycles, whereas the oxidation peak remains at ~ 2.70 V vs. Li/Li^+ , which is similar to the first cycle. Likewise, in C-VNF-15 and C-VNF-30, the reduction and oxidation peaks appear at ~ 2.30 and ~ 2.70 V vs. Li/Li^+ , respectively. Further, these redox peaks also appears to be sharper with less fade in current density compared to bare VNF

and indicates good reversibility during successive cycling. The improved performance is mainly attributed to the enhanced electronic conductivity enabled by carbon coating. A decrease in current density is observed for carbon-coated VNFs, for example current density of ~ 110 , ~ 90 and ~ 70 mA g⁻¹ peak potential at ~ 2.70 V vs. Li/Li⁺ for bare VNF, C-VNF-15 and C-VNF-30, respectively. Reddy *et al.*(2007)[40] also noticed similar kind of reduction in current density during CV analysis for V₂O₅-PEG nanobelt composites when compared to bare V₂O₅ nanobelts.

Figure 4.31 Typical galvanostatic traces of first two charge-discharge curves of (a) bare VNF, (b) C-VNF-15 and (c) C-VNF-30 cells between 1.75-4.0 V vs. Li/Li⁺ at 0.1 C rate in room temperature[180]

Galvanostatic discharge-charge profiles of half-cells (Li/VNFs) are cycled between 1.75– 4.0 V vs. Li/Li⁺ at 0.1 C rate (1 C is assumed to be 350 mA g⁻¹) in room temperature are shown in Figure 4.31. As expected, all the three samples showed multiple plateaus during first discharge, which is consistent with the CV analysis and representative phase transitions occurring during Li-intercalation/de-intercalation[7, 34,

37]. The first discharge plateau observed for bare VNF at ~ 3.20 V vs. Li/Li^+ is attributed to the reduction of V^{5+} to V^{4+} which enables the intercalation of Li-ions into layered V_2O_5 . Interestingly, the plateau at ~ 3.20 V vs. Li/Li^+ is not present in both C-VNFs, and it can be observed that the open circuit voltages (OCV) of C-VNFs are lower at ~ 3.0 V, as compared to bare VNF. The lower OCV results in the absence of the first V^{5+} to V^{4+} plateau, as well as the non-existence of the ~ 3.16 V reduction peak in the CV. It is possible that the $\text{V}^{5+} \rightarrow \text{V}^{4+}$ reduction occurs as a more gradual process during the first discharge. Also, the smaller amount of V^{5+} ions present in C-VNFs as compared to bare VNF could have resulted in this phenomenon. Upon further discharge, two prominent plateaus at ~ 2.28 and ~ 2.0 V vs. Li/Li^+ are observed for all the three VNFs. The plateau at ~ 2.28 V indicates formation of $\delta\text{-Li}_x\text{V}_2\text{O}_5$ phase and V^{4+} is partially reduced to V^{3+} forming δ - and $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ mixed phases. The plateau ~ 2.0 V vs. Li/Li^+ is believed to be the transformation of $\delta\text{-Li}_x\text{V}_2\text{O}_5$ into $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase. Further discharge to 1.75 V vs. Li/Li^+ causes the irreversible formation of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase, and this is in good agreement with CV traces obtained above. Bare VNF gives initial discharge capacity of 316 mAh g^{-1} , whereas C-VNF-15 and C-VNF-30 exhibited a capacity of ~ 280 and $\sim 300 \text{ mAh g}^{-1}$, respectively. Apparently, increasing carbon content leads to the higher initial discharge capacity (C-VNF-15 to C-VNF-30). On the other hand, lower initial capacity of the carbon-coated samples can be attributed to the reduced occurrence of the first phase transformation at ~ 3.20 V vs. Li/Li^+ . Chen *et al.* (2010)[115] also noted similar kind of absence of plateau region at ~ 3.20 V vs. Li/Li^+ in PANI- V_2O_5 composites and it is mainly due to the formation of VO_2 phase by reduction of V^{5+} from V_2O_5 .

Figure 4.32 illustrates the plot of discharge capacity vs. cycle number obtained from the galvanostatic discharge-charge curves of VNF cells cycled between 1.75 to 4.0 V vs. Li/Li^+ at 0.1 C rate (35 mA g^{-1}) at room temperature. The bare VNF delivered an initial discharge capacity of 316 mAh g^{-1} (~ 2.2 moles of lithium) and retained 43% of its

capacity after 50 cycles (Figure 4.34a). The carbon coated VNFs (C-VNF-15 and C-VNF-30) cycled under the same conditions retained ~67 and ~65% of the initial capacity after 50 cycles, in spite of the different amounts/thicknesses of carbon coating. The obtained discharge capacities are normalized and presented in Figure 4.32b. It is evident that, carbon coated VNFs (C-VNF-15 and C-VNF-30) exhibited good capacity retention characteristics compared to bare VNFs irrespective of the initial capacity values during extended cycling. There is only slight variation in the capacity retention properties noted for C-VNFs, hence C-VNF-15 was chosen for high temperature and rate performance studies.

Figure 4.32 Plots of specific discharge capacity vs. cycle number of VNF, C-VNF-15 and C-VNF-30 cycled at (a) 0.1 C rate at room temperature and (b) capacity retention (according to initial discharge capacity) vs. cycle number[180]

Figure 4.33 Plots of specific discharge capacity vs. cycle number of VNF and C-VNF-15 cycled at (a) 0.1 C rate at 55 °C and (b) 1 C rate at room temperature[180]

To explore the protective nature of carbon-coating towards electrolyte counterpart, C-VNF-15 and VNF cells were subjected to high temperature (55 °C) studies. The test cells were galvanostatically cycled at 0.1 C rate between 1.75 to 4.0 V vs. Li/Li⁺ at elevated temperature and presented in Figure 4.33a. As expected, in the elevated temperature conditions improved discharge capacity is noted for C-VNF-15 in the first cycle when compared to room temperature conditions (~280 to ~298 mAh g⁻¹). On the other hand, bare VNF showed the discharge capacity of ~284 mAh g⁻¹ at second cycle, which is ~32 mAh g⁻¹ less than its room temperature performance. The reduction of capacity in elevated temperature condition is mainly attributed to the severe reactivity of VNFs with electrolyte counterpart. In terms of cycling efficiency at elevated temperatures, ~65 and 45% capacity retention is observed after 50 cycles for VNF and C-VNF-15, respectively. In addition, the cells were also subjected to high current rate to study the effect of carbon coating towards electronic conducting properties of VNFs.

Figure 4.33b represents the high rate cycling performance of VNF and C-VNF-15 between 1.75 to 4.0 V vs. Li/Li^+ at 1 C (350 mA g^{-1}) at room temperature. Drastic differences between the cycling properties of C-VNF and VNFs are noted under high current cycling. The C-VNF-15 delivered higher initial capacity of $\sim 250 \text{ mAh g}^{-1}$ and $\sim 64\%$ capacity is retained after 50 cycles, whereas bare VNF showed only $\sim 100 \text{ mAh g}^{-1}$ of discharge capacity under the same test conditions. The presence of the carbon-coating acts as a physical layer of protection for the VNFs, preventing possible dissolution of vanadium and nucleophilic attack by the F^- ions from HF[48], especially at high temperatures, and at the same time improves the conductivity of VNF. These factors lead to the improved cycling stability of C-VNF over bare VNF.

4.2 Nanoparticle cathodes

For comparison with 1D nanostructures, nanoparticle-based cathode materials are synthesized using various methods and thoroughly studied using various characterization techniques and also electrochemical testing. Mainly, ionothermal and urea combustion syntheses are novel methods to obtain nano-particle olivine phosphate and vanadium pentoxide cathode materials. The results are presented in detail in the following sections.

4.2.1 Olivine nanoparticle cathodes

The most common synthesis method to obtain olivine phosphate (LiMPO_4 , where $\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) is usually the solid-state synthesis method. However, this method is often more energy intensive[205], requiring sintering at high temperatures and, consequentially, gives rise to larger particle sizes. Apart from solid-state synthesis, other methods such as sol-gel and ionothermal synthesis are explored and presented with the corresponding characterisation and electrochemical behavior.

4.2.1.1 LiMnPO₄ nanoparticle cathodes

Figure 4.34 FE-SEM images of (a) hydrothermal- (LMP-hyd), (b) ionothermal- (LMP-IL) and (c) sol-gel synthesized LiMnPO₄ (LMP-SG)

Under the FE-SEM (Figure 4.34), it could be observed that hydrothermally-synthesized LiMnPO₄ forms in rectangular morphology, with particle sizes ranging from about 800 nm – 1.2 μm. On the other hand, ionothermally-synthesized LiMnPO₄ gave rise to flakes ~1 μm in size, forming a 2D-morphology, similar to that synthesized by polyol methods[26]. Sol-gel synthesized LiMnPO₄ gave rise to large particles with irregular morphology.

Phase purity of the hydrothermally-synthesized LiMnPO₄ (LMP-hyd) and ionothermally-synthesized LiMnPO₄ (LMP-IL) was determined by XRD, in which the diffraction patterns were treated with Rietveld refinement using the Topas V3 software (Figure 4.35). XRD patterns of both samples could be matched to the calculated pattern of the *Lithiophilite Pnmb* phase of LiMnPO₄. Minute impurities could be noted in the hydrothermal synthesized sample LMP-hyd, from peaks noted at ~18 ° and ~34 ° 2θ, whereas ionothermal-synthesized LiMnPO₄ (LMP-IL) showed formation of 100 wt. % LiMnPO₄ phase. Attempts were made to re-synthesized LMP-hyd to reduce the impurities, but it was difficult to obtain reproducibility in subsequent samples. LiMnPO₄ obtained by solid-state method also gave 100 wt. % LiMnPO₄ phase.

Figure 4.35 XRD patterns of hydrothermal- (LMP-hyd), ionothermal- (LMP-IL) and solid-state (LMP-SS) synthesized LiMnPO_4 respectively

Sintering temperature (°C)	550	600	850
wt. % MnO	7	12	19
Wt. % LiMnPO_4	93	88	81
a (Å)	6.1069(1)	6.1053(8)	6.1075(3)
b (Å)	10.4591(3)	10.4532(1)	10.4564(4)
c (Å)	4.7458(1)	4.7446(8)	4.7467(3)
Crystal size (nm)	39.5(1)	64.9(2)	625.1(7)

Table 4.1 Lattice parameters of LMP-SG samples

Figure 4.36 XRD patterns of sol-gel synthesized LiMnPO_4 (LMP-SG) at various temperatures

Sol-gel synthesized LiMnPO_4 was achieved using the citric-acid assisted method (CAM). Following the sintering of the as-decomposed precursor at $400\text{ }^\circ\text{C}$ for 3 hours to remove the excess carbon, the LMP-SG precursors were heat-treated in Argon atmosphere at various temperatures to obtain minimal weight percentage of MnO impurity, in which the peaks are marked by asterisks (*) in Figure 4.36. Table 4.1

summarises the weight percentage (wt. %) of the phases and lattice parameters obtained from Rietveld refinement.

It can be derived that the formation of MnO impurity is favoured at higher temperatures, as the LMP-SG sample that was heat-treated at 850 °C gave rise to the highest proportion of 19 wt. % of MnO, as opposed to 81 wt. % LiMnPO₄ formation. Due to the high temperature used, the average crystal size is also much larger at ~625 nm. In subsequent samples, the lower heat treatment temperatures of 600 °C and 550 °C led to the formation of smaller crystals with sizes < 100 nm. While the lattice parameters (*a*, *b* and *c*) of the *Lithiophilite Pnmb* phase has negligible differences for the three samples, the wt. % of MnO impurity decreased to ~7 wt. % after heat treatment at 550 °C for 5 hours.

Figure 4.37 (a) Galvanostatic traces of LMP-IL and LMP-SS, cycling data of (b) LMP-IL, LMP-SG, LMP-hyd and LMP-SS up to 10 cycles and (c) LMP-IL and LMP-SS up to 30 cycles

The typical galvanostatic traces (Figure 4.37) of LMP-hyd, LMP-IL and LMP-SG are represented by that of LMP-IL, first charged to 4.5 V and discharged to 2.5 V vs. Li/Li⁺. The initial charge shows a formation of a sloping plateau starting from 4.0 V vs.

Li/Li⁺, which is indication that Li⁺ ions are deintercalating from the cathode. Upon discharge, no plateaus are observed, which could indicate that the Mn²⁺ / Mn³⁺ redox is not occurring reversibly. The galvanostatic traces of LMP-SG and LMP-hyd also have similar features. On the other hand, in the galvanostatic charge curve of LMP-SS, a sloping plateau starts at ~4.15 V and continues to 4.5 V, giving an initial charge capacity of ~45 mAh g⁻¹. Upon discharge, a plateau can be observed from ~4.0 V to ~3.7 V, which indicates reversibility in the Mn²⁺ / Mn³⁺ redox reaction.

It can be observed that LMP-SS has the highest initial capacity at ~60 mAh g⁻¹, which is comparable to that reported in the literature[23, 91]. LMP-IL, LMP-SG and LMP-hyd have respective initial capacities of ~20 mAh g⁻¹, ~5 mAh g⁻¹ and ~3 mAh g⁻¹. Further cycling to 10 cycles shows that the capacity fades to ~13 mAh g⁻¹ for LMP-IL, while the capacity of LMP-SS still increases. The higher capacity values of LMP-SS may be attributed to the synthesis method, which gives rise to larger particle size. Also, using the ionothermal synthesis method for LMP-IL enabled formation of phase-pure LiMnPO₄, as opposed to LMP-SG and LMP-hyd, which still contain impurities, thus giving slightly higher capacity values. Upon cycling to 30 cycles (Figure 4.37b), the specific capacity of LMP-SS is observed to stabilize at ~105 mAh g⁻¹, without further fading, while that of LMP-IL fades to ~10 mAh g⁻¹.

Overall, with the exception of LMP-SS, the capacity values of these LiMnPO₄ samples are low and it is possible that the inherent poor electrochemical properties[23] of LiMnPO₄ drastically affected the Li intercalation / deintercalation properties in these cases.

4.2.1.2 LiCoPO₄ nanoparticle cathodes

Following the work on LiMnPO₄, which has low conductivity and intercalation voltage ~4.1 V, it is imperative to synthesize and characterize the electrochemical properties of LiCoPO₄. LiCoPO₄ has high intercalation potential of ~5.1 V and it has the benefits of better conductivity over LiFePO₄ and LiMnPO₄. Moreover, these advantages have led to the doping of Co into other olivine phosphate structures to improve their electrochemical properties. To overcome the problem of electrolyte decomposition (EC: DEC organic electrolytes are unstable >4.5 V), electrolyte additives[94], such as LiBOB, can be added to prolong the lifespan of the electrolyte at higher voltages. In the following section, several routes have been employed to synthesize LiCoPO₄ nanoparticles are explored and the results are presented in detail.

Figure 4.38 FE-SEM images of (a) sol-gel synthesized LiCoPO₄ LCP-SG, (b) solid-state synthesized LiCoPO₄ LCP-SS and (c) ionothermally-synthesized LiCoPO₄ LCP-IL

LiCoPO₄ was synthesized using various methods including sol-gel and solid-state methods (Figure 4.38). Both methods gave rise to micron-sized particles with irregular morphology. On the other hand, the ionothermal method was also used to synthesize LiCoPO₄. Sub-micron particles were obtained from this method of synthesis, as shown in Figure 4.38c.

Figure 4.39 XRD patterns of LiCoPO_4 synthesized by various methods

Phase purity of as-synthesized LCP-IL, LCP-SG and LCP-SS were evaluated using XRD (Figure 4.39). All peaks match to the calculated *Pnma* structure of LiCoPO_4 , indicating that LiCoPO_4 is formed in all samples, without any impurities. The average crystal sizes were calculated by Rietveld refinement and are ~ 650 nm, ~ 600 nm and ~ 500 nm respectively for LCP-SS, LCP-SG and LCP-IL.

In LCP-SS, cyclic voltammograms of various voltage ranges were used to cycle the half-cells. Co-containing compounds (such as LiCoO_2) often undergo Co dissolution at higher voltages, which inevitably lead to large irreversible capacity upon further cycling. Figure 4.40 presents the CV data obtained. From Figures 4.40a to e, it is noticeable that there is a pair of redox peaks in each of the CV. In Figure 4.40a, the cell is cycled from 3.5 V to 5.0 V vs. Li/Li^+ , the oxidation peak is not obvious while a reduction peak at 4.67 V is formed. This could indicate that Li intercalation is occurring to a larger extent as compared to Li deintercalation. As the voltage range is increased to 3.5–5.1 V (Figure 4.40b & c), an oxidation peak around 5 V can be observed in the CV, and the reduction peak shifts from 4.67 V to 4.62 V. The shift in the reduction potential could be

related to the occurrence of oxidation at ~ 5.0 V. Further expansion of the voltage range to 3.5-5.2 V causes the reduction potential to shift to 4.59 V. In addition, it is observed that the larger voltage range leads to increased fading of the current densities in subsequent cycles. Figure 4.40f summarises the decrease in reduction potential vs. increasing voltage range.

Figure 4.40 Cyclic voltammograms of LCP-SS in various voltage ranges[206]

Figure 4.41 Cyclic voltammograms of (a) LCP-SG and (b) LCP-IL in the voltage range of 2.5- 5.5 V vs. Li/Li^+ with and without LiBOB additive

To study the effect of electrolyte additive on the electrochemical performance, LCP-SG and LCP-IL half cells were cycled in potentiostatic mode (CV) at a rate of 0.1 mV s^{-1} , comparing cells made with bare electrolyte and electrolyte with 3 wt. % LiBOB additive (Figure 4.41). In the sol-gel synthesized LiCoPO_4 (LCP-SG), it is evident that the presence of LiBOB additive increased the current density of LCP-SG by at least three times, when compared to that of bare electrolyte. One pair of redox peaks is observed in the CV of LCP-SG (bare electrolyte), where the oxidation peak is at 5 V and the reduction peak is $\sim 4.55 \text{ V}$ respectively. According to the literature[207] this redox pair is indicative of $\text{Co}^{2+} / \text{Co}^{3+}$ reaction. When LiBOB additive was added to the electrolyte, CV of LCP-SG showed two reduction peaks and one oxidation peak, the two reduction peaks are observed at ~ 4.85 and $\sim 4.5 \text{ V}$ vs. Li/Li^+ respectively, while the oxidation peak is at $\sim 5.1 \text{ V}$. It can also be noted that this oxidation peak is less sharp than the one observed for the LCP-SG cell without LiBOB additive. The redox couple related to 5.1 V (oxidation) and 4.8 V (reduction) may be due to the $\text{Co}^{3+} / \text{Co}^{4+}$ redox.

As for LCP-IL (Figure 4.41b), the cell made with bare electrolyte shows two oxidation peaks (5 and 5.2 V) and one reduction peak (4.6 V) in the CV. When LiBOB

additive was used, the redox peaks shifted to 5, 5.1 and 4.85 V respectively. Similar to LCP-SG, the current density is also much higher when LiBOB additive was used. The absence of the 4.5 V reduction peak in LCP-IL may be due to the crystal size, which is relatively smaller as compared to LCP-SG. Also, the smaller particle size may cause the shift in the reduction potential from 4.9 V (LCP-SG) to 4.85 V (LCP-IL) when electrolyte additive was used and from 4.55 V (LCP-SG) to 4.6 V (LCP-IL) when bare electrolyte was used. All voltages are reported vs. Li/Li^+ .

Figure 4.42 Cyclic voltammograms of LCP-SG up to 10 cycles (a) without and (b) with addition of LiBOB additive

Further cycling of LCP-SG in electrolytes with and without the addition of LiBOB did not show obvious fading upon cycling up to 10 cycles. In that of LCP-SG without LiBOB additive in the electrolyte (Figure 4.42a), the oxidation peak at ~ 5.1 V vs. Li/Li^+ faded upon further cycling and almost could not be observed by the third cycle, whereas the reduction peak ~ 4.55 V remained upon further cycling with some fading in current density. On the other hand, with the addition of LiBOB (Figure 4.42b), overall higher current density was achieved and less fading was also observed upon further cycling.

Similar electrochemical testing was carried out on LCP-IL cells, as shown in Figure 4.43. When the LCP-IL was cycled without addition of LiBOB, severe fading across further cycling can be observed. Also, the two oxidation peaks observed initially in the first cycle at ~ 5 and ~ 5.2 V vs. Li/Li^+ quickly faded to a broad peak at ~ 5.1 V by the third cycle. The reduction peak ~ 4.55 V remained intact, but also with severe fading. For LCP-IL with LiBOB additive, similar observations are made as that of LCP-SG, in which no sharp redox peaks are formed, with overall higher current density. Also, minimal fading upon further cycling was observed. It is possible that the addition of LiBOB additive helps to reduce capacity fading upon subsequent cycling of LiCoPO_4 active cathode materials.

Figure 4.43 Cyclic voltammograms of LCP-IL up to 10 cycles (a) without and (b) with addition of LiBOB additive

Different amounts of LiBOB additive were added to the bare electrolyte and tested in LCP-SS half cells. Galvanostatic cycling of the cells (Figure 4.44) were carried out at 0.05 C rate at room temperature. It can be observed that the discharge capacities of 115, 110, 109, 113 and 112 mAh g^{-1} were obtained for 0, 0.1, 0.5, 1 and 3 wt.% concentrations of LiBOB inclusion, respectively. Further cycling to 25 cycles show that the respective

capacity retention (based on initial capacity) values are 29 %, 28 %, 36.5 %, 53 % and 74 % for 0, 0.1, 0.5, 1 and 3 wt.% concentrations. It can be derived that addition of 3 wt. % of LiBOB enables improved cyclic retention properties in LiCoPO_4 , which is an indication of better reversibility of lithium intercalation / deintercalation during electrochemical charge / discharge.

Figure 4.44 (a) Galvanostatic discharge and (b) cycling data of LCP-SS with various concentrations of LiBOB addition to bare electrolyte[206]

Figure 4.45 (a) Galvanostatic discharge and (b) cycling data of LCP-IL and LCP-SG with variations of LCP-SG

Galvanostatic cycling of LCP-IL and LCP-SG cells based on bare electrolyte was carried out at 0.1 C rate at room temperature. As observed in Figure 4.45a, a plateau is formed at ~ 4.8 V, which is the deintercalation potential of the LCP samples. There is no variation of this potential for samples synthesized under various conditions. For

comparison, LCP-SG precursors with 10 wt. % Super P Li before heat treatment to obtain the LiCoPO_4 phase, using hand-mixing and ball-milling methods. Although there is no obvious variation in the XRD patterns of these variations, the initial specific capacities of LCP-SG-hand and LCP-SG-ball were higher than that of LCP-SG, synthesized without any additional carbon. The initial charge capacity of LCP-SG is $\sim 146 \text{ mAh g}^{-1}$, but there is large irreversible capacity, causing the first discharge capacity to be $\sim 35 \text{ mAh g}^{-1}$, corresponding to 24 % of initial charge capacity. LCP-SG-hand and LCP-SG-ball show higher initial charge capacities of 173 mAh g^{-1} and 154 mAh g^{-1} respectively, while the first discharge capacity values are 77 mAh g^{-1} (45% of charge capacity) and 53 mAh g^{-1} (34% of charge capacity). Comparatively, LMP-IL has lower initial charge and discharge capacities of 57 mAh g^{-1} and 43 mAh g^{-1} respectively.

Subsequent galvanostatic cycling to 30 cycles show discharge capacities of 10 mAh g^{-1} , 15 mAh g^{-1} , 13 mAh g^{-1} and 13 mAh g^{-1} for LCP-SG, LCP-SG-ball, LCP-SG-hand and LCP-IL respectively, giving corresponding capacity retention of 29 %, 28 %, 17 % and 30 %.

4.2.1.3 LiNiPO_4 nanoparticle cathodes

Like LiCoPO_4 , LiNiPO_4 has high intercalation voltage $>5 \text{ V}$, which makes it an attractive candidate for higher energy density applications as cathode materials in LIBs. However, the high operating voltage of such cathodes also requires research into high-voltage electrolytes. Current research on LiNiPO_4 is in the pioneering stages and some preliminary studies on LiNiPO_4 are presented in detail.

Figure 4.46 XRD patterns of LiNiPO_4 samples synthesized by ionothermal method

Temperature	Crystal size (nm)	wt. % LiNiPO_4	wt. % NiO
700 °C	180	95	5
800 °C	290	94	6
850 °C	290	93	7

Table 4.2 Summary of crystal size and phase purity for LiNiPO_4 (LNP-IL)

LiNiPO_4 precursors were reacted in ionothermally before being heat-treated in air at 700 °C, 800 °C and 850 °C for 5 hours. X-ray diffraction patterns (Figure 4.46) were collected to elucidate the phase formation of LiNiPO_4 in the LNP-IL samples. Rietveld refinement was carried out to provide insights on the phase purity of LiNiPO_4 . Heat-treatment of ionothermally-synthesized precursor at 850 °C for 5 hours gave rise to formation of 93 wt. % LiNiPO_4 phase and 7 wt. % of NiO as impurity, marked by asterisks (*) in Figure 4.46, when the temperature was reduced to 800 °C, the weight percent of NiO was increased slightly to 94 wt. % and subsequently, 95 wt. % at 700 °C. The reduction in sintering temperature to 700 °C also leads to reduction of particle size from ~290 nm to ~180 nm.

Cyclic voltammograms of LNP-IL-700 based half-cells were recorded at 0.1 mV s^{-1} rate in the range of 2.0-5.8 V. When the bare electrolyte was used (Figure 4.47b), a thin hysteresis loop is observed without any prominent peaks. Also, the oxidation and reduction curves cross at $\sim 5.3 \text{ V vs. Li/Li}^+$, indicating possible decomposition of the electrolyte. LiBOB additive was then added to the electrolyte and a second cell was tested under similar conditions (Figure 4.47a). Oxidation peaks can be noted at ~ 3.3 , ~ 5.0 and $\sim 5.5 \text{ V vs. Li/Li}^+$, while reduction peaks are noted at ~ 2.5 and $\sim 2.2 \text{ V}$. While the oxidation peak at $\sim 5.5 \text{ V}$ may be indicative of the $\text{Ni}^{2+} / \text{Ni}^+$ redox occurring in LiNiPO_4 cathode materials[31], the other peaks are not indicative and there does not seem to be formation of obvious paired redox peaks. This could indicate certain irreversibility in the Li intercalation / deintercalation for LiNiPO_4 .

Figure 4.47 Cyclic voltammograms (CV) of LNP-IL-700 (a) with LiBOB additive and (b) without LiBOB additive

4.2.2 V₂O₅ nanoparticle cathodes

Sluggish Li diffusion behavior, structural instability with lithium intercalation/de-intercalation and low electronic conductivity (10^{-2} - 10^{-3} S cm⁻¹) in bulk V₂O₅ are main cause for capacity fading over prolonged electrochemical cycling. Several approaches have been adopted to circumvent the aforementioned issues, such as modifying the crystal structure[137, 208, 209] to improve the Li⁺ ion diffusion by creating more open structures[34, 35], surface modification by conductive additives[38, 115] and patterning the 1D nanostructures[7, 34, 35, 103, 145]. As a result, research focus has progressively moved away from bulk V₂O₅ particles[39, 202, 210]. On the contrary, here sub-micron size V₂O₅ particles synthesized via urea-assisted combustion technique by controlling various parameters to achieve high performance material.

Figure 4.48 (a) Field emission secondary electron image (FE-SEM) and (b) transmission electron microscope (TEM) image with indexed selected area electron diffraction pattern (SAED) (inset) of VUC 600-1[33]

FE-SEM recorded on V₂O₅ powder sintered at 600 °C for 1 h in air (Figure 4.48a) revealed irregular shape V₂O₅ particle morphology with size ranging from 200-800 nm. The TEM image in Figure 4.48b shows the formation of crystalline V₂O₅ particle and it

was confirmed by SAED patterns. The observed diffraction spots of the crystal can be indexed to the (410) and (110) planes of the Shcherbinaite V_2O_5 phase.

Figure 4.49 (a) Rietveld refined XRD pattern of V_2O_5 prepared at 600 °C for 1 h and (b) family of XRD patterns of all samples sintered at 300, 400, 500 and 600 °C for durations of 1, 2 and 3 h respectively[33]

A representative X-ray powder diffraction (XRD) pattern evaluated by Rietveld refinement is presented in Figure 4.49a. The family of XRD patterns of sintered V_2O_5 powders are collected and presented in Figure 4.49b. Herein, the following labeling system has been used to describe the synthesized V_2O_5 powders, for example, VUC 600-1 here, VUC represents V_2O_5 by urea combustion, sintered at 600°C for duration of 1h.

Rietveld refinements are carried out for all the powders prepared using TOPAS V3 software. Observed reflections indicate the formation of single phase orthorhombic V_2O_5 corresponding to the layered Shcherbinaite structure ($Pmn2_1$), without any impurity phases.

Figure 4.50 Rietveld refinement parameter values (a) a , (b) b , (c) c lattice parameters, and (d) crystal sizes of all samples sintered at 300, 400, 500 and 600 °C for durations of 1, 2 and 3 h respectively[33]

Calculated lattice parameters and crystallite sizes obtained from Scherrer equation are presented in Figure 4.50a-c and d, respectively. It can be observed that, increasing sintering temperature results increase of lattice parameter values. Such increasing trends are also observed while increasing sintering time as well. Nevertheless, the observed values for lattice parameters a and c are slightly less than the literature values (JCPDS 89-2482 $a=11.544$ (2) Å, $b=4.383$ (1) Å and $c=3.571$ (1) Å) given in the corresponding Figures 4.51a, b and c), whereas the lattice parameter b value is slightly higher than reported. The variation of the lattice parameters with sintering temperature and time could be attributed to the removal of organic impurities and possibly the removal of oxygen vacancies[211-213]. The longer sintering time could enable more adequate reaction of vanadium precursor with ambient oxygen, while the higher sintering temperature enables a higher rate of reaction, to form the V_2O_5 structure. Furthermore, increasing the sintering temperature from 300-600 °C leads to a nearly exponential increase in crystallite size and it is clearly seen from Figure 4.50d. Overall increase in sintering duration (for example, 2 or 3 h) reveals noticeable increase in lattice parameter values and this effect is also more pronounced at higher sintering temperatures (400, 500 and 600 °C). Also, higher sintering temperature leads to increase in crystallite size, as given in Figure 4.50d. As the crystallite sizes obtained from the refinement data are much smaller than that observed from FE-SEM analysis and it is possible reason that the agglomeration of the crystallites may have occurred. The crystallite sizes are compared with V_2O_5 particles obtained at 600 °C for 1 h and subsequently ball-milled for 1 h. Average crystallite sizes of the ball-milled particles are reduced from 200 to 20 nm, obtained via Rietveld refinement. At the same time, when the particles are ball-milled with conducting carbon (3:1 w/w), the average crystallite sizes are further reduced from 200 to 28 nm.

Thermogravimetric studies (TGA) are carried out on the as-combustion synthesized precursor and results are presented in Figure 4.51a. Noticeable amount of

(~20 wt.%) weight loss is observed from the TGA of the as-combustion synthesized powder around 400 °C. This weight loss is an indication of the complete decomposition of organic components during sintering >400 °C in air.

Figure 4.51 (a) Thermogravimetric analysis (TGA) of as-combustion synthesized precursor and (b) Fourier-transform infrared spectra (FTIR) of samples sintered at 300, 400, 500 and 600 °C for 3 h respectively[33]

In order to confirm the formation of organic-moieties-free V_2O_5 powders, FTIR spectra has been recorded for all the powders and selectively presented in Figure 4.51b. All the recorded FTIR spectra of V_2O_5 comprise three characteristic bands at 1009, 817

and 527 cm^{-1} , irrespective of the sintering temperature. The sharp peak around 1009 cm^{-1} corresponds to the V=O stretching vibration and broad peaks at 827 and 527 cm^{-1} are assigned to asymmetric and symmetric stretching modes of V-O-V bonds respectively[101, 114]. The peak at 1009 cm^{-1} in the various spectra show increasing sharpness with increasing sintering temperature, which could indicate a strengthening of the V=O bond, and this supports the explanation for the lattice parameter expansions as observed in the XRD. Few additional peaks are observed in the case of $300\text{ }^{\circ}\text{C}$ sintered materials for all durations. The peaks around 1392 , 1612 and 1717 cm^{-1} are related to the presence of urea, as well as O-H bond vibrations[214-216]. This clearly indicates that the urea is not fully decomposed during the sintering process at $300\text{ }^{\circ}\text{C}$, whereas there is no such peaks are observed in the samples heat treated at 400 , 500 and $600\text{ }^{\circ}\text{C}$ for all durations indicating the complete degradation of organic molecules. Hence, it can be concluded that high purity V_2O_5 particles could be obtained the sintering temperature above $300\text{ }^{\circ}\text{C}$. The observed FTIR spectrum is in good agreement with TGA observations.

BET surface area analysis of the synthesized V_2O_5 powders were investigated and presented as follows. The V_2O_5 obtained from the sintering temperatures of 600 and $500\text{ }^{\circ}\text{C}$ for $1\text{--}3\text{ h}$ exhibiting lowest surface area ($\sim 3\text{ m}^2\text{ g}^{-1}$) of the materials prepared. However, sintering the materials at $400\text{ }^{\circ}\text{C}$ gives rise to higher surface area of $6\text{--}8\text{ m}^2\text{ g}^{-1}$ whereas those prepared at $300\text{ }^{\circ}\text{C}$ showed highest surface area of $6\text{--}11\text{ m}^2\text{ g}^{-1}$. As expected, the ball-milling procedure with carbon yielded slightly higher surface area for V_2O_5 particles of $19\text{ m}^2\text{ g}^{-1}$.

Electrochemical properties of the synthesized V_2O_5 particles were evaluated by means of galvanostatic and potentiostatic modes in half-cell (Li/ V_2O_5) configuration. All the half-cells are cycled between $1.75\text{--}4.0\text{ V}$ at 0.1 C in room temperature conditions by galvanostatically. The insertion of lithium ions into V_2O_5 layers results the phase

transformation of V_2O_5 to $Li_xV_2O_5$ leading to distortion in layered structure due to the occupancy of Li^+ ions into the spaces between the layers of VO_5 octahedral unit. The galvanostatic cycling studies are carried out for all the temperature conditions and sintering durations at 0.1 C rate and we are presenting the best performing materials in each sintering temperature. The V_2O_5 powders obtained from sintering at 600 °C for 1 h showed best cycling performance, whereas material sintered at 300 °C for 2 h (VUC 300-2) presented the poorest performance among the VUC powders. The detailed analysis will be discussed in later sections.

Cyclic voltammograms (CV) of Li/V_2O_5 cells (VUC 600-1 and VUC 300-2) were collected in the range of 1.75-4.0 V vs. Li/Li^+ at the slow scan rate of 0.1 mV s⁻¹ to understand the phase transformation occurring during lithium intercalation/de-intercalation into VO_5 layers and presented in Figure 4.52.

The Li/V_2O_5 cells were first discharged to intercalate the Li^+ ions in to V_2O_5 lattice. In the 1st cycle (Figure 4.52a), several oxidation/reduction peaks are observed for both VUC 600-1 and VUC 300-2 powders and corresponding to the intercalation/de-intercalation processes of Li^+ in V_2O_5 . The reduction (cathodic) peaks are observed at ~3.37, ~3.16, ~2.22, and ~1.81 V vs. Li/Li^+ , whereas two oxidation peaks only observed at ~2.70 and ~3.45 V vs. Li/Li^+ , respectively in both materials with different current densities. This variation in the current density may be attributed to the nature of crystallinity of materials synthesized. The appearance of cathodic peaks indicates that the reduction of V^{5+} in V_2O_5 takes place as a multistep process within the voltage range 1.75 to 4.0 V. The cathodic peaks at ~3.37 and ~3.16 V indicates the reduction of V^{5+} to V^{4+} , leads to the formation of $\epsilon-Li_xV_2O_5$ phase. It can be noted that the peak at ~3.16 V is at smaller current density as compared to that of electrospun V_2O_5 , (VNF, Section 4.1.3). This could generally refer to less amount of Li^+ intercalation occurring at this potential due to the relatively smaller surface-area-to-bulk ratio of VUC as compared to VNF, thus

the extent of phase transformation could be more gradual over the first electrochemical discharge. The other cathodic peaks ~ 2.22 and ~ 1.81 V belongs to partial reduction of V^{4+} to V^{3+} and this reduction reveal the formation of δ - and γ - $Li_xV_2O_5$ mixed phases. Cycling below 2.0 V vs. Li/Li^+ leads to the formation of irreversible γ - $Li_xV_2O_5$ phase which is confirmed by the appearance of reduction peak at ~ 1.81 V. This reduction process enables the accommodation of more than 2 Li per V_2O_5 formula unit. However, reversible reactions take place only in the potentials at ~ 2.70 and ~ 3.45 V vs. Li/Li^+ during anodic scan.

During subsequent cycles (Figure 4.52b & c), only one main well-defined oxidation/reduction pair is present for VUC 600-1. Further, the reduction peak is shifted to ~ 2.42 V, whereas oxidation peak remains at ~ 2.84 V vs. Li/Li^+ . These peaks are intact upon further cycling to 20 cycles, indicating the reversibility of the redox reactions. Whereas, the CV of VUC 300-2 is concerned, in the first cycle, it also undergoes similar reduction (cathodic) process of VUC 600-1 and exhibiting characteristic potentials at ~ 3.4 , ~ 3.18 , ~ 2.2 and ~ 1.9 V vs. Li/Li^+ respectively. In addition to above, two more additional reduction peaks can be observed at ~ 2.46 and ~ 2.81 V. These extra peaks can be attributed to the unwanted side reactions of organic impurities present in the VUC 300-2 sample. However, it shows the prominent oxidation peak at ~ 2.68 V in the first cycle rather than VUC 600-1. In the subsequent cycles (Figure 4.52b & c), two reduction peaks remains at ~ 2.49 and ~ 2.81 V vs. Li/Li^+ . The difference in the oxidation peaks of VUC 300-2 (~ 2.68 V) and VUC 600-1 (~ 2.84 V) in subsequent cycles may also be attributed to the incomplete formation of crystalline V_2O_5 phase, which provides sluggish kinetics during insertion/extraction of Li^+ ions results slight shift in the potentials. At the same time, organic impurities present in VUC 300-2 cannot be ruled out.

Figure 4.52 Cyclic voltammograms of VUC 300-2 and VUC 600-1 showing (a) first cycle, (b) second cycle and (c) 20th cycle, in which metallic lithium serves as both counter and reference electrodes in two electrode coin cell configuration with the scan rate of 0.1 mV s^{-1} between 1.75-4.0 V vs. Li/Li^+ [33]

The galvanostatic cycling profiles of VUC 600-1 and VUC 300-2 coin cells cycled between 1.75– 4.0 V *vs.* Li/Li⁺ at 0.1 C rate (or 35 mA g⁻¹) at room temperature are shown in Figure 4.53. Both samples show multiple plateaus during first discharge are more prominent in the VUC 600-1 cell when compared to VUC 300-2 (Figure 4.53a). The first discharge plateau occurs at 3.18 V *vs.* Li/Li⁺ this can be correlated to the reduction of V⁵⁺ to V⁴⁺ to enable the intercalation of Li into the layered V₂O₅. As a result, a mixture of α+ε-Li_xV₂O₅ phases are formed. Upon further discharge, two stable plateaus at ~2.24 and ~1.90 V are observed. The plateau at ~2.24 V is an indication of the formation of δ-Li_xV₂O₅ and further V⁴⁺ is partially reduced to V³⁺ forming the δ- and γ-Li_xV₂O₅ mixed phase. The plateau ~1.9 V is believed to be the transformation of δ-Li_xV₂O₅ to γ-Li_xV₂O₅ phase. Further discharging into 1.75 V causes the irreversible formation of γ-Li_xV₂O₅ and this holds good agreement with reduction potential in the CV ~1.81 V *vs.* Li/Li⁺.

In the case of VUC 300-2, the first discharge profile plateaus are not prominent when compared to VUC 600-1, which can be attributed to the incomplete crystallization of V₂O₅, thereby preventing the diffusion of Li⁺ ions and presence of impurities cannot be excluded (Figure 4.53b). In turn, incomplete reduction of V⁵⁺ to V⁴⁺ and V³⁺ takes place which leads to considerably less initial discharge capacity (250 mAh g⁻¹) when compared to VUC 600-1 at 0.1 C (320 mAh g⁻¹). In subsequent cycles, plateaus are not prominent in both cases and exhibiting the monotonous charge and discharge curves, which indicates that the Li⁺ intercalation/de-intercalation occurred reversibly in mixed phases of Li_xV₂O₅ formed after the first discharge. The specific discharge capacities of 320 and 250 mAh g⁻¹ are obtained for first and second cycles, respectively for VUC 600-1. The VUC 300-2 delivered the discharge capacities of 250 and 240 mAh g⁻¹ for first and second cycle. This improved capacity retention of VUC 300-2 rather VUC 600-1 is ascribed to the incomplete formation of Li_xV₂O₅ phases. As expected, highly crystalline

phase V_2O_5 (VUC 600-1) experiences large irreversible capacity loss, which is similar to the previous reports on the V_2O_5 system[7, 34, 35, 37, 100, 103, 145].

Figure 4.53 Typical galvanostatic cycles showing first and second charge and discharge curves of (a) VUC 600-1 and (b) VUC 300-2 cells between 1.75-4.0 V vs. Li/Li^+ at 0.1 C rate[33]

As mentioned earlier, all V_2O_5 powders obtained using urea combustion synthesis were cycled galvanostatically at 0.1 C rate (35 mA g⁻¹) and presented in Figure 4.54. Other than VUC 600-1 and VUC 300-2, the cycling performance of other samples VUC 400-3 (sintered at 400 °C for 3 h) and VUC 500-1 (sintered at 500 °C for 1 h) are also presented in Figure 4.54a. The powder VUC 600-1 delivered initial specific discharge capacity of 320 mAh g⁻¹ and maintains stable discharge capacity of ~230 mAh g⁻¹ (72 %

of initial discharge capacity) after 50 cycles. Such initial specific capacity is comparable than those reported in literature[35, 37] especially 1D nanostructures, as given in Table 2.3. Despite the relatively lower BET surface area, VUC 600-1 has comparable initial discharge capacity to 1D nanostructures, and along with much improved cyclic retention properties.

Figure 4.54 Plot of specific discharge capacity vs. cycle number (a) VUC 600-1, 500-1, 400-3 and 300-2, (b) VUC 600-1, ball-milled VUC 600-1 and ball-milled VUC 600-1 with carbon, and (c) VUC 600-1, NUC 600-1 (non-combustion synthesized) and commercial V₂O₅ powder[33]

On the other hand, VUC 500-1 presented an initial specific discharge capacity of 270 mAh g⁻¹ and 59 % of its initial discharge capacity only retained after 50 cycles. Similarly, VUC 400-3 and VUC 300-2 exhibited initial specific discharge capacity of 350 and 250 mAh g⁻¹, respectively. The capacity retention of VUC 400-3 and 300-2 is found to be 49 and 50 % respectively after 50 cycles. The poor cyclic retention of VUC 400-3 could be attributed to the smaller crystallite size, and for VUC 300-2 there is the additional factor of incomplete removal of organic moieties, as observed in TGA and FTIR. The relatively larger surface area of VUC 400-3, as compared to VUC 500-1 and VUC 600-1, could contribute to higher initial capacity and also capacity fading, as more unwanted side reactions could occur with the electrolyte. From VUC 500-1, and then to VUC 600-1, it can be observed that the increase in sintering temperature leads to further improvement in cycling behavior.

In order to study the effect of particle size on the electrochemical properties V₂O₅ powders, the VUC 600-1 was subsequently ball-milled using high energy milling with and without carbon. The cycling performance of the ball milled and native V₂O₅ are illustrated in Figure 4.54b. The ball-milled powder showed slightly lower initial discharge capacity of 260 mAh g⁻¹ than the native compound, but an improved cyclic retention of 77 % after 50 cycles is noted. Similarly, the powder, which is ball-milled with conductive carbon showed initial capacity of 245 mAh g⁻¹ and better capacity retention of 82 % is observed after 50 cycles than rest of its counterparts and this result is expected. Apart from the size reduction, ball-milling with carbon particles provides enhanced contact towards active material particulates than conventional mixing and thereby improving the performance of the cell. The powder morphology of the sample enables further improvement of cycling stability by a simple ball-milling procedure, which is not possible for other nanostructures as mentioned in Table 3.1, as the morphology would be destroyed.

Furthermore, the role of combustion synthesis on the performance of V_2O_5 is compared by direct sintering of the starting material at 600 °C for 1 h (Non-Urea Combustion, NUC 600-1). The electrochemical properties of above material was evaluated and compared with VUC 600-1 and commercially available material. The NUC 600-1 cell delivered the lower initial discharge capacity of 220 mAh g^{-1} when compared to 320 and 278 mAh g^{-1} for VUC 600-1 and commercial powders, respectively. The capacity retention of VUC 600-1 and NUC 600-1 powders are almost same ~71 % after 50 cycles. However, the urea combustion synthesis leads to slightly increased initial discharge capacity than rest.

Based on the electrochemical performance of V_2O_5 particles prepared by various conditions as stated above, the VUC 600-1 powder rendered better electrochemical performance among the samples tested. The same material has been subjected to rate performance studies with different C-rates conducted between 1.75 to 4.0 V and presented in Figure 4.55 with two duplicate cells. In both cells, it is evident that specific discharge capacity tends to decreases slowly at low current rate (0.1 C) during prolonged cycling. However, capacity fading is significantly improved when the cells are cycled at high currents, for example 0.5 or 1 or 2 C-rates. For the rate performance studies, the test cells are initially cycled to 50 cycles at 0.1 C and subsequently employed for high current rates. In the first cell, the C rate is increased from 0.1 to 1 C, the specific discharge capacity is decreased from 190 to 125 mAh g^{-1} and the capacity is maintained over 99 % for 10 cycles. Such behavior is expected in high current rates, while cycling the cell at high C rates, the surface of active material only involves the reaction rather than bulk. When the C rate is switched back to 0.1 C, the capacity is retained from 120 to 190 mAh g^{-1} .

Similarly, in the duplicate cell, the C-rate is increased from 0.1 to 0.2 C, a small amount of capacity fading (from 175 to 165 mAh g^{-1}) is noted. With further increase in

current to 0.5, 1 and 2 C rates, the cell delivered excellent discharge capacitive properties with negligible capacity fade. Finally, the current rate is relaxed to 0.1 C, and the discharge capacity is retained for its original state and maintained at 145 mAh g⁻¹ for after 20 cycles. From the above analysis, it can be concluded that the V₂O₅ prepared at 600 °C for 1 h by urea combustion shows good cell capabilities and capacity retention is maintained following cycling at higher C rates.

Figure 4.55 Rate capability studies of two duplicate cells comprising VUC 600-1 sub-micron size powders at room temperature[33]

4.2.2.1 Effect of aluminium-insertion (Al-insertion) in V_2O_5 nanoparticles

To further evaluate the effects of Al-intercalation on the electrochemical performance of V_2O_5 , Al-inserted urea-combustion synthesized V_2O_5 powders (VUC) were also studied and the results are presented as follows.

Figure 4.56 XRD of (a) Al-inserted V_2O_5 urea combustion powder (VUC), and (b) showing broadening of peaks with increasing Al-insertion

The XRD patterns of Al-inserted VUC were collected and compared to that of bare VUC (Figure 4.56a). The XRD pattern of bare VUC can be indexed to that of pure V_2O_5 , corresponding to the Shcherbinaite structure ($Pmn2_1$). It can be observed that the normalized XRD patterns of the Al-inserted powders have the same reflections as that of the bare VUC, without other impurities, along with the broadening of peaks (Figure 4.56b). The absence of Al-related peaks indicates that the Al-ions may be residing within the interlayers, similar to the case in the Al-inserted VNF discussed in the previous sections. Also, the increased concentration of Al-insertion leads to formation of smaller

particle sizes, which can be deduced from the broader peaks and lower intensity of reflections in the XRD.

Figure 4.57 XPS (V2p 3/2) of Al-inserted V_2O_5 urea combustion powder (VUC)

To evaluate the amount of Al inserted into the V_2O_5 structure, elemental dispersive spectroscopy (EDS) and inductively coupled plasma (ICP) were performed and the Al:V molar ratio of $Al_{0.66}VUC$ and $Al_{1.1}VUC$ are about 1:3 and 1.1:2 respectively. These results are also in agreement with those of and X-ray photoelectron spectroscopy (XPS). As seen in Figure 4.57 above, it can be noted that the binding energy of the V2P 3/2 spectra of Al-inserted VUC is reduced from the bare VUC. In $Al_{0.66}VUC$, the V2p 3/2 peak is observed at ~ 516.5 eV, similar to that of VO_2 [198], while in $Al_{1.1}VUC$, the peak is observed at ~ 516.0 eV, indicating the possible presence of a mixture of V^{3+} and V^{4+} ions. Taking into consideration the charge balance, the formulae of $Al_{0.66}VUC$ and $Al_{1.1}VUC$ are then determined to be $Al_{0.66}V^{4+}_2O_5$ and $Al_{1.1}V^{3+}_{1.3}V^{4+}_{0.7}O_5$ respectively.

Figure 4.58 Cyclic voltammograms of bare VUC and Al-inserted VUC showing (a) first cycle and (b) subsequent cycle.

Cyclic voltammograms (CV) of bare VUC and Al-inserted VUC half cells are collected in the range of 1.75-4.0 V vs. Li/Li^+ , at the slow scan rate of 0.1 mV s^{-1} , in order to understand the phase transformations occurring during lithium intercalation/de-intercalation between the VO_5 layers and presented in Figure 4.58.

The cells were first discharged to intercalate the Li^+ ions into V_2O_5 lattice. In the 1st cycle (Figure 4.58a), several oxidation/reduction peaks are observed for both bare and Al-inserted VUC, corresponding to the intercalation/de-intercalation processes of Li^+ in V_2O_5 . For bare VUC, the reduction (cathodic) peaks are observed at ~ 3.36 , ~ 2.10 , and

~ 1.85 V vs. Li/Li^+ , whereas only two oxidation peaks are observed at ~ 2.70 and ~ 3.46 V vs. Li/Li^+ . In $\text{Al}_{0.66}\text{VUC}$, reduction peaks can be observed ~ 3.0 , ~ 2.50 , ~ 2.20 and ~ 1.90 V, while two oxidation peaks are observed at ~ 2.70 and ~ 3.37 V in the first cycle. Similar reduction peaks are observed for $\text{Al}_{1.1}\text{VUC}$, with shift in the voltages to ~ 2.83 , ~ 2.50 , ~ 2.20 and ~ 1.90 V for reduction peaks and only one oxidation peak is observed at ~ 2.70 V for the first cycle. The appearance of cathodic peaks indicates that the reduction of V^{5+} in V_2O_5 takes place as a multistep process within the voltage range 1.75 to 4.0 V. In the bare VUC, the cathodic peak at ~ 3.36 indicates the reduction of V^{5+} to V^{4+} , leading to the formation of $\epsilon\text{-Li}_x\text{V}_2\text{O}_5$ phase. The other cathodic peaks ~ 2.10 and ~ 1.85 V belongs to partial reduction of V^{4+} to V^{3+} and this reduction reveal the formation of δ - and $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ mixed phases. Cycling below 2.0 V vs. Li/Li^+ leads to the formation of irreversible $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase which is confirmed by the appearance of reduction peak at ~ 1.85 V. This reduction process enables the accommodation of more than 2 Li per V_2O_5 formula unit. On the other hand, in the Al-inserted VUC, the first reduction peak is shifted to ~ 3.0 and ~ 2.83 V for $\text{Al}_{0.66}\text{VUC}$ and $\text{Al}_{1.1}\text{VUC}$, and an extra reduction peak is observed at ~ 2.83 and ~ 2.50 V respectively. This could be an indication that the insertion of Al-ions into the V_2O_5 structure led to reduction of the oxidation state of vanadium (V^{5+}). As a result, phase transformations related to the $\text{V}^{5+}/\text{V}^{4+}$ redox are reduced, and occurrence of the $\text{V}^{4+}/\text{V}^{3+}$ redox may be increased. Further reduction peaks at ~ 2.20 and ~ 1.90 V vs. Li/Li^+ indicate similar reactions occurring in Al-inserted VUC and bare VUC. The oxidation peaks in the CV of $\text{Al}_{0.66}\text{VUC}$ are at ~ 2.70 and ~ 3.37 V, similar to that of bare VUC. However, in $\text{Al}_{1.1}\text{VUC}$, it can be noted that there is no oxidation peak above 3V and only one oxidation peak is observed at ~ 2.70 V in the first cycle of the CV. It may be concluded that phase transitions related to Li intercalation occurred to a smaller extent in Al-inserted VUC as compared to VUC. The smaller current density of the CV cycles in Al-inserted VUC may indicate lower initial capacity as compared to bare VUC.

During subsequent cycles (Figure 4.58b), only one main well-defined oxidation/reduction pair is present for VUC. Further, the reduction peak is shifted to ~ 2.30 V, whereas oxidation peak is at ~ 2.67 V vs. Li/Li^+ . These peaks are intact upon further cycling to 20 cycles, indicating the reversibility of the redox reactions. In the subsequent CV cycles of Al-inserted VUC, the one pair of reduction / oxidation peaks are observed at ~ 2.50 V and ~ 2.70 V respectively.

Galvanostatic charge / discharge cycles were recorded on bare VUC and Al-inserted VUC based half-cells between 1.75-4.0 V at 0.1 C rate (35 mA g^{-1}). In all samples, several plateaus may be observed in the first discharge, indicative of the multiple phase transformations related to Li-intercalation into the V_2O_5 structure. In bare VUC (Figure 4.59a), plateaus are observed at ~ 3.0 , ~ 2.20 and ~ 1.96 V, which are indicative of reduction of V^{5+} to V^{4+} , V^{4+} to V^{3+} and formation of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase respectively. For $\text{Al}_{0.66}\text{VUC}$ (Figure 4.59b), plateaus are observed at ~ 3.10 , ~ 2.60 , ~ 2.26 and ~ 1.99 V, in agreement with the reduction peaks in the CV. $\text{Al}_{1.1}\text{VUC}$ reveal discharge plateaus at ~ 2.51 , ~ 2.31 and ~ 1.99 V. The first plateau > 3.0 V vs. Li/Li^+ is not present for that of $\text{Al}_{1.1}\text{VUC}$ (Figure 4.59c), indicating that the V^{5+} to V^{4+} reduction is not occurring, due to the absence of V^{5+} ions in the structure. The plateau at ~ 2.31 V is comparatively shorter than that of bare VUC and $\text{Al}_{0.66}\text{VUC}$, indicating presence of less V^{4+} ions in the structure of $\text{Al}_{1.1}\text{VUC}$. Finally the plateau at ~ 1.99 V is indicative of the $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase formation. Comparatively, in the galvanostatic charge, no obvious plateaus are observed. The first discharge capacities for bare VUC, $\text{Al}_{0.66}\text{VUC}$ and $\text{Al}_{1.1}\text{VUC}$ are $\sim 300 \text{ mAh g}^{-1}$, $\sim 320 \text{ mAh g}^{-1}$ and $\sim 160 \text{ mAh g}^{-1}$ respectively. It is possible the inserted Al^{3+} ions are residing between the V_2O_5 interlayers, occupying the spaces where intercalated Li^+ could possibly reside, resulting in the reduced specific capacity due to decreased Li intercalation. Subsequent charge / discharge cycles are without obvious

plateaus, indicating the reversible Li intercalation / deintercalation upon further cycling.

This data is in agreement with the CV as above.

Figure 4.59 First and second galvanostatic charge / discharge profiles of (a) bare VUC, (b) $\text{Al}_{0.66}\text{VUC}$ and (c) $\text{Al}_{1.1}\text{VUC}$

Figure 4.60 Discharge capacities vs. cycle number of bare VUC and Al-inserted VUC at (a) 0.1 C rate and (b) 1 C rate

Galvanostatic cycling was continued up to 50 cycles for all cells at 0.1 C and 1 C rates, as shown in Figure 4.60. During low rate cycling (0.1 C), the discharge capacity for bare VUC was $\sim 168 \text{ mAh g}^{-1}$, equivalent to $\sim 56 \%$ retention of initial capacity after 50 cycles. For Al-inserted VUC, the capacity retention was $\sim 55 \%$ and $\sim 70\%$ of initial capacity for $\text{Al}_{0.66}\text{VUC}$ and $\text{Al}_{1.1}\text{VUC}$ respectively. Insertion of small amount of Al in $\text{Al}_{0.66}\text{VUC}$ gives rise to slightly higher initial capacity but overall, no improvement in cyclic retention properties. The capacity retention of $\text{Al}_{1.1}\text{VUC}$ is the highest among the samples, however, it must be taken into account that the initial capacity of $\text{Al}_{1.1}\text{VUC}$ is low. Thus there is the possibility that Al^{3+} ions may occupy the interlayer spaces (between the V_2O_5 layers) which Li intercalation is expected to occur, thus the overall

capacity is reduced. The reduction of phase transformations may also be attributing to the lower overall specific capacity.

Cycling the cells at elevated temperature of 55 °C (0.1 C rate) was also carried out, but the bare VUC and $\text{Al}_{0.66}\text{VUC}$ cells experienced drastic degradation in electrochemical cycling behavior. Cycling of $\text{Al}_{1.1}\text{VUC}$ cell at high temperature (Figure 4.60a) increased initial capacity to 260 mAh g^{-1} , from $\sim 160 \text{ mAh g}^{-1}$. Upon cycling to 50 cycles, the capacity retention was $\sim 70 \%$, similar to performance of the same material at room temperature 0.1 C rate cycling. It is possible that the higher concentration of this $\text{Al}_{1.1}\text{VUC}$ sample led to the improved high temperature electrochemical properties.

The effect of Al-insertion was also studied based on high rate (1 C) cycling at room temperature (Figure 4.60b). $\text{Al}_{1.1}\text{VUC}$ has the highest initial capacity of $\sim 290 \text{ mAh g}^{-1}$ and further cycling to 50 cycles decreases the capacity to $\sim 180 \text{ mAh g}^{-1}$, $\sim 60\%$ retention of initial capacity. $\text{Al}_{0.66}\text{VUC}$ also has higher initial capacity of $\sim 230 \text{ mAh g}^{-1}$ and retained $\sim 64 \%$ of initial capacity after cycling for 50 cycles at 1 C rate. Finally, bare VUC has much lower initial capacity of $\sim 156 \text{ mAh g}^{-1}$, and $\sim 85 \%$ retention of initial capacity based. It can be derived that the insertion of Al^{3+} ions into VUC leads to improved electrochemical rate performance of the cells, judging from the good cycleability and higher initial capacity values.

4.3 Application of V_2O_5 powder (VUC) in full cell (vs. LTO anode)

To demonstrate the applicability of the V_2O_5 cathode materials in full cells, urea-combustion synthesized V_2O_5 (VUC 600-1) was prepared by electrochemical lithiation, by discharging it to 1.75 V vs. Li/Li^+ , in a Swagelok cell with Lithium as anode. The lithiated V_2O_5 electrode was then re-assembled in vs. Lithium titanate spinel (LTO) (Sigma-Aldrich) anode in an Argon-filled glovebox.

Figure 4.61 Cyclic voltammogram (CV) of V_2O_5 -LTO full cell

To elucidate the electrochemical reactions occurring in the V_2O_5 -LTO full cell, cyclic voltammogram (Figure 4.61) was done in the range of 0.005 to 3.0 V vs. Li/Li^+ , at 0.1 mV s⁻¹. The electrochemically lithiated V_2O_5 was used as the cathode. One main oxidation peak can be observed at 1.21 V vs. Li/Li^+ and two reduction peaks are observed at 2.33 and 0.60 V. Subsequent cycling does not show significant fading and the redox peaks also remain, indicating that the reactions are reversible throughout the Li intercalation / deintercalation processes.

Figure 4.62 Typical galvanostatic charge / discharge trace of V_2O_5 -LTO full cell

In Figure 4.62, the V_2O_5 -LTO full cell was cycled galvanostatically from 0.3 to 3 V vs. Li/Li^+ at 0.1 C (30 mA g^{-1}) rate. In the charge curve, the plateaus can be observed at ~ 1.2 and ~ 2.8 V, corresponding to the oxidation peaks in the CV. In the discharge, two plateaus can be observed at ~ 2.5 and ~ 0.90 V, corresponding to the reduction peaks in the CV. All subsequent charge / discharge cycles have similar profiles, indicating reversible electrochemical Li intercalation / deintercalation.

Figure 4.63 Specific capacity vs. cycle number for V₂O₅-LTO full cell

Galvanostatic cycling (Figure 4.63) was carried out up to 100 cycles on the full cell. The V₂O₅-LTO full cell shows initial high charge and discharge capacities of ~100 and ~82 mAh g⁻¹ respectively. Further cycling to 50 cycles reveals about 63-67 % retention of initial capacity. The full cell demonstrates good cyclic retention properties, stabilizing at ~65 mAh g⁻¹ after 100 galvanostatic cycles.

5. Discussion

5.1 Effect of nanoarchitectures on electrochemical performance of cathodes

It has been mentioned in literature that using nanoarchitectures in active electrode materials for LIBs have possible advantages such as reduced ion diffusion path lengths and improved stability[4, 5, 196]. In this thesis, several morphologies such as nanofibrous structures and sub-micron particles have been applied to cathode materials for LIBs and their electrochemical performances presented in the previous chapter. The following sections discuss nanoarchitectures and their effects on the electrochemical mechanisms and in turn, performance.

5.1.1 Effect of electrospinning morphology on electrochemical performance

The electrospinning technique was employed to synthesize several materials, namely LiFePO_4 , LiMnPO_4 and V_2O_5 , into fibrous structures. The 1D nanostructure is expected to bring about improved conductivity via presence of in-situ carbon coatings, as well as electrochemical stability.

5.1.1.1 LiFePO_4 -C nanocomposites

Figure 5.1 Schematic of LiFePO_4 -Carbon nanocomposites

LiFePO_4 nanoparticles were co-synthesized with carbon fibers, which have good wettability with the electrolyte and conductivity. As observed in Chapter 4, the

LFP-carbon co-synthesized composite LFP-C (Figure 5.1a) has the highest capacity ($\sim 160 \text{ mAh g}^{-1}$) among all the samples. The high carbon content ($\sim 84 \text{ wt. \%}$) provided enhancement of the electrochemical performance, but decreased the overall energy density of the cell. For the LFP-PAN sample (Figure 5.1b), the cyclic retention was not ideal and, judging from the morphology as observed in the TEM (Figure 4.2b) it is possible that the active LiFePO_4 particles were fully embedded and covered in the carbon nanofiber matrix, instead of being externally-connected via a porous network of electrospun carbon fibers as in LFP-C. Hence, the intercalation / deintercalation capability of the LiFePO_4 particles in LFP-PAN were greatly reduced, due to minimised direct contact with the electrolyte, where the mobile Li^+ ions were present. This observation is corroborated by the CV observation of LFP-PAN sample. Also LFP-PAN contained LiFePO_4 particles (other than the amorphous carbon nanofiber phase), which were pre-synthesized hydrothermally, and then mixed into the carbon precursor solution before being electrospun into nanofibers. The high temperature used to carbonized the carbon fibers led to the growth of large LiFePO_4 particles, which were in nanopowder form when first obtained from the hydrothermal synthesis. In addition, the large LiFePO_4 particles were widely spaced apart in the nanofibrous carbon matrix. The large distance between the active LiFePO_4 particles could have led to the reduced cyclability and lowered capacity of the LFP-PAN sample. Hence, the co-spinning of LiFePO_4 powder and PAN-precursor solution to obtain LFP-PAN proved to be less effective due to the continuous carbon coating on the exterior of the LiFePO_4 particles, which reduced the specific capacity.

By contrast, LFP-C, which have the active LiFePO_4 phase on the surface of the carbon-nanofibers, could achieve higher specific capacity. Taking into consideration the physical structure of the LiFePO_4 nanoparticles and carbon nanofibers, it is possible that the carbon nanofibers provided an electronically-conductive network,

doubling as a scaffold for the LiFePO_4 nanoparticles to chemically-attach during the hydrothermal synthesis. This structure is more beneficial due to the exposed LiFePO_4 nanoparticles, which means the electrochemically-active surface area is increased, as compared to LFP-PAN. In addition, the smaller particle size of the hydrothermally-synthesized LiFePO_4 could benefit the Li-intercalation properties of LFP-C.

The physically-mixed L-CNF has similar electrochemical performance as that of LFP-hyd, although the presence of CNF could have increased the polarization difference between the intercalation / deintercalation plateaus. From the results, it can be inferred that physical attachment of LiFePO_4 nanoparticles to the CNF had negligible effect on the electrochemical performance. On the other hand, chemically-attached LiFePO_4 -nanoparticles, as in LFP-C, have increased intermittent contact with the CNF, leading to better electrochemical performance.

5.1.1.2 LiMnPO_4 core-shell nanofibers

In an attempt to improve the intermittent contact between the LiMnPO_4 nanoparticles and carbon nanofibers, the core-shell nanostructure was applied to form C-LMP and LMP-C fibers. Electrochemical impedance spectra (EIS) were recorded for LMP-C and C-LMP half-cells, after fabrication and allowed to reach equilibration (Figure 5.2). According to the literature[184, 217], the high-to-middle frequency semicircle is related to the lithium-ions migration through the solid electrolyte interphase (SEI) layer and surface film capacitance, another semicircle at the low-frequency is related to lithium ion (charge) transfer as well as on the lithium ion concentration in an electrolyte and interfacial capacitance between electrode/electrolyte interface.

Figure 5.2 EIS of LMP-C, C-LMP and LMP-hyd

As seen above (Figure 5.2), the C-LMP equilibrated half cell has a relatively larger high-to-middle frequency circle than that for LMP-C. Thus, LMP-C could have higher conductivity[185], contributed by the carbon-nanofiber (CNF) shell, as noted in its higher initial capacity (8 mAh g^{-1}). On the other hand, it is also interesting to note that C-LMP has larger SEI formation than LMP-C. In C-LMP, the covering of the carbon core by the poorly conducting LiMnPO_4 shell results in lower conductivity than that of LMP-hyd, which consists of pristine LiMnPO_4 nanoparticles (not containing carbon) synthesized by hydrothermal method. In contrast to LFP-PAN, as observed in the previous section, the LiMnPO_4 nanofibers (LMP-C), which are encased in the CNF structure, are not fully covered by the carbon layer, due to the lower flow rate of the shell during the electrospinning process. Also, the formation of the LiMnPO_4 -carbon nanofibrous core-shell structure ensures that the nanoparticles do not agglomerate or become spaced out, as in the case of LFP-PAN, forming an evenly distribution of active

nanoparticles which are well-connected within the physical network structure. Although the conductivity of C-LMP (7 mAh g^{-1}) is lower than that of LMP-hyd, the larger SEI formation could have resulted in the higher initial capacity over LMP-hyd (3 mAh g^{-1}).

Figure 5.3 EIS of LMP-C, C-LMP and ball-milled variations

From Figure 5.3, it can be observed that the ball-milled LMP-C and C-LMP fibers lead to an overall decrease in the Z' values of the high-to-middle frequency semicircles. This is expected as the ball-milling process broke down the 1D nanostructure provided by the core-shell fibers and thus surface area for SEI formation was drastically reduced. It is also interesting to note that the slope of the Warburg element, which is corresponding to the linear, low frequency portion of the EIS, is at a larger angle as compared to the non-ball-milled fibers. LMP-C and C-LMP have a linear slope $\sim 45^\circ$ in the EIS, which indicates diffusion-dependent electrochemical reactions, related to Li intercalation / deintercalation. Thus, in the ball-milled samples, it may be noted that the larger angle of the Warburg slope could mean that less diffusion-dependent reactions could occur during

electrochemical charge / discharge. Ball-milling of the fibers led to overall decrease in diffusion-active surface area, as compared to the fibers, leading to less charge / discharge cycles required to reach maximum capacity.

5.1.1.3 V₂O₅ nanofibers (VNF)

The possible mechanism behind the formation of these high-purity VNF is suggested in the schematic shown in Figure 5.4. The vanadium-containing precursor VO(acac)₃ is dissolved in a solution of ethanol and acetic acid, with addition of PVP to increase the viscosity of the solution. During the electrospinning process, the PVP forms a polymeric scaffold in which the droplets of dissolved VO(acac)₃ are evenly dispersed. This enables the formation of a random network of as-spun fibers. Upon sintering, the degradation of PVP and the growth of the V₂O₅ nanoparticles, via the oxidation of VO(acac)₃, occur simultaneously. In order to maintain the fibrous morphology of the VNF, a slow rate of temperature increase (2 °C min⁻¹) is required. The sintering process has an annealing effect on the V₂O₅ nanoparticles and allows the nanoparticles to join together, forming porous nanofibers. In addition, the slow sintering rate enables sufficient time for the PVP to be totally degraded, as proven by the FTIR studies. Formation of such nanofibers with large aspect ratios prevents the agglomeration of nanoparticles.

Figure 5.4 Schematic diagram showing the formation of VNF during sintering[34]

In addition, the VNF precursor solution was sintered without electrospinning, giving rise to the formation of VNF-powder. It can be noted from the FTIR spectra that the formation of the V₂O₅ phase was not complete, resulting in overall poorer electrochemical performance (~200 mAh g⁻¹ initial capacity). Therefore, the porous structure of electrospun VNF fibers led to the formation of V₂O₅ phase and complete decomposition of organic moieties during the short sintering time of 15 mins, thus contributing to the high initial capacity (316 mAh g⁻¹).

Figure 5.5 Nyquist plots of VNF (a) fresh cell and after cycling and (b) Bode phase angle plot of the impedance data with equivalent circuit used for fitting the Nyquist plots. Symbols present experimental spectra and continuous lines represent fitted data using equivalent electrical circuit[34]

Electrochemical impedance spectra (EIS) for coin-cells of electrospun VNF were recorded in the frequency range 100 kHz to 10 mHz. Nyquist (Z'' vs. Z') plots after

stabilizing the fresh cell and after 10 cycles are shown in Figure 5.5a. The cells display two partially overlapped semicircles in the low and middle frequency range and a straight line in the low-frequency range, suggesting VNF electrode kinetics[39]. For the fresh cell, the Nyquist plots consist of three parts, a high-to-middle frequency semicircle between 100 kHz to 10 Hz, another semicircle at the low-frequency (5 to 0.25 Hz) and a sloping line with a phase angle of about 45° to the real axis (Z') in the lower frequency range (< 0.1 Hz), corresponds to Warburg-type element. The ionic diffusion from the bulk of electrolyte to the reaction sites affects impedance mostly at high frequencies. As before, the high-to-middle frequency semicircle is related to the lithium-ions migration through the solid electrolyte interphase (SEI) layer and surface film capacitance, another semicircle at the low-frequency is related to lithium ion (charge) transfer as well as on the lithium ion concentration in an electrolyte and interfacial capacitance between VNF/electrolyte interface. The sloping straight line at very low frequency corresponds to the dominant mass transport and is indicative of controlled diffusion of electroactive species across the interface between surface films in the VNF matrix; it also involves the capacitive effect of the conducting carbon used in electrode preparation.

To perform a quantitative analysis, a simple equivalent circuit was configured to simulate the EIS, shown in Figure 5.5b and circuit parameters are calculated by using the series combination of R_s , R_{SEI+ct}/CPE_{SEI+dl} , R_b/CPE_b and W_o , the finite length Warburg resistance (open-circuit terminus). At high characteristic frequency, intercept of the semicircle extended to the Z' axis is reflected by an ohmic resistance (R_s), which includes ionic resistance from the separator and resistance of the electrolyte. R_{SEI+ct} is ascribed to resistance due to the lithium ion migration through the interface between the surface layer of the VNF electrode/electrolyte and surface film resistance. CPE_{SEI+dl} corresponds to the surface film and double-layer capacitance at the porous VNF electrode surface. The bulk resistance (R_b) arises due to combination of electronic resistivity of active material (VNF)

and ionic conductivity of electrolyte filled by the pores of the composite electrode (active material, conducting carbon and binder). The constant phase element CPE_b is the bulk capacitance arising due to the complicated electrochemical processes. The constant phase element is an empirical impedance function of the type, $CPE_{SEI+dl/b} = A(j\omega)^{-\alpha_{SEI+dl/b}}$, replaced with capacitance by taking into account the rough nature of the electrode, where ω is the angular frequency, and A and $\alpha_{dl/b}$ are the constants. The degree of distortion of the impedance spectra can be obtained from the value of $\alpha_{SEI+dl/b}$ [218, 219].

The experimental data were subjected to a nonlinear least square fitting procedure and equivalent circuit parameters are obtained for VNF fresh cell and after cycling. The semicircles with a characteristic frequency of 63 Hz and 1 Hz before cycling and a single semicircle at 31 Hz after cycling evaluate degree of intercalation and deintercalation of lithium ions at VNF electrode / electrolyte interface. Cells, before and after cycling, show almost constant value of ohmic resistance, $R_s \sim 2.84 \Omega$ arising mainly from the resistance of electrolyte. R_{SEI+ct} is observed to decrease from 485 to 37 Ω for VNF. The contribution due to SEI formation is negligible in the case of freshly made cell. After cycling, the decrease in impedance observed for VNF, indicates the evidence of SEI formation in the higher frequency region, overlapped with the bulk resistance region. The presence of two semicircles is clearly apparent in the phase angle vs. log frequency (Bode plot shown in Figure 5.5c) of the cycled cell. It is expected that during long-term cycling, the surface reactions at electrolyte/electrode interface can also lead to the worsening of the electrochemical properties of active electrode materials, forming insoluble products (mixture of $Li_xV_2O_5$ phases) which exhaust Li^+ content in electrodes, blocking the pores of the electrodes, resulting in the increased charge transfer impedance[220]. The capacitance CPE_{SEI+dl} is also observed to decrease during cycling from 8.88 to 4.02 μF for VNF electrode. This slight decrease for VNF can be ascribed to the available electroactive surface area facilitated by VNF matrix through which charge transfer

occurs. During every discharge process, the thickness of double layer decreases along with the active charge-transfer processes (or Li^+ transfer in the VNF matrix). When the CPE_{dl} reaches the maximum value, the vacancies of VNF are fully occupied by Li^+ . The further transformation to $\text{Li}_x\text{V}_2\text{O}_5$ phases gives rise to the rebuilding of new capacitive double layer. This process repeats until the VNF electrode reaches to the full discharged state[221]. The significant increase in bulk resistance from 483.9 to 1173 Ω after cycling is observed. Therefore, it is expected that an increase in bulk resistance to electron or ion transfer will result in slow kinetics, large activation polarizations and leads to a significant loss of cycling efficiency and capacity fading. The Warburg diffusion resistance W_0 increased from 0.19 to 103 m Ω after cycling thus showed decrease in the low frequency bulk capacitance CPE_b from 0.55 to 0.02 mF. This rather high capacitance before cycling could be due to the accumulating of charge before the Faradic reaction takes place. After cycling, the change in bulk structure and cathode surface has reduced the amount of diffusion pathways, and decreases the utilization of active materials thus increasing Warburg resistance for VNF. Therefore VNF, having porous interconnected morphology, are considered to have potential in minimizing diffusion barriers, and ionic and electronic resistances to decrease the internal resistance as well as to facilitate electrolyte accessibility in the cathode network.

As clearly seen, Nyquist plots of VNF has a much larger diffusivity constant, as shown by the Warburg element. This indicates that more lithium ions are entering the nanofibrous structure of VNF, which is contributed by the electrospinning method of synthesis. The porous, randomly interconnected network of VNF gives rise to a large surface area, which allows increased contact of the electrolyte and the electrode material, and facilitates the movement of lithium ions into and from the VNF cathode.

5.1.2 Effect of chemical / physical modifications on electrochemical performance

5.1.2.1 Effect of Al-insertion on V_2O_5 crystal structure and electrochemical performance

Reduction in the crystallite size values are apparently reflected from the decrease in the intensity and broadening of the peaks evidenced from XRD patterns (Figure 4.22a and b). From the increase in the lattice parameters from the native VNF to the Al-inserted VNF, it can be deduced that the chemically-inserted Al^{3+} ions are likely to reside between the VO_5 slabs and forming the $[AlO_6]$ octahedra with oxygen atoms in the V_2O_5 structure[112, 117]. Schematic representations of the layered V_2O_5 crystal structure, formed by the VO_5 polyhedra, and the possible positions of Al^{3+} ions residing within the V_2O_5 layers, are given in Figure 4.22b and c, respectively. The occupancy of Al^{3+} will stabilise the VO_5 layers and thereby improving the facile insertion and extraction of Li-ions under high current operations.

EIS were recorded for the equilibrated half-cells of VNF and Al-inserted VNF. The high-to-middle frequency semicircles are related to the formation of solid electrolyte interphase (SEI) layer and surface film capacitance, while the middle-to-low frequency region refers to the charge transfer (CT) and interfacial capacitance across the electrode/electrolyte interface. The inclined vertical line at 45° in low frequency regions refer to the lithium-diffusion-related kinetics[204]. In Figure 5.6, it is clearly observed that the diameter of the high-frequency semicircles shows an increasing trend from bare VNF to $Al_{0.5}VNF$, while the semicircle for that of $Al_{1.0}VNF$ shows a smaller diameter. The Al-insertion to VNF could increase the conductivity of the electrode, as observed in compounds of having the formula $M_xV_2O_5$ [111, 121], where M= metallic ions, while further insertion of Al-ions into the structure could reduce the porosity of the $Al_{1.0}VNF$, as observed in the FE-SEM (Figure 4.20) thus reducing overall SEI formation. On the

other hand, the bare VNF and $\text{Al}_{0.5}\text{VNF}$ are comparatively more porous, and could possibly have more SEI formation, leading to the larger diameter of the high frequency semicircle in the EIS.

Figure 5.6 EIS of VNF and Al-inserted VNF[197]

In general, Al-insertion to VNF is observed to improve the high-rate and high temperature cycling properties to a certain extent. Firstly, the addition of Al^{3+} ions into the V_2O_5 structure during the *in-situ* synthesis leads to the reduction of V^{5+} to V^{4+} (for both $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$) and also to V^{3+} (for $\text{Al}_{1.0}\text{VNF}$) of Al-VNFs. The presence of these pre-reduced vanadium ions (V^{4+} and V^{3+}) before the electrochemical Li-intercalation/de-intercalation reduces the extent of electrochemically induced phase changes, related to the conversion of V_2O_5 to $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase. Further, Al^{3+} insertion leads to increased *c*-spacing in the layered structure and it is believed to occupy between the VO_5 layers, thus provides the necessary structural stability for V_2O_5 phase. Once the crystal structure is stabilized, it becomes less susceptible distortion due to the

intercalation/de-intercalation of Li-ions during electrochemical cycling[112, 117]. In comparison, $\text{Al}_{0.5}\text{VNF}$ has more similar phase transitions during Li-intercalation/de-intercalation with native VNF due to the smaller increase in the lattice parameters and presence of V^{5+} ions remains within the structure. On the other hand, $\text{Al}_{1.0}\text{VNF}$ has a much larger deviation in a and c lattice parameters, and also the complete reduction of V^{5+} ions to a mixed valence states of V^{4+} and V^{3+} ions which leads to the larger differences in phase transitions related to Li-intercalation/de-intercalation during electrochemical cycling. From the galvanostatic studies, it is evident that, irrespective of the inclusion of Al^{3+} at low and high current rates and testing temperature, the layered V_2O_5 showed capacity fading during cycling. There are several reasons believed for such fading, which includes vanadium dissolution[48], poor compatibility of vanadium towards linear carbonates (eg. DEC)[222, 223] and also intrinsic nature of the native compound[195]. Further, the presence of Al^{3+} drastically improved the electrochemical performance of V_2O_5 by stabilizing the structure during high current rate and elevated temperature operations. Similar kind of improvement in the elevated temperature performance for Al^{3+} inclusion has also been noticed in other systems like LiMn_2O_4 [201] and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [47]. At the same time, 1D fibrous morphology of V_2O_5 nanofibers cannot be ruled out, which enables facile insertion/extraction of Li-ions during high current testing. The presences of voids in the fibers enable more contact area towards electrolyte solution leads to the faster diffusion of Li-ions. In addition, the retention of fibrous morphology during electrochemical testing is also one of the factors for such performance as shown by ex-situ electrode analysis.

5.1.2.2 Effect of Al-insertion on V₂O₅ (VUC) crystal structure and electrochemical performance

Al-insertion was also carried out on the as-combustion synthesized V₂O₅ precursor, using Al(NO₃)₃ as the aluminium precursor. From the Rietveld refinement of the XRD patterns, it can be noted that the crystallinity of the Al-inserted samples decreased.

Sample	VUC	Al _{0.66} VUC	Al _{1.1} VUC
Lattice parameter <i>a</i> (Å)	11.513 (6)	11.513 (3)	11.535 (6)
Lattice parameter <i>b</i> (Å)	4.385 (2)	4.387 (1)	4.395 (2)
Lattice parameter <i>c</i> (Å)	3.564 (1)	3.562 (5)	3.571 (2)

Table 5.1 Lattice parameters for bare VUC and Al-inserted VUC

The XRD patterns of bare and Al-inserted VUC can be indexed to that of pure V₂O₅, corresponding to the Shcherbinaite structure (*Pmn*2₁). A summary of the lattice parameter values obtained from Rietveld refinement (Table 5.1) shows that all the lattice parameters vary slightly with increasing Al-insertion, especially in Al_{1.1}VUC. The larger amount of Al³⁺ ions within the crystal structure possibly leads to increased strain within the crystal structure, leading to the broadening of the XRD peaks (Figure 4.56b) and affecting the structural properties.

Figure 5.7 Schematic (not-to-scale) of possible positions of inserted Al^{3+} ions in layered structure of V_2O_5 in (a) VNF and (b) VUC

It is possible that the Al is residing in the interlayer spaces, between the V_2O_5 layers, where Li^+ ions will reside in the case of Li intercalation, as illustrated in Figure 5.7b. If so, then the Al-inserted VUC will have lower specific capacity values than that of bare VUC. In addition, the electrochemical stability of Al-inserted VUC should be improved, due to the possible support (or bonding) given to the interlayer space by the Al^{3+} ions, in agreement with the galvanostatic cycling results.

Figure 5.8 EIS of bare VUC and Al-inserted VUC

To further elucidate the effect of Al-insertion on the electrochemical performance of V_2O_5 powder (VUC), electrochemical impedance spectroscopy (EIS) was carried out on bare VUC, $Al_{0.66}VUC$ and $Al_{1.1}VUC$ respectively (Figure 5.8). The high-to-middle frequency semicircles observed is usually related to the formation of solid electrolyte interphase (SEI) layer and surface film capacitance, while the middle-to-low frequency region refers to the charge transfer (CT) and interfacial capacitance across the electrode/electrolyte interface. The inclined vertical line at 45° in low frequency regions refer to the lithium-diffusion-related kinetics. It can be observed that the semicircles show a decreasing trend in the diameter, with increasing Al-insertion into the VUC. The bare VUC has the largest diameter for the high frequency semicircle, indicating better charge transfer and more SEI formation as compared to the Al-inserted VUC. The decreasing trend of the semicircles possibly indicates higher conductivity with increasing Al-insertion into VUC[185]. It is also interesting to note that the larger gradient (inclination towards the y-axis) of the linear region at low frequency regions is more for Al-inserted VUC, indicating that less lithium-diffusion-related kinetics may occur in these samples. This data is in agreement with the electrochemical data, which shows that the Al-inserted VUC have relatively poorer electrochemical performance at room temperature, compared to bare VUC.

5.1.2.3 Effect of carbon coating on electrochemical performance of VNF

Figure 5.9 Electrochemical impedance spectra (EIS) bare VNF, C-VNF-15 and C-VNF-30 with enlarged high frequency region (inset)[180]

Electrochemical impedance spectroscopy (EIS) was carried out on bare VNF, C-VNF-15 and C-VNF-30 respectively, and presented in Figure 5.9. The high-to-middle frequency semicircle were observed which are related to the formation of solid electrolyte interphase (SEI) layer and surface film capacitance, while the middle-to-low frequency region refers to the charge transfer (CT) and interfacial capacitance across the electrode/electrolyte interface. The inclined vertical line at 45° in low frequency regions refer to the lithium-diffusion-related kinetics. It is clearly observed that the diameter of the high-frequency semicircles showed a decreasing trend with increasing carbon coating, suggesting that there is CT occurring in the C-VNF electrodes. This confirms that the electronic conductivity of VNF increased with larger amount of carbon coating and it was well-reflected in the electrochemical cycling studies.

From the galvanostatic studies, it is evident that amorphous carbon-coating plays a dual role to improve the electrochemical properties of VNFs. First, the electronic conductivity has been improved by the presence of the carbon layer, which has been clearly seen from electrochemical properties of C-VNFs at high current densities. Unfortunately, low current rates improvement of electrochemical properties is not obvious which is mainly due to the presence of VO_2 phase. Improvement in conductivity enables the facile Li-intercalation/de-intercalation during charge-discharge processes. Secondly, the homogeneous coating effectively prevents the nucleophilic attack on the electrode material by fluoride ions (F^-) from hydrofluoric acid (HF), especially at elevated temperature operations[190], as observed in Figure 4.33a. Apart from the carbon coating, presences of voids in the fibers enable more contact area towards electrolyte solution leads to the faster diffusion of Li-ions cannot be ruled out. At the same time, capacity fading of VNFs are inevitable, which can be related to vanadium dissolution, poor compatibility of vanadium compounds towards linear carbonates and also intrinsic nature of the native compound. The electrochemical cyclic stability of C-VNFs is improved from that of bare VNF, via the protective carbon layer.

5.1.2.4 Effect of carbon coating on electrochemical performance of VUC

Figure 5.10 Electrochemical impedance spectra (EIS) VUC 600-1, VUC 600-1 ball-milled and VUC 600-1 ball-milled with carbon[33]

Electrochemical impedance spectra (EIS) for VUC 600-1 and ball-milled powders VUC 600-1bm and VUC 600-1bmC (with carbon) were recorded in the frequency range 100 kHz to 5 mHz. The typical Nyquist (Z'' vs. Z') plots for freshly made cells after stabilization of 24 h are shown in Figure 5.10. The Nyquist plots consist of two main parts, a high-to-middle frequency semicircle related to SEI layer formation and charge transfer kinetics, and a sloping line to the real axis (Z') in the lower frequency range corresponding to Warburg-type element, relating to lithium diffusion kinetics.

For V_2O_5 electrode kinetics, a simple equivalent circuit was configured to simulate the EIS and shown in Figure 5.12. The circuit parameters have been calculated by using the series combination of R_s , R_{SEI+ct}/CPE_{SEI+dl} , R_b/CPE_b and W_o , the finite

length Warburg resistance (open-circuit terminus). At high characteristic frequency, intercept of the semicircle extended to the Z' axis is reflected by an ohmic resistance (R_s), which includes resistance from separator and electrolyte solution. The R_{SEI+ct} is ascribed to resistance due to the lithium ion migration through the interface between the surface layer of the V_2O_5 cathode/electrolyte and surface film resistance. CPE_{SEI+dl} correspond to the surface film and double-layer capacitance at the V_2O_5 electrode surface. The bulk resistance (R_b) arises due to combination of electronic resistivity of active material (V_2O_5) and ionic conductivity of electrolyte filled by the pores of the composite electrode (active material, conducting carbon and binder). The constant phase element CPE_b is the bulk capacitance arising due to the complicated electrochemical processes. The constant phase element is an empirical impedance function of the type, $CPE_{SEI+dl/b} = A(j\omega)^{-\alpha_{SEI+dl/b}}$, replaced with capacitance by taking into account the rough nature of the electrode, where ω is the angular frequency, and A and $\alpha_{dl/b}$ are the constants. The degree of distortion of the impedance spectra can be obtained from the value of $\alpha_{SEI+dl/b}$.

The experimental data are subjected to a non-linear least square fitting procedure and equivalent circuit parameters are obtained for V_2O_5 cells after the same length of equilibration period. For the ball-milled sample, reduction of particle size leads to increase in electro-active surface area, thus increasing the film formation. This can be seen from the increase in R_{SEI+ct} value and there is a slight decrease in CPE_{SEI+dl} (32 μF to 14 μF) is noted when compared to native compound. The R_b and CPE_b are also reduced to 46 Ω and 5 mF respectively, compared to VUC 600-1. This may be correlated to the decrease in the porosity of the ball-milled sample[220]. Similarly, Warburg resistance is also noticeably reduced from ~ 1.75 k Ω to 25 m Ω . The decrease in Warburg impedance values indicate that diffusion pathways have been increased in the ball-milled sample due to the reduction in the particles size. Further ball-milling with conductive carbon (Super P Li) to the VUC 600-1 sample leads to the increase in R_{SEI+ct} and CPE_{SEI+dl} values to ~ 1.30

k Ω and 17 μ F respectively from ball milled powders. This is believed to be due to the capacitive effect of Super P Li carbon, in which ball-milling further enabled more homogeneous mixing of the active material and conductive species. The R_b is also increased to 323 Ω , however, there is no major variation in the CPE_b value (~ 5 mF) upon addition of Super P Li carbon. The decrease in Warburg resistance to 1.7 m Ω indicates that the addition of conductive carbon leads to a faster diffusion of lithium ion during electrochemical reaction, which has been reflected in the cycling performance of the cells.

Unlike the case of C-VNF, where the carbon coating improves the conductivity of the VNF, and also acts as a protective layer, the addition of conductive Super P Li carbon to VUC merely increases the capacitive effect and charge transfer properties, via the larger surface-area-to-volume ratio provided by the ball-milling of the V_2O_5 sub-micron particles. Hence, the presence of carbon in ball-milled VUC improves the cyclic stability via the capacitive effect, instead of acting as a protective layer.

5.1.3 Effect of sintering temperature

5.1.3.1 Sol-gel synthesis of $LiMnPO_4$

In the sol-gel synthesis of $LiMnPO_4$, different sintering temperatures were used to reduce the amount of impurities. As noted in the previous section (Table 4.1), higher sintering temperature of 850 $^{\circ}$ C led to formation of ~ 19 wt. % of MnO impurities, while decreasing the temperature to 550 $^{\circ}$ C reduces the MnO phase to ~ 7 wt. %. Although Argon atmosphere was used during the sintering, the higher temperature could induce the formation of MnO, and other impurities, as noted in the literature. In contrast, lowering the sintering temperature can reduce the amount of impurities. Consequentially, variation of the sintering temperature also affects the average crystal size. At higher temperatures, the rate of reaction increases exponentially and growth of crystallites is favoured, leading

to formation of ~625 nm crystals at 850 °C. Lower temperatures, in turn, lead to less crystal growth and formation of much smaller crystals (< 100 nm).

5.1.3.2 Post-ionothermal sintering of LiNiPO₄

Ionothermal synthesis of LiNiPO₄ was carried out similar to that of LiMnPO₄ and LiCoPO₄. However, the LiNiPO₄ phase did not form due to the lower temperature conditions used in ionothermal synthesis. Thus, the ionothermal samples were sintered at higher temperatures (700-850 °C) in air. Like LiMnPO₄ above, it can also be observed that the NiO impurities show an increasing trend with increasing sintering temperature. As seen in Table 4.2, LiNiPO₄ obtained from sintering at 850 °C for 10 hours contained 7 wt. % NiO impurities, and decreasing the sintering temperature to 700 °C enabled the NiO impurities to decrease to 5 wt. %. Similarly, the crystal size is smaller at 180 nm after sintering at 700 °C, and increased to ~290 nm after sintering at 850 °C.

5.1.3.3 Effect of sintering temperature on electrochemical performance of urea-combustion synthesized V₂O₅ (VUC)

As-combustion synthesized V₂O₅ precursors were sintered at different temperatures (300-600 °C) for durations 1-3 hours. It can be observed that the lattice parameters (a, b and c) and crystal sizes all increased with increasing sintering duration and temperature. FTIR spectra also show formation of V₂O₅ phase after sintering at temperatures > 300 °C. In general it is observed that sintering at 600 °C gave the best electrochemical performance, in terms of high initial capacity and good cyclic retention properties, while samples sintered at 300 °C gives overall low initial capacity, due to incomplete formation of the V₂O₅ phase and small crystal size.

For VUC powders prepared by sintering at the various temperatures (300, 400, 500 and 600 °C), EIS for the equilibrated fresh cells were recorded in the frequency range 100 kHz to 5 mHz. The Nyquist plots consist of two parts, a high-to-middle frequency semicircle and a sloping line to the real axis (Z') in the lower frequency range corresponds to Warburg-type element, related to V_2O_5 electrode kinetics.

Figure 5.11 EIS for VUC sintered at various temperatures[33]

Figure 5.12 Equivalent circuit for EIS of VUC[33]

Sample	R_{SEI+ct} (Ω)	CPE_{SEI+dl} (μF)	R_b (Ω)	CPE_b (mF)	W_o (Ω)
VUC 300-2	1.177	2.75×10^{-8}	145.7	0.0249	359
VUC 400-3	265.4	35.3	74.65	2.99	700
VUC 500-1	8.301	0.615	160.3	0.0375	208
VUC 600-1	275.0	32.0	53.86	10.2	1750

Table 5.2 Summary of EIS values for VUC prepared at different temperatures[33]

After non-linear least squares fitting, similar to that in section 5.1.2.3, results are presented in Figure 5.11. VUC 600-1 shows a semicircle with a characteristic frequency of 200 Hz, whereas VUC 500-1 shows a semicircle with a characteristic frequency of 158 Hz. The characteristic frequencies for VUC 400-3 and VUC 300-2 are observed to be at 126 and 256 Hz respectively. The value R_{SEI+ct} is observed highest for VUC 600-1 sample ($\sim 275 \Omega$), followed by VUC 400-3 ($\sim 265 \Omega$), whereas for VUC 500-1 and VUC 300-2, the value of R_{SEI+ct} is found to be $< 10 \Omega$. Similarly, the highest capacitance CPE_{SEI+dl} is observed for 600-1 ($\sim 32 \mu F$) and lowest for VUC 300-2 (275 pF). The R_{SEI+ct} and CPE_{SEI+dl} values can be correlated to the available electro-active surface area facilitated by V_2O_5 cathode through in which charge transfer (CT) occurs. This clearly inferred that the difference in surface area affects the formation of surface film and charge transfer properties. The high R_{SEI+ct} and CPE_{SEI+dl} values of VUC 600-1 sample indicate the more active formation of surface films on the surface of the electrode. Consequentially, VUC 600-1 exhibited the lowest R_b value among the other samples, whereas it shows highest CPE_b value (~ 10 mF). Due to lower bulk resistance (R_b), the cycling stability is certainly improved[113]. The Warburg diffusion resistance (W_o) is slightly higher for VUC 600-1 (~ 1.75 k Ω) as compared to the other VUC prepared at lower temperatures, indicating that it possess lower number of diffusion pathways than the latter. It is possible that less lithium-diffusion related kinetics are occurring in VUC 600-1 and this could have contributed to the overall better cyclic efficiency.

Figure 5.13 EIS of VUC 600-1 and NUC 600-1[33]

In addition to the above, the powder NUC 600-1 (non-urea combustion synthesized V_2O_5 powder, obtained by sintering vanadium precursor directly) showed highest R_{SEI+ct} values (545 Ω) and capacitive effect of the interphase is reduced from 32 μF to 23 μF when compared to the combustion sample VUC 600-1. The bulk resistance is also increased to 194 Ω whereas bulk capacitance (CPE_b) is reduced to 2 mF. Finally, the high Warburg resistance (W_o) ~ 13.9 k Ω indicated the large decrease in number of diffusion pathways, which results in poor performance during cycling.

From the EIS analysis, it can be concluded that larger particle size of VUC 600-1 enabled better cycling stability, though it exhibited slightly lower initial discharge capacity when compared to rest of the samples prepared at different conditions. Ball-milling is one of the approaches to reduce the particle size, which increases the contribution towards more robust surface film formation via larger available area. However, overall bulk resistivity is reduced when compared to VUC 600-1. Hence, ball-milling of V_2O_5 powder increases number of diffusion pathways for Li^+ ion transport, which is observed from the improved capacity retention properties. Moreover, urea

combustion method provides improved the capacitive properties of V_2O_5 powders and also increased the electro-active surface which is reflected in the reduced Warburg resistance value when compared to that of non-combustion synthesized sample NUC 600-1. This result is also in good agreement with higher initial capacity and cycling profile observed for VUC 600-1 when compared to NUC 600-1.

5.2 Fundamental studies on mechanism of lithium intercalation

Lithium intercalation into V_2O_5 occurs via the reduction of V^{5+} in V_2O_5 and subsequent phase transformations in V_2O_5 , according to equation 3 below.

Typically, half cells Li/V_2O_5 are first discharged to enable intercalation of Li into the structure. During the first discharge, one can observe the multistep reduction process occurring as plateaus in galvanostatic discharge and reduction peaks in the cyclic voltammogram. Usually a first reduction peak (or plateau) occurs ~ 3.2 V, indication the reduction of V^{5+} to V^{4+} , leading to the formation of ϵ - $Li_xV_2O_5$, as indicated in equation (6) below.

Further, reduction peaks around ~ 2.2 V and 2.1 V refer to the partial reduction of V^{4+} to V^{3+} , leading to the formation of a mixed phase of δ - and γ - $Li_xV_2O_5$, as shown in equations (5) and (6).

Upon cycling below 2.0V vs. Li/Li^+ , the γ - $Li_xV_2O_5$ phase is irreversibly formed, as shown by the reduction peak at 1.95V. This irreversible reduction process of the vanadium ion enables the accommodation of more than 2 Li per V_2O_5 . The continuous

insertion of Li causes the V_2O_5 layers to distort, in order to accommodate more Li into the interlayer spaces.

At the end of the first discharge, the distorted $Li-V_2O_5$ structure which forms retains this structure and subsequent charge / discharge cycles are based on this final form and usually only one pair of oxidation / reduction peaks are observed in the subsequent cycles of CV.

5.2.1 Pre-lithiation studies on $Li_xV_2O_5$

In order to elucidate the phase transformations occurring in $Li_xV_2O_5$, prelithiation was carried out on VUC 600-1 powders, as the bare V_2O_5 cathode material. The prelithiation was carried out in tandem with the predicted Li intercalation concentrations as above, corresponding to the plateaus in the first discharge. Concentrations of 0.2, 0.5, 1, 2 and 3 mol BuLi were used to obtain similar extent of lithiation as those of electrochemically lithiated samples.

FE-SEM was carried out on bare VUC 600-1 V_2O_5 powder and the prelithiated samples as shown in Figure 5.14. It is observed that 0.2 and 0.5 $Li-V_2O_5$ have similar morphology as VUC 600-1, indicating that the smaller amounts of Li intercalation did not affect the morphology of the VUC 600-1 drastically. From 1.0 $Li-V_2O_5$ (Figure 5.13d), it is seen that the morphology as less angular as compared to 0.2 and 0.5 $Li-V_2O_5$ (Figures 5.13b and c), it can be inferred that this is the intermediate stage in which the V_2O_5 undergoes a structural change to accommodate >1 Li per V_2O_5 . At the lithiation of 2.0 Li per V_2O_5 , it is noted that the powder-like morphology is no longer present (Figure 5.13e). The formation of $Li_xV_2O_5$ phase leads to the formation of a rod-like morphology at the intercalation of 3 Li per V_2O_5 (Figure 5.13f).

Figure 5.14 Field-emission scanning electron microscope (FE-SEM) images of (a) bare VUC 600-1 (V_2O_5 urea combustion), (b) $0.2\text{Li-V}_2\text{O}_5$, (c) $0.5\text{Li-V}_2\text{O}_5$, (d) $1.0\text{Li-V}_2\text{O}_5$, (e) $2.0\text{Li-V}_2\text{O}_5$ and (f) $3.0\text{Li-V}_2\text{O}_5$

Figure 5.15 XRD of prelithiated V_2O_5 samples

In the X-ray diffraction patterns (Figure 5.15) of the prelithiated V_2O_5 samples, it can be observed that $0.2Li-V_2O_5$, which marks the beginning of the Li intercalation into V_2O_5 , shows an extra peak $2\theta = \sim 20^\circ$. Rietveld refinement shows that the extra peak is belonging also to the V_2O_5 *Shcherbinaite* $Pmn2_1$ phase, but with a relatively larger crystal size. Thus, two V_2O_5 phases are observed, both with different sets of lattice parameters. The first is *Shcherbinaite* $Pmn2_1$ ($a = 11.435$ (1) Å, $b = 4.487$ (1) Å, $c = 3.5691$ (1) Å, crystal size = 103 (2) nm) and the second of similar phase ($a = 11.503$ (1) Å, $b = 4.393$ (2) Å, $c = 3.567$ (20) Å and crystal size = 155 (4) nm). It is possible that lithiation occurred in the latter phase, as increase in the a lattice parameter is observed, while there is slight reduction in those of b and c . The larger crystal size could also be an indication of phase change. It is possible that at the concentration of 0.2 Li per V_2O_5 , partial Li

intercalation occurs, leading to the formation of a mixture lithiated and non-lithiated V_2O_5 phases.

Prelithiated V_2O_5 at 0.5 BuLi (0.5Li- V_2O_5) mainly shows an extra reflection in the XRD at $2\theta = \sim 18^\circ$, along with peaks related to the V_2O_5 structure. Rietveld refinement shows the presence of two phases, the original V_2O_5 phase and a LiV_2O_5 *Pnma* phase. The respective lattice parameters of the two phases are derived to be V_2O_5 , Shcherbinaite *Pmn*₂ ($a = 11.411$ (5) Å, $b = 4.515$ (4) Å, $c = 3.568$ (5) Å and crystal size = 72 (1) nm) and LiV_2O_5 , *Pnma* ($a = 9.942$ (1) Å, $b = 3.638$ (1) Å and $c = 9.908$ (1) Å and crystal size = 100 (2) nm). It is evident that the c parameters of both phases are drastically different, thus leading to the large distortion of the V_2O_5 structure upon Li intercalation. The V_2O_5 phase has lower overall crystal size, as compared to 0.2Li- V_2O_5 . It could be that the V_2O_5 phase undergoes amorphisation to convert to the LiV_2O_5 phase. Incorporation of 1 Li into V_2O_5 means that the oxidation state of V^{5+} is partially reduced to V^{4+} .

Subsequently, LiV_2O_5 phase is fully formed at 1 BuLi per V_2O_5 (1.0Li- V_2O_5), with the following lattice parameters ($a = 9.623$ (1) Å, $b = 3.780$ (1) Å and $c = 10.341$ (7) Å, crystal size = 49 (1) nm). This can be correlated to the formation of δ - LiV_2O_5 . According to the literature, discharging the V_2O_5 to a voltage ~ 2.5 V leads to the formation of this phase, and more importantly, at this point, the lithium intercalation of V_2O_5 is still reversible, as the main structure of V_2O_5 is still intact.

As broad peaks are observed in the XRD pattern of 2.0Li- V_2O_5 , prelithiation of V_2O_5 carried out at a higher concentration of 2M BuLi (2.0Li- V_2O_5), possibly led to the formation of an amorphous phase, which could be correlated to the beginning of phase change to the irreversible formation of $Li_{2.2}V_2O_5$. The intercalation of larger amount of Li ions into the layered structure could have caused considerable strain, rendering the structure amorphous. This data is in agreement with that observed in the FESEM (Figure

5.13e), where the angular, particulate morphology could not be observed. Due to the high concentration of Li, this phenomenon has never been reported before, in which up to 1.16 Li has been prelithiated per V_2O_5 via chemical routes[105-107], while Eguchi and Ogawa (2007)[108] previously reported the existence of $Li_{2.2}V_2O_5$, that was synthesized via the reaction of lithium and vanadium alkoxides. Finally, prelithiation of 3 M BuLi to V_2O_5 ($3.0Li-V_2O_5$), forms the heavily lithiated phase of V_2O_5 . The peaks could be matched to that of $Li_xV_2O_5$ phase[107], indicating the reformation of a distorted V_2O_5 structure with accommodation of Li^+ ions from $2.0Li-V_2O_5$. It may be assumed to be the ω - LiV_2O_5 phase, similar to the phase irreversibly formed at the end of the first electrochemical discharge of V_2O_5 below 2.0 V.

Figure 5.16 XPS for (a) Li 1s and (b) V2p_{3/2} of prelithiated V_2O_5 samples

In order to confirm the presence of Li in the lithiated phases, XPS was carried out the Li-V₂O₅ powders, as shown in Figure 5.16a. Peaks can be observed in all the lithiated phases at ~55.7 eV, similar to that of lithium vanadate compound[198]. However it was difficult to determine the amount of Li present in the phases. On the other hand, the XPS of vanadium (V2p_{3/2}) was also carried out. A relatively sharp peak could be observed at ~517.6 eV, corresponding to that of V₂O₅ (presence of V⁵⁺) in the NIST database, for that of bare V₂O₅ powder before the prelithiation. Increasing the lithiation concentrations of BuLi to 0.2, 0.5 and 1 mol per V₂O₅ respectively caused a slight shift, due to the appearance of a smaller peak at ~516.3 eV, similar to that of VO₂, indicating the presence of a mixture of V⁵⁺ and V⁴⁺ ions. When the lithiation content was increased to 2 and 3 Li per V₂O₅, broad peaks are observed, including binding energies of ~516.3 and ~515.8 eV, indicating the presence of V⁴⁺ and V³⁺ ions.

Prelithiated phase	Li: V ratio
0.2Li-V₂O₅	1.4:10
0.5Li-V₂O₅	1: 4
1.0Li-V₂O₅	8:10
2.0Li-V₂O₅	2:1
3.0Li-V₂O₅	2.5:2

Table 5.3 Summary of ICP analyses

Further analyses were then carried out using inductively coupled plasma analyses (ICP), as presented in Table 5.3. For 0.2 and 0.5Li-V₂O₅, it could be noted that the Li: V ratio are in agreement with the concentration of BuLi and V₂O₅ used. As the concentration of Li is increased in 1.0 and 2.0Li-V₂O₅, the amount of Li present is more than the prelithiated amount, with respect to V₂O₅. This indicates that there may be some phase change occurring in the layered V₂O₅ structure to accommodate more Li into the

V_2O_5 structure. This result is in agreement with that observed in XRD (Figure 5.14), especially so for $2.0\text{Li-V}_2\text{O}_5$ where the structure is observed to become nearly amorphous with. Interestingly, the mole ratio for Li: V translates to 4 Li per V_2O_5 , this could be an indication that the V_2O_5 structure is not intact during the reaction of 2 mol BuLi per mol of V_2O_5 . From the prelithiation carried out with 3 mol of BuLi per mol of V_2O_5 , the maximum amount of lithium then seems to be ~ 2.5 Li per V_2O_5 . In consideration of the information derived from XRD (Figure 5.15), it could be possible that the intercalation of 2.0 Li per V_2O_5 leads to collapse of the structure but the reaction of V_2O_5 with 2.5 Li gives rise to the formation of a distorted $\omega\text{-Li}_x\text{V}_2\text{O}_5$ structure. The final formula of $\text{Li}_x\text{V}_2\text{O}_5$ can be thus derived to be $\text{Li}_{2.5}\text{V}_2\text{O}_5$.

Figure 5.17 Cyclic voltammograms (CV) of $0.2\text{Li-V}_2\text{O}_5$ showing (a) first and (b) subsequent cycles

The electrochemical properties of the pre-lithiated V_2O_5 were studied. The half-cells of Li/ lithiated V_2O_5 were first charged to 4.0 V vs. Li/Li^+ , to deintercalate the pre-inserted Li and then subsequently discharged. In Figure 5.17 above, the CV of $0.2\text{Li-V}_2\text{O}_5$ shows similar peaks to that of V_2O_5 , with no extra peaks. However it is noticeable

that the reduction peaks at ~ 3.35 and ~ 3.12 V vs. Li/Li^+ in the first cycle are more pronounced than those in VUC 600-1, for which the corresponding peaks are at 3.37 V and 3.16 V. Subsequent cycling behavior is similar to that of VUC 600-1, showing one main pair of oxidation peaks. It is possible that the low amounts of Li present in the V_2O_5 structure enabled further electrochemical intercalation of Lithium into the layered structure. The CV is also in agreement with the XRD, which shows the formation of two V_2O_5 phases with slightly different lattice parameters.

Figure 5.18 Cyclic voltammograms (CV) of $0.5\text{Li-V}_2\text{O}_5$ showing (a) first and (b) subsequent cycles

In the CV of $0.5\text{Li-V}_2\text{O}_5$, the first cycle of the CV is relatively the same, with much higher current density as compared to VUC 600-1 and $0.2\text{Li-V}_2\text{O}_5$. All peaks remain the same, except for the appearance of a small oxidation peak at ~ 3.4 V vs. Li/Li^+ and also, the formation of a redox pair at ~ 3.64 V (ox) and ~ 3.61 V (red). These extra peaks may indicate the presence of LiV_2O_5 , as observed in the XRD. Therefore, extra Li is deintercalating from the lithiated V_2O_5 cathode. In the subsequent cycles, extra reduction peaks at ~ 3.15 , ~ 2.37 , ~ 2.27 and ~ 1.93 V can be observed. These peaks

indicate that there may be some reversibility of Li intercalation / deintercalation during the second charge / discharge cycle for the LiV_2O_5 phase.

At $1.0\text{Li-V}_2\text{O}_5$, where the formation of LiV_2O_5 is derived to occur, the CV (Figure 5.19) shows a drastically different shape from VUC 600-1. In the first cycle, one oxidation peak is observed at 2.70 V vs. Li/Li^+ and two reduction peaks are observed at 3.25 and 2.42 V respectively. The other peaks related to V_2O_5 are not observed in the CV, therefore it confirms that the structure of V_2O_5 has changed upon intercalation of 1 Li per V_2O_5 .

Figure 5.19 Cyclic voltammograms (CV) of $1.0\text{Li-V}_2\text{O}_5$ showing (a) first and (b) subsequent cycles

In the second cycle, oxidation peaks are observed at 2.70, 3.16 and 3.50 V, while reduction peaks are observed at 3.30 V and 2.43 V. The appearances of these peaks indicate that further Li intercalation / deintercalation may lead to other phase changes in the LiV_2O_5 structure. Also it may be noted that the overall area of the CVs are reduced by one order as compared to VUC 600-1. Further cycling to 10 cycles note that the oxidation peaks at 3.50 V and 2.70 V fade away and the reduction peak shifts from 3.30 to 3.17 V. Also it can be noted that the 5th cycle shows extra peaks at 2.15 V and 1.94 V. The

appearance and disappearance of the peaks during subsequent cycles are an indication that several irreversible reactions may be occurring during subsequent electrochemical Li intercalation / deintercalation.

According to the XRD, the lithiation of 2.0 Li into V_2O_5 leads to the formation of an amorphous structure. In the CV (Figure 5.20), two main oxidation peaks are observed at 2.90 and 3.48 V while main reduction peaks are observed at 3.38, 3.18, 2.30 and 1.90 V. The presence of many small redox peaks in the CV may indicate the occurrence of Li intercalation / deintercalation into the disordered structure of $2.0Li-V_2O_5$. The area inside the CV curves is still relatively small, similar to those in $1.0Li-V_2O_5$. The presence of Li inside the V_2O_5 structure before the electrochemical reactions could lead to overall reduced initial capacities, as less Li can electrochemically intercalate into the structure.

Figure 5.20 Cyclic voltammograms (CV) of $2.0Li-V_2O_5$ showing (a) first and (b) subsequent cycles

Subsequent cycling to 10 cycles show that while the oxidation peak at 2.90 V remains, the 3.48 V becomes a broad peak, encompassing the other small peaks observed initially. Reduction peaks at 3.38 and 3.18 V fade and disappear by the 10th cycle while the reduction peak at 2.30 V reduces in intensity and shifts to 2.14 V by the 10th cycle.

The reduction peak at 1.93 V only appears in the first cycle, indicative of an irreversible reaction.

Pre-intercalation of high concentration of lithium into V_2O_5 led to the formation of $3.0Li-V_2O_5$, in which the first cycle of the CV shows oxidation peaks at 2.30, 2.60, 3.33, 3.46, 3.50 and 3.66 V, with forming corresponding redox pairs with reduction peaks at 2.33, 2.40, 3.16, 3.37, 3.45 and 3.60 V. The oxidation peaks appear at similar voltages to the reduction peaks of VUC 600-1, indicating the de-intercalation of the prelithiated Lithium ions. It can be noted that the first oxidation peak should occur at 1.90 V if lithium intercalation > 2.0 Li per V_2O_5 is reversibly occurring. The absence of the 1.90 V oxidation peak at the first cycle of CV for $3.0Li-V_2O_5$ indicates that some lithium has led to irreversible phase transformation of the V_2O_5 structure by intercalation of > 2.0 Li.

Figure 5.21 Cyclic voltammograms (CV) of $3.0Li-V_2O_5$ showing (a) first and (b) subsequent cycles)

Subsequent cycles only show two pairs of redox peaks at 2.69 / 2.45 (ox / red) and 2.33 / 1.90 V respectively, indicating that subsequent electrochemical Li intercalation / deintercalation occur reversibly.

The prelithiated V_2O_5 cathodes were first charged at constant current rate (0.05 C , $\sim 17 \text{ mA g}^{-1}$) to $4.0 \text{ V vs. Li/Li}^+$ to determine the amount of Li that was intercalated chemically into the V_2O_5 structure. The first charge cycles are presented in Figure 5.22.

$0.2\text{Li-V}_2\text{O}_5$ shows first charge capacity of $\sim 26 \text{ mAh g}^{-1}$, corresponding to approximately 0.2 Li per V_2O_5 , which is in agreement with the prelithiated concentration. $0.5\text{Li-V}_2\text{O}_5$ and $1.0\text{Li-V}_2\text{O}_5$ show initial capacities of $\sim 66 \text{ mAh g}^{-1}$ and $\sim 70 \text{ mAh g}^{-1}$ respectively, both corresponding to $\sim 0.5 \text{ Li per V}_2\text{O}_5$. While the pre-intercalation of 0.5 Li is in agreement with the concentration of the BuLi (as Li precursor) used, it is noted that the $1.0\text{Li-V}_2\text{O}_5$ shows that less than 1.0 Li per V_2O_5 was pre-intercalated into the V_2O_5 structure. A possible explanation could be that the formation of LiV_2O_5 structure, as observed in the XRD above, led to some of the Li^+ ions being bonded to the V_2O_5 structure and thus, they could not be de-intercalated during the first charge cycle. This result is similar to that mentioned by Garcia *et al.* (1999)[36, 105], in which it was mentioned that the deinsertion of prelithiated Li^+ ions was incomplete for $\text{Li} > 0.9$ per V_2O_5 .

Figure 5.22 First galvanostatic charge of prelithiated V_2O_5 cathodes

The first galvanostatic charge for 2.0Li-V₂O₅ led to a specific capacity of ~100 mAh g⁻¹, corresponding to ~0.7 Li per V₂O₅. This result is in agreement with the case of 1.0Li-V₂O₅, in which some of the pre-intercalated Li was bonded in the V₂O₅ crystal structure. Also, it should be taken into account that the amorphization of the crystal structure as observed in the XRD of 2.0Li-V₂O₅ could lead to reduced chemical intercalation of Li, leading to overall, much lower charge capacity. In addition, it is possible that the formation of LiV₂O₅ and other intermediate phases may be irreversible, hence less Li⁺ ions could be reversibly deintercalated from the crystal structure. Finally for 3.0Li-V₂O₅, where the ω-LiV₂O₅ has most likely formed, the initial charge capacity is ~125 mAh g⁻¹, corresponding to slightly less than 0.9 Li per V₂O₅. This is in agreement with the previous explanations regarding the phase transformations of V₂O₅ upon the first discharge, where the formation of ω-LiV₂O₅ phase leads to larger irreversible capacity in the first two galvanostatic charge / discharge cycles.

Figure 5.23 (a) First galvanostatic discharge and (b) second charge cycle of prelithiated V₂O₅ cathodes, with comparison to first charge / discharge cycles of unlithiated V₂O₅

Subsequent galvanostatic charge / discharge cycles of the prelithiated V_2O_5 are presented in Figure 5.23. For $0.2Li-V_2O_5$ and $0.5Li-V_2O_5$, it can be observed that the discharge curves have similar plateaus and also capacities as in the first discharge curve of unlithiated V_2O_5 . The equivalent amounts of Li intercalated per V_2O_5 are ~ 2.4 , ~ 2.5 and ~ 2.2 for $0.2Li-V_2O_5$, $0.5Li-V_2O_5$ and unlithiated V_2O_5 (VUC 600-1) respectively. This indicates that the similar Li-intercalation is occurring during the first discharge cycles for both 0.2 and $0.5Li-V_2O_5$, eventually leading to the irreversible formation of ω - LiV_2O_5 phase, after discharging to < 2.0 V vs. Li/Li^+ . Also, this indicates that the pre-intercalation of 0.2 Li and 0.5 Li concentrations into V_2O_5 does not change the structure of V_2O_5 a lot, therefore, > 2 Li could still be intercalated into the structure.

In the discharge curves of 1.0, 2.0 and 3.0 $Li-V_2O_5$, no obvious plateaus can be observed. Also it is interesting to note that the $1.0Li-V_2O_5$ and $2.0Li-V_2O_5$ have much lower initial discharge capacities of ~ 210 mAh g^{-1} and ~ 88 mAh g^{-1} respectively, corresponding to intercalation of ~ 1.4 Li and ~ 0.6 Li. It can be inferred that the structural changes occur between $1.0 < x < 2.0$, where x represents the amount of Li in $Li_xV_2O_5$. Possible amorphization could occur during this structural change, leading to overall lower intercalation of Li, and discharge capacity. Finally at $3.0Li-V_2O_5$, in which the ω -Li V_2O_5 structure is expected to have formed, the discharge curve does not have obvious plateaus, similar to the second discharge curves observed in bare V_2O_5 cathode materials. At the same time, the highly-distorted V_2O_5 structure enables the accommodation of ~ 2.2 mol of Li per mol of active material, giving high discharge capacity of ~ 330 mAh g^{-1} , almost similar to bare V_2O_5 (320 mAh g^{-1}).

As observed in Figure 5.23b, there are no plateaus observed in all the charge cycles for the various concentrations of prelithiated V_2O_5 , and the galvanostatic charge traces take on the typical profile of subsequent charge cycles observed in V_2O_5 . The respective second charge capacities are ~ 334 mAh g^{-1} (~ 2.25 Li), ~ 348 mAh g^{-1} (~ 2.3 Li),

$\sim 190 \text{ mAh g}^{-1}$ ($\sim 1.3 \text{ Li}$), $\sim 80 \text{ mAh g}^{-1}$ ($\sim 0.6 \text{ Li}$) and $\sim 325 \text{ mAh g}^{-1}$ ($\sim 2.2 \text{ Li}$) for $0.2\text{Li-V}_2\text{O}_5$, $0.5\text{Li-V}_2\text{O}_5$, $1.0\text{Li-V}_2\text{O}_5$, $2.0\text{Li-V}_2\text{O}_5$ and $3.0\text{Li-V}_2\text{O}_5$, as compared to the first specific charge capacity of unlithiated V_2O_5 , $\sim 290 \text{ mAh g}^{-1}$, equivalent to $\sim 2 \text{ Li}$ per V_2O_5 .

Figure 5.24 Discharge capacity vs. cycle number for prelithiated V_2O_5 and V_2O_5 in voltage ranges of (a) 1.75- 4.0 V and (b) 3.0-4.0 V vs. Li/Li^+

All half-cells were cycled galvanostatically at 0.1 C (35 mAh g^{-1}) rate at room temperature. It can be observed in Figure 5.24a that $0.2\text{Li-V}_2\text{O}_5$, $0.5\text{Li-V}_2\text{O}_5$ and $3\text{Li-V}_2\text{O}_5$ have higher initial capacity than unlithiated V_2O_5 , but further cycling to 50 cycles refer give rise to similar capacity retention trends. The higher initial capacity could be attributed to the presence of Li^+ ions present in the lithiated V_2O_5 samples in the case of $0.2\text{Li-V}_2\text{O}_5$ and $0.5\text{Li-V}_2\text{O}_5$. It is also interesting to note that the first discharge and second discharge show large capacity drop for VUC 600-1, 0.2 and $0.5\text{Li-V}_2\text{O}_5$. The second discharge capacities for VUC 600-1 and $0.2\text{Li-V}_2\text{O}_5$ are ~ 245 , ~ 290 and $\sim 280 \text{ mAh g}^{-1}$ respectively, corresponding to $\sim 20 \%$ capacity decrease from the initial discharge capacity. The large irreversible discharge capacity difference can be correlated to the irreversible phase transformations occurring at the end of the first discharge, and because the second discharge does not cause the now-lithiated V_2O_5 cathode to undergo further irreversible phase changes, the capacity decreases. This is further confirmed by

comparing the second discharge values of the higher pre-lithiated V_2O_5 samples, in which the $Li-V_2O_5$ phases are expected to be already forming. For $3.0Li-V_2O_5$, there is ~15 % difference between the first and second discharge capacity values. For the 0.2 and 0.5 Li -prelithiated V_2O_5 , the improved cyclic stability are similar to that reported in literature[36, 105]. $1.0Li-V_2O_5$ and $2.0Li-V_2O_5$ do show larger differences between the first and second discharge capacities, with the discharge capacity values decreasing by 13 and 10 % respectively. This larger irreversible capacity loss may be attributed to the more disordered structure in the latter two samples.

Furthermore, the lithiated V_2O_5 samples were cycled from 3.0-4.0 V vs. Li/Li^+ . The smaller voltage range enables reversibility of Li intercalation / deintercalation, without further formation of irreversible phases. Therefore, it is logical to note that the capacity values are quite stable, remaining at ~100 % capacity retention for up to 50 cycles. It is very interesting to observe that the stable cathodic capacity of $0.2Li-V_2O_5$ is low at ~70 $mAh\ g^{-1}$, as compared to $0.5Li-V_2O_5$, $1.0Li-V_2O_5$ and $3.0Li-V_2O_5$. From this data, it is possible to conclude that the low concentration of Li pre-intercalation did not change the structure of V_2O_5 . Also, it can be understood that, for the higher initial capacity to be achieved, the V_2O_5 cathode must undergo adequate extent of phase transformations. These phase transformations may aid in slight spacing / distortion of V_2O_5 , similar to the case of $0.5Li-V_2O_5$ and $1.0Li-V_2O_5$, in order to accommodate more Li^+ ions, and in turn, corresponding higher initial capacity. It can also be noted that $0.5Li-V_2O_5$ has the highest stable capacity in the 3-4 V range cycling, which indicates that the formation of LiV_2O_5 structure creates stability within the crystal structure. $1.0Li-V_2O_5$ and $3.0Li-V_2O_5$ have almost same stable capacity at ~80 $mAh\ g^{-1}$, indicating that the reversible Li intercalation / deintercalation occurs up to ~0.55 Li in this voltage range. $2.0Li-V_2O_5$ then has the lowest capacity of ~50 $mAh\ g^{-1}$, which can be attributed to the poorer crystallinity of this compound.

Figure 5.25 EIS of prelithiated V_2O_5 and bare V_2O_5

The electrochemical impedance spectra of the fresh cells based on the prelithiated V_2O_5 cathodes were taken after equilibration and compared to that of V_2O_5 half-cell. In general it is known that the high-to-middle frequency semicircle is related to the conductivity and solid-electrolyte interface (SEI) formation between the active cathode surface and the electrolyte, the middle-to-low frequency region is related to the charge transfer mechanisms and the low frequency region which is usually a sloping line is related to the Li-diffusion kinetics of the cell.

In Figure 5.25 above, the various EIS of the cells are presented. Firstly, it is obvious that the un-lithiated V_2O_5 cathode has a very large high frequency semicircle, indicating high formation of SEI layer. The circumference of the high frequency semicircles increase in the following order of prelithiation concentration: 3.0, 0.2, 0.5, 1.0 and 2.0Li- V_2O_5 . The increasing Li content in the prelithiated V_2O_5 can lead to increase in overall conductivity of the cathode material from 0.2 to 2.0 Li, whereas for 3.0Li- V_2O_5 ,

the irreversible formation of the 3.0Li-V₂O₅ compound possibly leads to less SEI formation.

In general, the prelithiation study enables a deeper understanding of the mechanism regarding Li intercalation into V₂O₅, as well as subsequent deintercalation from the lithiated compounds, through the comparison of chemically lithiated V₂O₅ with electrochemical data. X-ray diffraction studies elucidate the phase changes occurring during various stages of Li intercalation and also the effects on the crystal structure. Cyclic voltammetry and galvanostatic studies are in good agreement with the XRD analyses. Furthermore, the reversibility of the Li intercalation into V₂O₅ at different stages are thoroughly explored. Intercalation of <0.5 Li into the V₂O₅ structure (forming ε-Li_{0.5}V₂O₅) is considered to be reversible, while further intercalation of 0.5 < x < 1.0, in Li_xV₂O₅, (forming δ-LiV₂O₅) marks the first step where Li intercalation into V₂O₅ becomes irreversible and this can be observed from the irreversible capacity loss of 1.0Li-V₂O₅ from the first to second cycles. Then further intercalation to achieve γ-Li₂V₂O₅ (~2.0 Li) and ω-Li₂V₂O₅ (~3.0 Li) leads to irreversible formation of the highly distorted crystal structure. The transition between the γ and ω Li_x-V₂O₅ phases may then result in amorphization, before finally forming ω-Li_xV₂O₅ (discharge to < 2.0 V vs. Li/Li⁺).

Interestingly, 3.0Li-V₂O₅, which has intercalated 2.5 Li per V₂O₅ via the chemical route, has similar charge / discharge behavior to bare VUC, which is V₂O₅ from the second charge / discharge cycle onwards. Notably, more than 2 Li per V₂O₅ has intercalated into the layered structure of V₂O₅ after the first discharge, as simulated using the chemical prelithiation. It is shown that 1 Li per V₂O₅ is retained in the structure, forming the highly distorted structure of LiV₂O₅, in which further Li intercalation / deintercalation takes place. However, during the subsequent galvanostatic cycle, the specific discharge and charge capacity values of ~320 mAh g⁻¹ and ~280 mAh g⁻¹ (both ~330 mAh g⁻¹ for 3.0Li-V₂O₅) show that ~2.2 Li can enter the highly distorted structure

of LiV_2O_5 , and subsequently deintercalate from this structure. The better cyclic charge efficiency ($\sim 100\%$) for $3.0\text{Li-V}_2\text{O}_5$, as compared to $\sim 88\%$ for electrochemically lithiated V_2O_5 , could be due to the better stability of LiV_2O_5 structure formed via the chemical lithiation route. This provides a possible explanation to the improved cyclic stability as observed above, and also previously mentioned in literature[36]. Furthermore, the electrochemical lithiation of V_2O_5 , and eventual distortion of the layered structure, takes place over a shorter time range (~ 10 hours at 0.1 C rate) than the chemical lithiation route (~ 1 week), contributing to the instability of the V_2O_5 structure during further electrochemical cycling. Finally, it must be taken into consideration that the layered structure in V_2O_5 and multiple oxidation states of vanadium, enables accommodation of a variety of ions[7, 39, 40, 111, 112, 119, 122, 123, 125, 224-228], such as Cu, Ag, Al and water molecules. The presence of small amounts of such impurities could drastically affect the electrochemical behavior of V_2O_5 cathode materials in general and this provides the reason why such electrodes only reach stable capacity values after the first few initial cycles.

5.2.2 Electrochemical Thermodynamic Measurement Studies (ETMS)

The ETMS technique is a novel method, developed by Reynier and Yazami *et al.* (2006, 2007)[179, 186, 187], to enable in-situ calculations of entropy and enthalpy values related to phase transformations occurring during the electrochemical intercalation / deintercalation of Li into and from active electrode materials in LIBs.

$$\Delta G(x) = -FE_o(x) = \Delta H(x) - T \Delta S(x) \quad (9)$$

According to the Gibbs free energy equation (Equation 9) as mentioned in Section 3.3.2.3, the OCV of the electrochemical cell recorded at various temperatures can be used to calculate these thermodynamical values, which in turn give clues related to the phase transformations occurring in-situ. So far, this technique has only been applied to study the effect of Li intercalation to graphitic anodes.

Currently, as V_2O_5 cathode materials are known to undergo multiple phase transformations during Li intercalation. However, mainly ex-situ techniques have been employed to elucidate the effects of ion-insertion, carbon-coatings, as well as nanomorphologies. Herein, this method is used, for the first time, to study the related phase transformations in V_2O_5 . It is believed that while the enthalpy values give an indication of the thermal stability of the cathode materials, the changes in the entropy values provide an indication of phase change during the electrochemical processes.

The typical first discharge curve of V_2O_5 powder is shown in Figure 5.26, showing the three main plateaus at ~ 3.2 , ~ 2.3 and ~ 1.9 V vs. Li/Li^+ in which phase transformations are usually correlated. The original structure of α - V_2O_5 (Figure 5.26 inset a) has layered consisting of VO_5 square pyramids. The first plateau at ~ 3.2 V vs. Li/Li^+ can be correlated to the phase transformation into ϵ - LiV_2O_5 , according to Equation 4 below. To accommodate this structure change, V^{5+} is reduced to V^{4+} .

Figure 5.26 Typical first galvanostatic discharge curve of V_2O_5 powder cathode with corresponding V_2O_5 crystal structures (a) before and (b) after Li intercalation

Further discharging to ~ 2.3 V leads to intercalation of up to 1.5 Li per V_2O_5 , this causes the V^{4+} to be further reduced to V^{3+} and the formation of $\delta\text{-LiV}_2\text{O}_5$ and $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ as a mixture of phases. This phase transformation can also be observed via the chemical prelithiation of V_2O_5 urea combustion powders in Section 5.2.1. As more and more Li^+ ions intercalate into the V_2O_5 structure, the layers become increasingly distorted, as shown in Figure 5.26 inset b. Discharging to < 2.0 V leads to the irreversible formation of this distorted structure in which subsequent Li intercalation and deintercalation occurs during further charge / discharge cycles. During ETMS, it is expected to observed large

changes in entropy and enthalpy values during the abovementioned phase changes and at the corresponding voltages.

Figure 5.27 (a) First discharge cycles of VUC 600-1 and VNF with corresponding (b) entropy and (c) enthalpy traces

In-situ thermodynamic measurements of VUC-600-1 and VNF were carried out at different charge states to further elucidate the phase transformation processes. In the first galvanostatic discharge trace of the urea-combustion synthesized V₂O₅ VUC 600-1, the intercalation plateaus are noted at 3.20, 2.30 and 2.0 V vs. Li/Li⁺. The corresponding trends of the entropy and enthalpy values also show plateaus spanning the states of charge

where the cell is discharged to these voltages. In VUC 600-1, the entropy and enthalpy values show a sharp decrease at the corresponding discharge capacity of 80 – 110 mAh g⁻¹ (equivalent to 0.55-0.75 Li per V₂O₅), before increasing again at the next corresponding discharge plateau (Figure 5.27a) at ~2.30 V. These decreases in the thermodynamic values indicate phase transformations occurring, possibly from V₂O₅ to the formation of ε-Li_xV₂O₅.

In the case of the vanadium pentoxide electrospun nanofibers (VNF), the entropy and enthalpy values also show a sharp drop corresponding to discharge capacity of 20-30 mAh g⁻¹ (equivalent to 0.15-0.20 Li). Interestingly, the enthalpy values for the VNF are noted to be higher than that of VUC 600-1 in the initial measurement. It can also be noted that the porous nature of the VNF could lead to faster initial phase transformation. The first discharge plateau of ~3.20 V for VNF is much shorter as compared to that of VUC, it is up to 20 mAh g⁻¹ as compared to ~80 mAh g⁻¹ for VUC. The porous nature of the VNF could possibly increase the rate of Li diffusion and the intercalation of a smaller amount of Li can already induce a phase transformation in VNF than VUC 600-1.

Furthermore, the effects of Al-insertion and carbon-coating on VNF were also studied with the in-situ thermodynamic measurements (Figure 5.28). In general, it can be noted that the entropy change associated with the Al-inserted and carbon-coated VNF is to a lesser extent as compared to bare VNF. Especially in Al-inserted VNF, it is observed that the entropy values do not change much from the corresponding discharge plateaus from 3.20 to 2.30 V vs. Li/Li⁺ respectively. In that of carbon-coated VNF, the entropy values show a sharp decrease at the corresponding discharge plateau at ~2.30 V, it is possible that the phase change is delayed, as compared to VNF, where the decrease in the entropy values is observed between the discharge plateaus at 3.20 V and 2.30 V. Interestingly, the enthalpy values show an overall increasing trend in VNF. This could

mean that the phase transformations related to Li intercalation could increase the overall enthalpy of the cell.

Figure 5.28 (a) First discharge cycles of VNF, Al-inserted VNF and C-VNF with corresponding (b) entropy and (c) enthalpy traces

5.2.3 Lithium diffusion studies

The Randles-Sevcik equation is used to calculate the chemical diffusion coefficients of the materials, which can be evaluated by the CV measurements. The gradient of the peak current vs. the square root of the scan rate can be used to calculate the lithium diffusion coefficient in the case of lithium ion batteries, assuming that Li intercalation occurs mainly by diffusion kinetics during electrochemical charge / discharge. Herein, for consistency, the peak current of the main oxidation peak in the CVs are taken and plotted against the square root of the scan rate for different materials.

In general it can be observed in the CVs that, with increasing scan rate, the height and area of the peaks increase. Also, the cathodic (reduction) peaks shift to lower potentials and anodic (oxidation) peaks shift to higher potentials with increasing scan rate, similar to electrochemical behaviour observed in literature[46, 112]. The larger scan rate results in a higher peak current as the capacity of an electrode should be a constant, given by the peak area divided by the scan rate. The shift of the oxidation and reduction peaks indicates the manifestation of irreversible electrochemical behaviours, which become increasingly obvious with higher scan rates. Especially at scan rates $>0.5 \text{ mV s}^{-1}$, the time interval for Li intercalation / deintercalation is drastically reduced, and also contributes to the combination of peaks. Moreover, at higher scan rates or higher current rates, the pseudocapacitive lithium transport takes precedence over the lithium storage electrochemical processes[229]. This is an indication that the Li intercalation / deintercalation process is intrinsically slow and the variation in scan rate results in different charge-transfer kinetics occurring during charging / discharging.

Figure 5.29 Cyclic voltammograms of (a) VUC 600-1 (V₂O₅ urea combustion synthesized) and (b) V₂O₅ nanofibers (VNF) at various scan rates and (c) peak current vs. $v^{1/2}$

From the CVs of VUC 600-1 and VNF as presented in Figures 5.29a and b, it can be observed that in general, the CVs of VUC 600-1 has larger current density than those of VNF. This means that the overall specific capacity of VUC 600-1 is slightly higher than that of VNF, which is in agreement with the data from galvanostatic cycling. There is one main pair of redox peaks in each CV at lower scan rates 0.1 and 0.2 mV s⁻¹ and two pairs of redox peaks at higher scan rates 0.5, 1 and 2 mV s⁻¹. The appearance of the second pair of peaks at higher scan rate could possibly be related to small side reactions occurring, contributing to irreversible capacity fade during low C rates. At higher scan rates, this phenomena caused by irreversible electrochemical reactions become more pronounced. In addition, the peaks in the CVs of VUC 600-1 can be observed to shift consistently to higher potentials for oxidation peaks and lower potentials for reduction

peaks, indicating that the VUC 600-1 nanoparticle structure is more stable with Li intercalation / deintercalation even at higher C rates. In the case of VNF, it can be observed that the redox peaks exhibit irregularities at scan rates of 1 and 2 mV s⁻¹, which can be an indication that the nanofibrous morphology is breaking down at the high electrochemical cycling rate. Also, more irreversible reactions could be occurring in VNF during high rate cycling. In general, the VNF morphology is less stable at high C rates as compared to VUC 600-1.

From the peak currents, the specific lithium diffusion coefficients as calculated for VNF and VUC are $2.33 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ and $8.08 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ respectively. These values indicate that Li diffusion occurs more readily in the urea combustion synthesized V₂O₅ powder as compared to the VNF. Although the VUC 600-1 are of larger particle sizes, the urea combustion synthesis method may give rise to higher overall electroactive surface area. Also, the porous structure of the electrospun VNF may lead to the larger formation of SEI, which may inhibit the Li diffusion kinetics occurring in the VNF upon subsequent cycling.

Figure 5.30 Cyclic voltammograms of (a) VUC 300-2 (V₂O₅ urea combustion synthesized), (b) VUC 600-1 and (d) VUC 600-1 bmC (ball-milled with carbon) at various scan rates and (c) peak current vs. $v^{1/2}$

From Figure 5.30 it can be noted that the VUC 300-2 (Figure 5.30a) and VUC 600-1 bmC (Figure 5.30d) powders have one main pair of redox peaks. In the case of VUC 300-2, the V₂O₅ phase is not fully formed due to the lower sintering temperature, and this leads to overall lower current density. As for the VUC 600-1 bmC, the absence of the extra pair of redox peaks observed at higher potential indicated that the side reactions occurring in VUC 600-1 could have been reduced by the carbon-coating via the ball-milling process. It is possible that the charge-transfer kinetics of V₂O₅ were enhanced by the carbon coating[230], contributing to the better cyclic stability.

The specific lithium diffusion coefficients as calculated for VUC 300-2 and VUC 600-1 are $1.72 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ and $8.08 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ respectively. The much lower lithium diffusion coefficient could be attributed to the low temperature (300 °C) used to prepare VUC 300-2, as compared to 600 °C for VUC 600-1. The low sintering temperature led to formation of smaller average crystal size (~60 nm), as well as incomplete oxidation of vanadium to the V^{5+} state. In turn, less phase transformations occur during the electrochemical discharge process for VUC 300-2, leading to decreased lithium intercalation and overall lower initial capacity than VUC 600-1.

In comparing the VUC 600-1 and the same powder ball-milled with carbon (VUC 600-1 bmC), it can be noted that the latter sample has a lower lithium diffusion coefficient at $1.38 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$. This could be attributed to the agglomeration of particles during the ball-milling process, reducing available surface area for electrochemical activities. The lower lithium diffusion coefficient also contributed to the lower initial capacity ($\sim 250 \text{ mAh g}^{-1}$) as compared to VUC 600-1 ($\sim 320 \text{ mAh g}^{-1}$).

Figure 5.31 Cyclic voltammograms of (a) VNF, (b) Al_{0.5}VNF and (c) Al_{1.0}VNF at various scan rates and (d) peak current vs. $v^{1/2}$

The CVs of Al_{0.5}VNF show the presence of two pairs of redox peaks while those of Al_{1.0}VNF show one pair of redox peaks. The higher amount of Al³⁺ ions inserted prevented the irreversible side reactions, leading to overall better electrochemical performance at higher C rates.

Al-inserted VNFs Al_{0.5}VNF and Al_{1.0}VNF (Figure 5.31) have Li diffusion coefficients of $1.05 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ and $2.9 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ respectively. Compared to VNF, which has lithium diffusion coefficient of $2.33 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$, Al_{0.5}VNF has lower diffusion coefficient. The presence of Al³⁺ ions maintains the layered structure of V₂O₅, lending some rigidity to the structure, and also reduces the initial oxidation state of V⁵⁺, both effects reduce the number of Li ions that can enter the V₂O₅ structure. On the other hand, further insertion of Al³⁺ ions pushes the V₂O₅ layers further apart, leading to

increase in the interlayer spacing, thus increasing the amount of lithium diffusion in $\text{Al}_{1.0}\text{VNF}$, as observed from the higher Li diffusion coefficient.

Figure 5.32 Cyclic voltammograms of (a) VNF, (b) C-VNF-15 and (c) C-VNF-30 at various scan rates and (d) peak current vs. $v^{1/2}$

As observed in Figure 5.32b, the CVs of C-VNF-15 at higher scan rates show consistent increase in peak current and shifts in redox potentials, indicating that the carbon-coating on VNF increases the stability of VNF structure at higher current rates. Also the combination redox peaks in CVs of C-VNF-30 could indicate that less side reactions are occurring with increasing carbon-coating and contributes to overall structural stability of VNF.

Carbon-coated VNFs C-VNF-15 and C-VNF-30 have Li diffusion coefficients of $5.81 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ and $4.50 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$. The higher Li diffusion coefficients could be due to the improved electronic and ionic conductivity of the VNF via the carbon-

coating, in turn enabling faster transport of Li^+ ions through the fibrous network. This effect is observed in the improved cycling stability of the carbon-coated VNF.

Figure 5.33 Cyclic voltammograms of (a) bare VUC, (b) $\text{Al}_{0.66}\text{VUC}$ and (c) $\text{Al}_{1.1}\text{VUC}$ at various scan rates and (d) peak current vs. $\nu^{1/2}$

The CVs of Al-inserted VUC show consistent redox shifts with increasing scan rates. Also, the overall current densities of the CVs are smaller than that of the bare VUC, indicating lower capacities, but improved cyclic stabilities.

$\text{Al}_{0.66}\text{VUC}$ and $\text{Al}_{1.1}\text{VUC}$ have Li diffusion coefficients of $1.19 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$ and $0.53 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$, compared to the bare VUC, which had Li diffusion coefficient of $10.8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ g}^{-1}$. The insertion of Al into the V_2O_5 structure could lead to possible blockage of the Li intercalation sites, as the Al^{3+} ions possibly reside in the interlayer space between the V_2O_5 layers. In addition, increasing the amount of Al^{3+} ion insertion to VUC leads to further decrease in the Li diffusion coefficient, in agreement with EIS.

The differences in the possible positions of Al-inserted VNF and VUC affect the amount of Li entering the layered V_2O_5 structure. In summary, in VNF the Al-ions reside within the interlayers, lending support and rigidity to the layered crystal structure. Initial insertion of small amount of Al-ions limits the amount of Li intercalation, decreasing the Li diffusion coefficient, while insertion of larger amount of Al-ions could push the V_2O_5 layers apart, increasing the specific capacity via intercalation of larger amount of Li ions. However, in VUC, the inserted Al-ions possibly reside in the positions suitable for Li-intercalation, and the occupation of the aforementioned positions prevents the entry of Li-ions, thus reducing the lithium diffusion coefficient. Considering the synthesis routes of Al-inserted VNF and VUC, it could be possible that the in-situ synthesis method (as in VNF) involving the Al and vanadium precursors[197], as opposed to the reaction of as-formed V_2O_5 with Al precursor[112, 119], could lead to the formation of the MO_6 octahedra[117] within the interlayers which gives support to the layered structure.

6. Conclusion

This thesis provides an in-depth study on the effect of nanoarchitectures on the electrochemical behaviours of olivine phosphates and V_2O_5 cathodes. Synthesis methodologies such as electrospinning, urea combustion and ionothermal syntheses were explored to fabricate different nanostructures and their respective effects were studied through various structural / electrochemical characterization techniques. The electrospinning method was used to synthesize high capacity V_2O_5 nanofibers and high voltage olivine phosphate nanostructures. Co-synthesized olivine phosphate $LiFePO_4$ -carbon fiber nanostructures enabled achievement of stable capacity at $\sim 160 \text{ mAh g}^{-1}$, ($>20\%$ better than pristine $LiFePO_4$) near to theoretical capacity. In contrast, $LiFePO_4$ -carbon fiber nanostructures with $LiFePO_4$ nanoparticles grown onto the porous carbon fibrous structure proved to be better than the embedment of active nanoparticles fully in the carbon fiber matrix. The carbon fibrous structure provided a conductive network for the $LiFePO_4$ nanoparticles, improving overall specific capacity. Core-shell nanofibrous structure of $LiMnPO_4$ -carbon composites showed $>100\%$ increase in capacity, as compared to pristine $LiMnPO_4$ nanoparticles, owing to the improved conductivity.

On the other hand, porous, interconnected pristine V_2O_5 nanofibers (VNF) enabled intercalation of ~ 2.2 Li per V_2O_5 , which is vital to achieving high capacity values. Physical and chemical properties of VNF were also thoroughly studied via various techniques such as FE-SEM, FTIR, X-ray and electron diffraction methods. Further, insertion of aluminium ions into the V_2O_5 structure was carried out to improve the cyclic retention properties of VNF, by at least 50%, and also high temperature and high rate cycling performance. The amount of Al-insertion and possible atomic positions of inserted Al^{3+} ions were derived from XRD, EDS and XPS techniques. More importantly, with this study, the phase transformations and Li intercalation mechanisms occurring in

V₂O₅ were further elucidated. Carbon-coating was done on VNF using a non-destructive plasma enhanced chemical vapour deposition (PECVD) and the protective properties of such physical coatings were proven by high temperature and high rate electrochemical cycling. Ex-situ structural studies on the various VNF electrodes were carried out via FE-SEM. Interestingly, the bare VNF electrodes were rendered amorphous after electrochemical cycling, without retention of the original fibrous morphology, but the Al-inserted and carbon-coated VNF electrodes showed the presence of nanofibers in the cycled electrodes. Electrochemical impedance spectra (EIS) and lithium diffusion studies further corroborated the beneficial effects of chemical / physical modifications on VNF.

Ionothermal synthesis method was employed, for the first time, to synthesize olivine phosphate (> 4.5 V vs. Li/Li⁺) high voltage cathode materials, namely LiCoPO₄ and LiNiPO₄. With this method, single-phase LiMnPO₄ and LiCoPO₄ were achieved and the electrochemical properties were studied in comparison to sol-gel and hydrothermally synthesized counterparts. In LiCoPO₄, the effects of Co dissolution occurring at high voltages >5 V vs. Li/Li⁺ were studied by varying the voltage range, showing reduced fading of the oxidation peaks at smaller voltage ranges. In addition, high voltage instability in organic electrolytes was overcome by optimized addition of LiBOB additive. Finally high-purity LiNiPO₄ was synthesized with a systematic combination of ionothermal and heat-treatment methods and preliminary studies were conducted, showing promising results for future applications.

Self-propagating urea combustion method was used to synthesize V₂O₅ sub-micron particles (VUC). Herein, the effects of heat treatment temperatures and durations were thoroughly studied, with comparison of lattice parameters and crystal sizes. Also, the respective electrochemical performances and mechanisms were further compared and elucidated via CV, galvanostatic and EIS methods. Large crystallite sizes (~300 nm) achieved by heat-treatment at high temperature at 600 °C proved to give the best capacity

values ($\sim 320 \text{ mAh g}^{-1}$) and good cyclic retention properties of $\sim 80\%$ capacity retention after 50 cycles. Furthermore, the effects of carbon-coating were studied via ball-milling and brought about further improvements in electrochemical cycling properties. Al-insertion was carried out in V_2O_5 sub-micron particles and most interestingly, the positions of the Al^{3+} ions in the V_2O_5 structures for VNF and the VUC were within and between the V_2O_5 interlayers respectively, possibly for reasons related to the synthesis methodologies and morphological differences. Overall, insertion of Al-ions into the layered V_2O_5 structure also helped to improve high temperature and high C-rate properties. More significantly, the insertion of Al^{3+} ions into VNF and VUC confirmed the positions in which Li-ions occupy during intercalation within the V_2O_5 structure. This study concludes that insertion of ions between interlayers could provide support to the layered structure, and also increase the Li intercalation sites / space within the crystal structure improving the electrochemical performance of similar layered structures. However, the occupation of inserted ions between the layers would hinder the Li-intercalation process, leading to lower specific capacity. Similarly, EIS and Li diffusion studies were carried out to further compare the Li intercalation mechanisms between morphologies and effects of chemical / physical modifications.

The addition of carbon to framework structured olivine phosphate nanomaterials was achieved via co-electrospinning with carbon precursors, including core-shell nanostructures, in 1D nanoarchitectures, and also with in-situ carbon for 0D morphology, with synthesis methods such as sol-gel, solid-state and ionothermal methods. From the 1D nanostructure olivine phosphate materials, it can be concluded that the even distribution of active nanomaterials is vital to the electrochemical performance, whereas in 0D nanostructures, the presence of in-situ carbon enhances the connectivity of the active olivine phosphate materials. The high-voltage olivine phosphate cathode materials LiCoPO_4 and LiNiPO_4 were studied in 0D morphology and dissolution of active materials

at voltage >4.5 V vs. Li/Li^+ is important for the electrochemical stability of such materials.

In V_2O_5 , with its layered structure, high initial capacity was achieved in 1D nanoarchitected VNF via electrospinning. However, the relatively large surface-area-to-volume ratio possibly led to reaction of the active material with the electrolyte, other than Li intercalation, causing irreversible capacity fade. The chemical modification of the abovementioned fibers, via insertion of Al^{3+} ions and the physical modification with carbon coating were employed to successfully improve the electrochemical stability of the VNF. On the other hand, 0D V_2O_5 powder obtained using urea combustion showed excellent electrochemical performance, as opposed to bulk V_2O_5 . The larger particle size of VUC powder, as well as smaller surface area, led to very good cyclic stability. The effects of Al^{3+} insertion to VNF and VUC are different, due to the variation in the possible positions of Al^{3+} within the V_2O_5 structure. In VNF, cyclic stability was improved via reduced electrochemical phase transformations and support of the layered structure, whereas in VUC, the insertion of Al^{3+} ions led to distortion of the crystal structure, and also occupied the positions for Li intercalation. As for the addition of carbon to VUC, this merely had a capacitive effect, as opposed to the protective properties observed in VNF.

Furthermore, chemical lithiation by using BuLi as the lithium precursor was carried out on VUC in various concentrations, and could be directly correlated to the states of charge in the electrochemical discharge of V_2O_5 . Detailed studies involving XRD, CV, galvanostatic studies, EIS and Li diffusion techniques enabled analyses of the phase and structural changes occurring to V_2O_5 upon Li intercalation. These studies confirmed the phase transformations occurring to enable intercalation of > 2 Li into V_2O_5 , advancing the development of V_2O_5 towards practical applications in full-cell LIBs. A new method, known as the electrochemical thermodynamics measurement studies

(ETMS), enabled in-situ measurement of entropy and enthalpy values and was used to study the correlation of phase changes to the thermodynamics of the electrodes. Finally, the application of V_2O_5 /LTO full cell further proved the practical applicability of V_2O_5 as a LIB cathode material.

In this thesis, the study of Li intercalation into framework structured high voltage olivine phosphate and layered V_2O_5 high capacity cathode materials were studied. It can be noted that the framework structure of olivine phosphate provides a somewhat rigid, yet stable crystal structure, in which the intercalation of Li ions occur via 1D tunnels present within the structure. On the other hand, the layered V_2O_5 structure accommodates larger number of Li ions by distortion of the crystal structure, in which the variable oxidation states of transition metal vanadium plays an important role. In the 1D nanoarchitectures, it can be noted that the active material needs to be evenly distributed, with close connection to the carbon layer for effective electronic and ionic conduction, whereas for V_2O_5 (VNF) the electroactive surface area is increased in the network of 1D nanostructures. In the case of 0D nanostructure, the presence of in-situ carbon for olivine phosphates help to increase the interconnectivity between electroactive particles and the high surface area of urea-combustion synthesized V_2O_5 , as opposed to bulk, improves electrochemical stability without compromising capacity. The framework structure of olivine phosphate materials is difficult to modify chemically, as compared to the layered V_2O_5 , and carbon coating was carried out to improve the electrochemical properties. Chemical and physical modifications could be performed to improve the stability of the crystal structure of layered V_2O_5 . The differences in the effects of such modifications, especially on the electrochemical Li intercalation / deintercalation processes, could be attributed to the different crystal structures of olivine phosphates and V_2O_5 cathode materials.

6.1 Novel contributions from this thesis

Based on the studies carried out in this thesis, several scientific and technological contributions have been made and are summarized in the sections below.

6.1.1 Scientific contributions:

- Synthesis of cathode materials based on phase-pure vanadium pentoxide (V_2O_5) nanofibers and olivine phosphates $LiMPO_4$ ($M=Fe, Mn, Co, Ni$) nanofibrous composites by electrospinning, that demonstrates improved electrochemical performance.
- Optimization of urea combustion synthesis of V_2O_5 sub-micron powders with improved electrochemical cycling properties.
- Established new route based on ionothermal synthesis to fabricate single-phase high-voltage cathode materials $LiCoPO_4$ and $LiNiPO_4$.
- Demonstrated carbon coating method via core-shell technique on olivine nanofibers by electrospinning method.
- Effect of 1D nanofibers and nanoparticles on lithium intercalation behavior.
- Fundamental studies on Al-insertion and direct correlation via chemical prelithiation on V_2O_5 elucidate phase transformations during Li intercalation / deintercalation.
- Novel studies on correlation of electrochemical thermodynamics measurement studies (ETMS) correlated to phase transformations in occurring in V_2O_5 crystal structure.

6.1.2 Technological significance

- Non-destructive, protective carbon coating via PECVD method to improve cyclic stability of V_2O_5 nanofibers (VNF).
- Systematic studies on addition of LiBOB additives for high-voltage electrolyte applications.
- Lithium ion battery full-cell studies of V_2O_5 as cathode material vs. lithium titanate spinel (LTO) anode.

7. Future work

Based on the investigations performed in this thesis, some preliminary investigations have been carried out and the following possibilities for future work are recommended to further develop and understand the mechanisms and performances of future LIBs

7.1 Fundamental studies on LiFePO_4 and LiMnPO_4

In this thesis, core-shell carbon coating methods were applied via the electrospinning method to improve the conductivity of poorly conducting olivine phosphates LiFePO_4 and LiMnPO_4 . The electrochemical properties were improved, in terms of specific capacity. However, the inherent Jahn-Teller distortion in LiMnPO_4 drastically affects the electrochemical performance.

To enable further understanding of the structure and conducting mechanisms of LiFePO_4 and LiMnPO_4 , it is suggested to conduct systematic doping studies, ideally with the electrospinning method. For example, doping Fe to the Mn-site[89, 189] to LiMnPO_4 can reduce the impact of the Jahn-Teller distortion. A systematic doping study with varying Fe and Mn concentrations, combined with in-situ studies such as neutron / synchrotron studies would enable better understanding of the Li-intercalation mechanisms in LiMnPO_4 and hopefully, provide a solution to the Jahn-Teller distortion.

7.2 Investigations on LiCoPO_4 and LiNiPO_4

LiCoPO_4 and LiNiPO_4 are emerging potential cathode materials due to their high working voltages >4.5 V. In addition, they have better electronic conductivity than their predecessors LiFePO_4 and LiMnPO_4 . Currently, little research has been conducted on the electrochemical studies of LiCoPO_4 and LiNiPO_4 , due to difficulties in synthesis of these materials. So far, only the solid-state method has been used to synthesize these high voltage cathode materials. Novel synthesis methods could be employed to synthesize LiCoPO_4 and LiNiPO_4 to obtain different nanostructures and investigate their effects on the electrochemical behaviours.

7.2.1 High voltage studies

Another main obstacle to the study of LiCoPO_4 and LiNiPO_4 would be the high working voltage. LiCoPO_4 and LiNiPO_4 have working voltages ~ 5 V vs. Li/Li^+ , and this brings about issues regarding (1) dissolution of active materials into the electrolyte and (2) decomposition of conventional organic electrolytes >4.5 V.

Firstly, the dissolution of active materials into the electrolyte at high voltages would mean that the cyclic stability would be affected adversely. Such dissolution reduces the amount of active materials with each consequent charge / discharge cycle, and causes irreversible capacity fade. Protective fluoride[231] and oxide coatings[232, 233] may help to reduce the dissolution, by reacting with the electrolyte in place of the active materials, thereby improving the cyclic stability.

Secondly, new electrolytes which can be stable at voltages above 5 V without decomposition, even after prolonged electrochemical cycling, can be developed. Possible candidates include ionic liquids[98], which are predicted to be 6 V electrolytes. The

prerequisites of such electrolyte include excellent conductivity of Li^+ ions, and also compatibility with the electrode materials.

7.3 In-situ studies of LIBs

In this thesis, the in-situ thermodynamic studies of V_2O_5 -based half-cells were carried out based on electrochemical thermodynamics measurement studies (ETMS). While ex-situ chemical prelithiation into V_2O_5 enabled direct correlation of the various phases of $\text{Li}_x\text{V}_2\text{O}_5$ formed during the electrochemical discharge, preliminary ETMS studies also showed variation in the entropy and enthalpy values obtained at the respective states-of-charge (SOCs), elucidating the possible phase transformations occurring in V_2O_5 due to Li intercalation. The existence and species of intermediate phases can be detected by the subtle differences between the entropy and enthalpy values, bringing about further insights to the Li intercalation mechanisms of various active cathode / anode materials, as well as the intricate reactions occurring among the electrochemical species during the charge / discharge processes. Further studies and experiments are required to enable a complete understanding of these charge storage mechanisms and the associated redox reactions. Besides phase changes, the in-situ study of the thermodynamics can act as an evaluation tool regarding the thermal stability of the cathode material. This technique can be combined with other in-situ technologies such as in-situ X-ray / synchrotron techniques[234-240], nuclear magnetic resonance (NMR)[241] and another novel technique known as the scanning electrochemical potential microscopy (SECPM)[242-244], which enables in-situ mapping of the electrode surface during electrochemical processes.

These studies can also be extended to olivine phosphate materials and it is hoped to enable further insight into the phase transformations and Li intercalation mechanisms.

The effect of minute impurities, such as dopants, inserted ions and coatings, on subsequent electrochemical performances can also be studied. As research moves further onto the field of nanotechnology, the presence of such impurities must not be overlooked, as they can have drastic effects on the electrochemical / redox mechanisms and subsequently affect the cycle life. On a larger scale, such studies enable comparison between particle sizes, as well as other physical and chemical effects.

7.4 Full cell studies on V_2O_5

The first application of a V_2O_5 / LTO full cell was demonstrated in this thesis. Following the promising results, it is suggested to continue further research on the full cell by varying anode material (such as titanium dioxide, graphite) to obtain an optimized voltage range, and stable electrochemical performance. Further studies on the thermal stability and lifetime of the full cells should also be conducted. As mentioned before, the thermal stability of LIBs is vital in the progress to large scale applications. ETMS and other thermodynamics studies (eg. differential calorimetric studies, DSC) can be conducted to access the thermal safety of the LIBs. Also, prolonged cycling of the full cells should be conducted and research is to be continued to ensure that the full cell can sustain at least 1000-2000 cycles, to be considered for large-scale applications.

8. References

1. Cheng, F.Y., J. Liang, Z.L. Tao, and J. Chen, *Functional materials for rechargeable batteries*. Advanced Materials, 2011. **23**(15): p. 1695-1715.
2. Etacheri, V., R. Marom, R. Elazari, G. Salitra, and D. Aurbach, *Challenges in the development of advanced Li-ion batteries: A review*. Energy & Environmental Science, 2011. **4**(9): p. 3243-3262.
3. Bazito, F.F.C. and R.M. Torresi, *Cathodes for lithium ion batteries: The benefits of using nanostructured materials*. Journal of the Brazilian Chemical Society, 2006. **17**(4): p. 627-642.
4. Cai, C. and Y. Wang, *Novel nanocomposite materials for advanced Li-ion rechargeable batteries*. Materials, 2009. **2**: p. 1205-1238.
5. Guo, Y.-G., J.-S. Hu, and L.-J. Wan, *Nanostructured materials for electrochemical energy conversion and storage devices*. Advanced Materials, 2008. **20**: p. 2878-2887.
6. Wang, Y. and G. Cao, *Developments in nanostructured cathode materials for high-performance lithium-ion batteries*. Advanced Materials, 2008. **20**: p. 2251-2269.
7. Ban, C.M., N.A. Chernova, and M.S. Whittingham, *Electrospun nano-vanadium pentoxide cathode*. Electrochemistry Communications, 2009. **11**(3): p. 522-525.
8. Pitchai, R., V. Thavasi, S.G. Mhaisalkar, and S. Ramakrishna, *Nanostructured cathode materials: a key for better performance in Li-ion batteries*. Journal of Materials Chemistry, 2011. **21**(30): p. 11040-11051.
9. Landi, B.J., M.J. Ganter, C.D. Cress, R.A. DiLeo, and R.P. Raffaele, *Carbon nanotubes for lithium ion batteries*. Energy & Environmental Science, 2009. **2**(6): p. 638-654.

10. Zhou, F., M. Cococcioni, K. Kang, and G. Ceder, *The Li intercalation potential of LiMPO_4 and LiMSiO_4 olivines with $M = \text{Fe, Mn, Co, Ni}$* . Electrochemistry Communications, 2004. **6**: p. 1144-1148.
11. Yazami, R. and P. Touzain, *A reversible graphite lithium negative electrode for electrochemical generators*. Journal of Power Sources, 1983. **9**(3-4): p. 365-371.
12. Thackeray, M.M., W.I.F. David, P.G. Bruce, and J.B. Goodenough, *Lithium insertion into manganese spinels*. Materials Research Bulletin, 1983. **18**(4): p. 461-472.
13. Wakihara, M., *Recent developments in lithium ion batteries*. Materials Science & Engineering R-Reports, 2001. **33**(4): p. 109-134.
14. Ellis, B.L., K.T. Lee, and L.F. Nazar, *Positive electrode materials for Li-ion and Li-batteries*. Chemistry of Materials, 2010. **22**: p. 691-714.
15. Scrosati, B. and J. Garche, *Lithium batteries: Status, prospects and future*. Journal of Power Sources, 2010. **195**(9): p. 2419-2430.
16. He, Y.B., F. Ning, Q.H. Yang, Q.S. Song, B.H. Li, F.Y. Su, H.D. Du, Z.Y. Tang, and F.Y. Kang, *Structural and thermal stabilities of layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ materials in 18650 high power batteries*. Journal of Power Sources, 2011. **196**(23): p. 10322-10327.
17. Chen, J.-M., C.-H. Hsu, Y.-R. Lin, M.-H. Hsiao, and G.T.-K. Fey, *High-power LiFePO_4 cathode materials with a continuous nano carbon network for lithium-ion batteries*. Journal of Power Sources, 2008. **184**: p. 498-502.
18. Choi, D. and P.N. Kumta, *Surfactant based sol-gel approach to nanostructured LiFePO_4 for high rate Li-ion batteries*. Journal of Power Sources, 2007. **163**(1064-1069).

19. Croce, F., A.D. Epifanio, J. Hassoun, A. Deptula, T. Olczac, and B. Scrosati, *A novel concept for the synthesis of an improved LiFePO_4 lithium battery cathode*. *Electrochemical and Solid-State Letters*, 2002. **5**(3): p. A47-A50.
20. Hosono, E., Y. Wang, N. Kida, M. Enomoto, N. Kojima, M. Okubo, H. Matsuda, Y. Saito, T. Kudo, I. Honma, and H. Zhou, *Synthesis of triaxial LiFePO_4 nanowire with a VGCF core column and a carbon shell through the electrospinning method*. *ACS Applied Materials & Interfaces*, 2010. **2**(1): p. 212-218.
21. Gong, Z. and Y. Yang, *Recent advances in the research of polyanion-type cathode materials for Li-ion batteries*. *Energy & Environmental Science*, 2011. **4**: p. 3223-3242.
22. Bakenov, Z. and I. Taniguchi, *Physical and electrochemical properties of LiMnPO_4/C composite cathode prepared with different conductive carbons*. *Journal of Power Sources*, 2010. **195**(21): p. 7445-7451.
23. Barpanda, P., K. Djellab, N. Recham, M. Armand, and J.M. Tarascon, *Direct and modified ionothermal synthesis of LiMnPO_4 with tunable morphology for rechargeable Li-ion batteries*. *Journal of Materials Chemistry*, 2011. **21**(27): p. 10143-10152.
24. Martha, S.K., B. Markovsky, J. Grinblat, Y. Gofer, O. Haik, E. Zinigrad, D. Aurbach, T. Drezen, D. Wang, G. Deghenghi, and I. Exnar, *LiMnPO_4 as an advanced cathode material for rechargeable lithium batteries*. *Journal of The Electrochemical Society*, 2009. **156**(7): p. A541-A552.
25. Ni, J.F., Y. Kawabe, M. Morishita, M. Watada, and T. Sakai, *Improved electrochemical activity of LiMnPO_4 by high-energy ball-milling*. *Journal of Power Sources*, 2011. **196**(19): p. 8104-8109.

26. Wang, D.Y., H. Buqa, M. Crouzet, G. Deghenghi, T. Drezen, I. Exnar, N.H. Kwon, J.H. Miners, L. Poletto, and M. Graetzel, *High-performance, nano-structured LiMnPO₄ synthesized via a polyol method*. Journal of Power Sources, 2009. **189**(1): p. 624-628.
27. Bramnik, N.N., K. Nikolowski, C. Baehtz, K.G. Bramnik, and H. Ehrenberg, *Phase transitions occurring upon lithium insertion-extraction of LiCoPO₄*. Chemistry of Materials, 2007. **19**(4): p. 908-915.
28. Gu, H.B., B. Jin, D.K. Jun, and Z. Han, *Improved electrochemical performance of LiCoPO₄ nanoparticles for lithium ion batteries*. Journal of Nanoscience and Nanotechnology, 2007. **7**(11): p. 4037-4040.
29. Huang, X., J. Ma, R. Wu, Y. Hu, J. Dai, Z. Zhu, H. Chen, and H. Wang, *Hydrothermal synthesis of LiCoPO₄ cathode materials for rechargeable lithium ion batteries*. Materials Letters, 2004. **59**: p. 578-582.
30. Wolfenstine, J. and J. Allen, *LiNiPO₄-LiCoPO₄ solid solutions as cathodes*. Journal of Power Sources, 2004. **136**: p. 150-153.
31. Wolfenstine, J. and J. Allen, *Ni³⁺/Ni²⁺ redox potential in LiNiPO₄*. Journal of Power Sources, 2005. **142**(1-2): p. 389-390.
32. Ban, C.M. and M.S. Whittingham, *Nanoscale single-crystal vanadium oxides with layered structure by electrospinning and hydrothermal methods*. Solid State Ionics, 2008. **179**(27-32): p. 1721-1724.
33. Cheah, Y.L., V. Aravindan, and S. Madhavi, *Electrochemical lithium insertion behavior of combustion synthesized V₂O₅ cathodes for lithium-ion batteries*. Journal of The Electrochemical Society, 2012. **159**(3): p. A273-A280.
34. Cheah, Y.L., N. Gupta, S.S. Pramana, V. Aravindan, G. Wee, and M. Srinivasan, *Morphology, structure and electrochemical properties of single phase electrospun*

- vanadium pentoxide nanofibers for lithium ion batteries*. Journal of Power Sources, 2011. **196**(15): p. 6465-6472.
35. Mai, L., L. Xu, C. Han, X. Xu, Y. Luo, S. Zhao, and Y. Zhao, *Electrospun ultralong hierarchical vanadium oxide nanowires with high performance for lithium ion batteries*. Nano Letters, 2010. **10**(11): p. 4750-4755.
 36. Mai, L.Q., L. Xu, B. Hu, and Y.H. Gu, *Improved cycling stability of nanostructured electrode materials enabled by prelithiation*. Journal of Materials Research, 2010. **25**(8): p. 1413-1420.
 37. Pitchai, R., S. Shivakumara, H.N. Vasan, and N. Munichandraiah, *Preparation of nanostrip V_2O_5 by the polyol method and its electrochemical characterization as cathode material for rechargeable lithium batteries*. Journal of Physical Chemistry C, 2008. **112**: p. 16700-16707.
 38. Ponzio, E.A., T.M. Benedetti, and R.M. Torresi, *Electrochemical and morphological stabilization of V_2O_5 nanofibers*. Electrochimica Acta, 2007. **52**: p. 4419-4427.
 39. Reddy, C.V.S., A.-P. Jin, X. Han, Q.-Y. Zhu, L.-Q. Mai, and W. Chen, *Preparation and characterization of (PVP+ V_2O_5) cathode for battery applications*. Electrochemistry Communications, 2006. **8**: p. 279-283.
 40. Reddy, C.V.S., J. Wei, Z. Quan-Yao, D. Zhi-Rong, C. Wen, S.-i. Mho, and R.R. Kalluru, *Cathodic performance of (V_2O_5 +PEG) nanobelts for Li ion rechargeable battery*. Journal of Power Sources, 2007. **166**: p. 244-249.
 41. Pan, A., J. Liu, J.-G. Zhang, G. Cao, W. Xu, Z. Nie, X. Jie, D. Choi, B.W. Arey, C. Wang, and S. Liang, *Template free synthesis of LiV_3O_8 nanorods as a cathode material for high-rate secondary lithium batteries*. Journal of Materials Chemistry, 2010. **21**(1153-1161).

42. Zhang, H.-L., J.R. Neilson, and D.E. Morse, *Vapor-diffusion-controlled sol-gel synthesis of flaky lithium vanadium oxide and its electrochemical behaviour*. Journal of Physical Chemistry C, 2010. **114**: p. 19550-19555.
43. Huang, B., X.D. Zheng, and M. Lu, *Synthesis and electrochemical properties of carbon nano-tubes modified spherical $\text{Li}_2\text{FeSiO}_4$ cathode material for lithium-ion batteries*. Journal of Alloys and Compounds, 2012. **525**: p. 110-113.
44. Gover, R.K.B., P. Burns, A. Bryan, M.Y. Saidi, J.L. Swoyer, and J. Barker, *LiVPO_4F : A new active material for safe lithium-ion batteries*. Solid State Ionics, 2006. **177**(26-32): p. 2635-2638.
45. Zhou, F., X.M. Zhao, and J.R. Dahn, *Reactivity of charged LiVPO_4F with 1 M LiPF_6 EC:DEC electrolyte at high temperature as studied by accelerating rate calorimetry*. Electrochemistry Communications, 2009. **11**(3): p. 589-591.
46. Rui, X.H., N. Ding, J. Liu, C. Li, and C.H. Chen, *Analysis of the chemical diffusion coefficient of lithium ions in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material*. Electrochimica Acta, 2010. **55**(7): p. 2384-2390.
47. Cho, A.R., J.N. Son, V. Aravindan, H. Kim, K.S. Kang, W.S. Yoon, W.S. Kim, and Y.S. Lee, *Carbon supported, Al doped- $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a high rate cathode material for lithium-ion batteries*. Journal of Materials Chemistry, 2012. **22**(14): p. 6556-6560.
48. Patoux, S., C. Wurm, M. Morcrette, G. Rousse, and C. Masquelier, *A comparative structural and electrochemical study of monoclinic $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$* . Journal of Power Sources, 2003. **119–121**(0): p. 278-284.
49. Qiao, Y.Q., X.L. Wang, Y. Zhou, J.Y. Xiang, D. Zhang, S.J. Shi, and J.P. Tu, *Electrochemical performance of carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials derived from polystyrene-based carbon-thermal reduction synthesis*. Electrochimica Acta, 2010. **56**(1): p. 510-516.

50. Li, Y.J., L. Hong, and F. Wu, *Preparation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material for power Li-Ion batteries*. Progress in Chemistry, 2012. **24**(1): p. 47-53.
51. Koleva, V., R. Stoyanova, and E. Zhecheva, *Nano-crystalline LiMnPO_4 prepared by a new phosphate-formate precursor method*. Materials Chemistry and Physics, 2010. **121**: p. 370-377.
52. Padhi, A., K. Nanjundaswamy, and J. Goodenough, *Phospho-olivines as positive-electrode materials for rechargeable lithium batteries*. Journal of The Electrochemical Society, 1997. **144**(4): p. 1188-1194
53. Thackeray, M., *Lithium-ion batteries: An unexpected conductor*. Nature Materials, 2002. **1**: p. 81-82.
54. Chan, C.K., H. Peng, R.D. Twisten, K. Jarausch, X.F. Zhang, and Y. Cui, *Fast, completely reversible Li insertion in vanadium pentoxide nanoribbons*. Nano Letters, 2007. **7**(2): p. 490-495.
55. Thomas, J., *Lithium Batteries: A spectacularly reactive cathode*. Nature Materials, 2003. **2**: p. 705-707.
56. Liu, H., Y.P. Wu, E. Rahm, R. Holze, and H.Q. Wu, *Cathode materials for lithium ion batteries prepared by sol-gel methods*. Solid State Electrochemistry, 2004. **8**: p. 450-466.
57. Yamada, H., K. Tagawa, M. Komatsu, I. Moriguchi, and T. Kudo, *High power battery electrodes using nanoporous V_2O_5 /carbon composites*. Journal of Physical Chemistry C, 2007. **111**: p. 8397-8402.
58. Gangulibabu, D. Bhuvaneswari, N. Kalaiselvi, N. Jayaprakash, and P. Periasamy, *CAM sol-gel synthesized LiMPO_4 ($M=\text{Co}, \text{Ni}$) cathodes for rechargeable lithium batteries*. Journal of Sol-gel Science and Technology, 2009. **49**: p. 137-144.

59. Yamada, A., M. Hosoya, S.-C. Chung, Y. Kudo, K. Hinokuma, K.-Y. Liu, and Y. Nishi, *Olivine-type cathodes: Achievements and problems*. Journal of Power Sources, 2003. **119-121**: p. 232-238.
60. Milke, B., P. Strauch, M. Antonietti, and C. Giordano, *Synthesis of $\text{Li}_y\text{MnSiO}_x$ and LiMnPO_4 nanostructures*. Nanoscale, 2009. **1**: p. 110-113.
61. Jin, B., E.M. Jin, K.-H. Park, and H.-B. Gu, *Electrochemical properties of LiFePO_4 -multiwalled carbon nanotubes composite cathode materials for lithium polymer battery*. Electrochemistry Communications, 2008. **10**: p. 1537-1540.
62. Lai, C.Y., Q.J. Xu, H.H. Ge, G.D. Zhou, and J.Y. Xie, *Improved electrochemical performance of LiFePO_4/C for lithium-ion batteries with two kinds of carbon sources*. Solid State Ionics, 2008. **179**(27-32): p. 1736-1739.
63. Meligrana, G., C. Gerbaldi, A. Tuel, S. Bodoardo, and N. Penazzi, *Hydrothermal synthesis of high surface LiFePO_4 powders as cathode for Li-ion cells*. Journal of Power Sources, 2006. **160**: p. 516-522.
64. Oh, S.W., S.T. Myung, H.J. Bang, C.S. Yoon, K. Amine, and Y.K. Sun, *Nanoporous structured LiFePO_4 with spherical microscale particles having high volumetric capacity for lithium batteries*. Electrochemical and Solid-State Letters, 2009. **12**(9): p. A181-A185.
65. Howard, W.F. and R.M. Spotnitz, *Theoretical evaluation of high-energy lithium metal phosphate cathode materials in Li-ion batteries*. Journal of Power Sources, 2007. **165**: p. 887-891.
66. Kim, J., D.-H. Seo, S.-W. Kim, W.-U. Park, and K. Kang, *Mn based olivine electrode material with high power and energy*. Chemical Communications, 2010. **46**: p. 1305-1307.
67. Li, H.H., J. Jin, J.P. Wei, Z. Zhou, and J. Yan, *Fast synthesis of core-shell LiCoPO_4/C nanocomposite via microwave heating and its electrochemical Li*

- intercalation performances*. Electrochemistry Communications, 2009. **11**: p. 95-98.
68. Morgan, D., A. Van der Ven, and G. Ceder, *Li conductivity in Li_xMPO_4 ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) olivine materials*. Electrochemical and Solid-State Letters, 2004. **7**(2): p. A30-A32.
 69. Konarova, M. and I. Taniguchi, *Preparation of LiFePO_4/C composite powders by ultrasonic spray pyrolysis followed by heat treatment and their electrochemical properties*. Materials Research Bulletin, 2008. **43**: p. 3305-3317.
 70. Lin, Y., M.X. Gao, D. Zhu, Y.F. Liu, and H.G. Pan, *Effects of carbon coating and iron phosphides on the electrochemical properties of LiFePO_4/C* . Journal of Power Sources, 2008. **184**: p. 444-448.
 71. Heo, J.B., S.B. Lee, S.H. Cho, J. Kim, S.H. Park, and Y.S. Lee, *Synthesis and electrochemical characterizations of dual doped $\text{Li}_{1.05}\text{Fe}_{0.997}\text{Cu}_{0.003}\text{PO}_4$* . Materials Letters, 2009. **63**: p. 581-583.
 72. Jang, I.C., H.H. Lim, S.B. Lee, K. Karthikeyan, V. Aravindan, K.S. Kang, W.S. Yoon, W.I. Cho, and Y.S. Lee, *Preparation of LiCoPO_4 and LiFePO_4 coated LiCoPO_4 materials with improved battery performance*. Journal of Alloys and Compounds, 2010. **497**: p. 321-324.
 73. Wang, D., H. Li, S. Shi, X. Huang, and L. Chen, *Improving the rate performance of LiFePO_4 by Fe-site doping*. Electrochimica Acta, 2005. **50**(2955-2958).
 74. Liang, G.C., L. Wang, X.Q. Ou, X. Zhao, and S.Z. Xu, *Lithium iron phosphate with high-rate capability synthesized through hydrothermal reaction in glucose solution*. Journal of Power Sources, 2008. **184**(2): p. 538-542.
 75. Murugan, A.V., T. Muraliganth, and A. Manthiram, *One-pot microwave-hydrothermal synthesis and characterization of carbon-coated LiMPO_4 ($M=\text{Mn}$,*

- Fe, and Co) cathodes*. Journal of The Electrochemical Society, 2009. **156**(2): p. A79-A83.
76. Zhang, D., X. Yu, Y.F. Wang, R. Cai, Z.P. Shao, X.Z. Liao, and Z.F. Ma, *Ballmilling-assisted synthesis and electrochemical performance of LiFePO₄/C for lithium-ion battery adopting citric acid as carbon precursor*. Journal of The Electrochemical Society, 2009. **156**(10): p. A802-A808.
 77. Wang, L., Y. Huang, R. Jiang, and D. Jia, *Nano-LiFePO₄/MWCNT cathode materials prepared by room-temperature solid-state reaction and microwave heating*. Journal of The Electrochemical Society, 2007. **154**(11): p. A1015-A1019.
 78. Silva, D., O. Crosnier, G. Ouvrard, J. Greedan, A. Safa-Sefat, and L. Nazar, *Reversible lithium uptake by FeP₂*. Electrochemical and Solid-State Letters, 2003. **6**(8): p. A162-A165.
 79. Song, G.-M., Y. Wu, G. Liu, and Q. Xu, *Influence of AlF₃ coating on the electrochemical properties of LiFePO₄/ graphite Li-ion batteries*. Journal of Alloys and Compounds, 2009. **487**: p. 214-217.
 80. Hu, Y.S., Y.G. Guo, R. Dominko, M. Gaberscek, J. Jamnik, and J. Maier, *Improved electrode performance of porous LiFePO₄ using RuO₂ as an oxidic nanoscale interconnect*. Advanced Materials, 2007. **19**(15): p. 1963-1966.
 81. Kavan, L., I. Exnar, J. Cech, and M. Graetzel, *Enhancement of electrochemical activity of LiFePO₄ (olivine) by amphiphilic Ru-bipyridine complex anchored to a carbon nanotube*. Chemistry of Materials, 2007. **19**(19): p. 4716-4721.
 82. Kavan, L., I. Exnar, and M. Graetzel, *Molecular wiring of LiFePO₄ (Olivine)*. Chemistry of Materials, 2008. **20**(9): p. 3163-3168.
 83. Kavan, L., I. Exnar, S.M. Zakeeruddin, and M. Graetzel, *Molecular wiring of olivine LiFePO₄ by ruthenium(II)-bipyridine complexes and by their assemblies*

- with single-walled carbon nanotubes*. Journal of Physical Chemistry C, 2008. **112**(23): p. 8708-8714.
84. Kavan, L., M. Zukalova, I. Exnar, S.M. Zakeeruddin, and M. Graetzel, *Molecular wiring of LiMnPO₄ (olivine) by ruthenium(II)-bipyridine complexes*. Electrochemistry Communications, 2009. **11**(11): p. 2137-2140.
 85. Chen, J., S. Wang, and M.S. Whittingham, *Hydrothermal synthesis of cathode materials*. Journal of Power Sources, 2007. **174**: p. 442-448.
 86. Kumar, P.R., M. Venkateswarlu, M. Misra, A.K. Mohanty, and N. Satyanarayana, *Carbon coated LiMnPO₄ nanorods for lithium batteries*. Journal of The Electrochemical Society, 2011. **158**(3): p. A227-A230.
 87. Chen, G.Y., J.D. Wilcox, and T.J. Richardson, *Improving the performance of lithium manganese phosphate through divalent cation substitution*. Electrochemical and Solid-State Letters, 2008. **11**(11): p. A190-A194.
 88. Wang, Y.R., Y.F. Chen, S.Q. Cheng, and L.N. He, *Improving electrochemical performance of LiMnPO₄ by Zn doping using a facile solid state method*. Korean Journal of Chemical Engineering, 2011. **28**(3): p. 964-968.
 89. Kim, J.-K., G.S. Chauhan, J.-H. Ahn, and H.-J. Ahn, *Effect of synthetic conditions on the electrochemical properties of LiMn_{0.4}Fe_{0.6}PO₄/C synthesized by sol-gel technique*. Journal of Power Sources, 2009. **189**: p. 391-396.
 90. Kim, J., Y.U. Park, D.H. Seo, S.W. Kim, and K. Kang, *Mg and Fe co-doped Mn based olivine cathode material for high power capability*. Journal of The Electrochemical Society, 2011. **158**(3): p. A250-A254.
 91. Yang, G., H.A. Ni, H.D. Liu, P. Gao, H.M. Ji, S. Roy, J. Pinto, and X.F. Jiang, *The doping effect on the crystal structure and electrochemical properties of LiMn_xM_{1-x}PO₄ (M = Mg, V, Fe, Co, Gd)*. Journal of Power Sources, 2011. **196**(10): p. 4747-4755.

92. Doan, T.N.L., Z. Bakenov, and I. Taniguchi, *Preparation of carbon coated LiMnPO_4 powders by a combination of spray pyrolysis with dry ball-milling followed by heat treatment*. Advanced Powder Technology, 2010. **21**(2): p. 187-196.
93. Doan, T.N.L. and I. Taniguchi, *Cathode performance of LiMnPO_4/C nanocomposites prepared by a combination of spray pyrolysis and wet ball-milling followed by heat treatment*. Journal of Power Sources, 2011. **196**(3): p. 1399-1408.
94. Dalavi, S., M.Q. Xu, B. Knight, and B.L. Lucht, *Effect of added LiBOB on high voltage ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) spinel cathodes*. Electrochemical and Solid-State Letters, 2012. **15**(2): p. A28-A31.
95. Li, S.Y., Y.Y. Zhao, X.M. Shi, B.C. Li, X.L. Xu, W. Zhao, and X.L. Cui, *Effect of sulfolane on the performance of lithium bis(oxalato)borate-based electrolytes for advanced lithium ion batteries*. Electrochimica Acta, 2012. **65**: p. 221-227.
96. Borgel, V., E. Markevich, D. Aurbach, G. Semrau, and M. Schmidt, *On the application of ionic liquids for rechargeable Li batteries: High voltage systems*. Journal of Power Sources, 2009. **189**(1): p. 331-336.
97. Seki, S., Y. Mita, H. Tokuda, Y. Ohno, Y. Kobayashi, A. Usami, M. Watanabe, N. Terada, and H. Miyashiro, *Effects of alkyl chain in imidazolium-type room-temperature ionic liquids as lithium secondary battery electrolytes*. Electrochemical and Solid-State Letters, 2007. **10**(10): p. A237-A240.
98. Galinski, M., A. Lewandowski, and I. Stepniak, *Ionic liquids as electrolytes*. Electrochimica Acta, 2006. **51**(26): p. 5567-5580.
99. Liu, D., Y. Liu, B.B. Garcia, Q. Zhang, A. Pan, Y.-H. Jeong, and G. Cao, *V_2O_5 xerogel electrodes with much enhanced lithium-ion intercalation properties with N_2 annealing*. Journal of Materials Chemistry, 2009. **19**: p. 8789-8795.

100. Zhai, T., H. Liu, H. Li, X. Fang, M. Liao, L. Li, H. Zhou, Y. Koide, Y. Bando, and D. Golberg, *Centimeter-long V_2O_5 nanowires: From synthesis to field-emission, electrochemical, electrical transport and photoconductive properties*. *Advanced Materials*, 2010. **22**: p. 2547-2552.
101. Xiong, C., A.E. Aliev, B. Gnade, and K.J. Balkus Jr., *Fabrication of silver vanadium oxide and V_2O_5 nanowires for electrochromics* *ACS Nano*, 2008. **2**(2): p. 293-301.
102. Pan, A.Q., J.G. Zhang, Z.M. Nie, G.Z. Cao, B.W. Arey, G.S. Li, S.Q. Liang, and J. Liu, *Facile synthesized nanorod structured vanadium pentoxide for high-rate lithium batteries*. *Journal of Materials Chemistry*, 2010. **20**(41): p. 9193-9199.
103. Ren, X., Y. Jiang, P. Zhang, J. Liu, and Q. Zhang, *Preparation and electrochemical properties of V_2O_5 submicron-belts synthesized by a sol-gel H_2O_2 route*. *Journal of Sol-Gel Science and Technology*, 2009. **51**: p. 133-138.
104. Whittingham, M.S. and M.B. Dines, *Normal-Butyllithium - Effective, general cathode screening agent*. *Journal of The Electrochemical Society*, 1977. **124**(9): p. 1387-1388.
105. Garcia, B., M. Millet, J.P. Pereira-Ramos, N. Baffier, and D. Bloch, *Electrochemical behaviour of chemically lithiated $Li_xV_2O_5$ phases ($0.9 \leq x \leq 1.6$)*. *Journal of Power Sources*, 1999. **81**: p. 670-674.
106. Pecquenard, B., D. Gourier, and N. Baffier, *EPR identification of $Li_xV_2O_5$ phases generated by chemical and electrochemical lithium intercalation in V_2O_5* . *Solid State Ionics*, 1995. **78**(3-4): p. 287-303.
107. Murphy, D.W., P.A. Christian, F.J. Disalvo, and J.V. Waszczak, *Lithium incorporation by vanadium pentoxide*. *Inorganic Chemistry*, 1979. **18**(10): p. 2800-2803.

108. Eguchi, M. and K. Ozawa, *Lithium insertion property of $Li_{2.2}V_2O_5 \cdot nH_2O$* . *Electrochimica Acta*, 2007. **52**(7): p. 2657-2660.
109. Koltypin, M., V. Pol, A. Gedanken, and D. Aurbach, *The study of carbon-coated V_2O_5 nanoparticles as a potential cathodic material for Li rechargeable batteries*. *Journal of The Electrochemical Society*, 2007. **154**(7): p. A605-A613.
110. Li, X., W. Li, H. Ma, and J. Chen, *Electrochemical lithium intercalation / deintercalation of single-crystalline V_2O_5 nanowires*. *Journal of The Electrochemical Society*, 2007. **154**(1): p. A39-A42.
111. Wei, Y., C.-W. Ryu, and K.-B. Kim, *Improvement in electrochemical performance of V_2O_5 by Cu doping*. *Journal of Power Sources*, 2007. **165**(1): p. 386-392.
112. Zhan, S., Y. Wei, X. Bie, C. Wang, F. Du, G. Chen, and F. Hu, *Structural and electrochemical properties of Al^{3+} doped V_2O_5 nanoparticles prepared by an oxalic acid assisted soft-chemical method*. *Journal of Alloys and Compounds*, 2010. **502**: p. 92-96.
113. Huguenin, F., E.M. Girotto, R.M. Torresi, and D.A. Buttry, *Transport properties of V_2O_5 /polypyrrole nanocomposite prepared by a sol-gel alkoxide route*. *Journal of Electroanalytical Chemistry*, 2002. **536**: p. 37-45.
114. Navone, C., R. Baddour-Hadjean, J.P. Pereira-Ramos, and R. Salot, *A kinetic study of electrochemical lithium insertion into oriented V_2O_5 thin films prepared by rf sputtering*. *Electrochimica Acta*, 2008. **53**: p. 3329-3336.
115. Chen, Y.P., G. Yang, Z.H. Zhang, X.Y. Yang, W.H. Hou, and J.J. Zhu, *Polyaniline-intercalated layered vanadium oxide nanocomposites-One-pot hydrothermal synthesis and application in lithium battery*. *Nanoscale*, 2010. **2**(10): p. 2131-2138.

116. Boyano, I., M. Bengoechea, I.d. Meatza, O. Miguel, I. Cantero, E. Ochoteco, J. Rodriguez, M. Lira-Cantu, and P. Gomez-Romero, *Improvement in the Ppy/V₂O₅ hybrid as a cathode material for Li ion batteries using PSA as an organic additive*. Journal of Power Sources, 2007. **166**: p. 471-477.
117. Giorgetti, M., M. Berrettoni, and W.H. Smyrl, *Doped V₂O₅-based cathode materials: Where does the doping metal Go? An X-ray absorption spectroscopy study*. Chemistry of Materials, 2007. **19**(24): p. 5991-6000.
118. Parent, M.J., S. Passerini, B.B. Owens, and W.H. Smyrl, *Composites of V₂O₅ aerogel and nickel fiber as high rate intercalation electrodes*. Journal of The Electrochemical Society, 1999. **146**(4): p. 1346-1350.
119. Zhan, S., C. Wang, G. Chen, F. Du, and Y. Wei, *Preparation and electrochemical properties of nano AlV₂O₅ cathode materials for rechargeable lithium batteries*. Ionics, 2010. **16**(3): p. 209-213.
120. Chu, Y.-Q. and Q.-Z. Qin, *Fabrication and characterization of silver-V₂O₅ composite thin films as lithium-ion insertion materials*. Chemistry of Materials, 2002. **14**: p. 3152-3157.
121. Coustier, F., S. Passerini, and W.H. Smyrl, *Dip-coated silver-doped V₂O₅ xerogels as host materials for lithium intercalation*. Solid State Ionics, 1997. **100**: p. 247-258.
122. Zhan, S.Y., G. Chen, D.L. Liu, A. Li, C.Z. Wang, and Y.J. Wei, *Effects of Cr doping on the structural and electrochemical properties of V₂O₅*. Journal of Alloys and Compounds, 2009. **479**(1-2): p. 652-656.
123. Zhan, S.Y., C.Z. Wang, K. Nikolowski, H. Ehrenberg, G. Chen, and Y.J. Wei, *Electrochemical properties of Cr doped V₂O₅ between 3.8 V and 2.0 V*. Solid State Ionics, 2009. **180**(20-22): p. 1198-1203.

124. Li, H.X., L.F. Jiao, H.T. Yuan, M. Zhao, M. Zhang, and Y.M. Wang, *High-performance Cu-doped vanadium oxide ($\text{Cu}_x\text{V}_2\text{O}_5$) prepared by rapid precipitation method for rechargeable batteries*. Materials Letters, 2007. **61**: p. 101-104.
125. Wei, Y., C.-W. Ryu, and K.-B. Kim, *Cu-doped V_2O_5 as a high-energy density cathode material for rechargeable lithium batteries*. Journal of Alloys and Compounds, 2008. **459**(1–2): p. L13-L17.
126. Zhu, D., H. Liu, L. Lv, Y.D. Yao, and W.Z. Yang, *Hollow microspheres of V_2O_5 and Cu-doped V_2O_5 as cathode materials for lithium-ion batteries*. Scripta Materialia, 2008. **59**: p. 642-645.
127. Liu, C.-K., K. Lai, W. Liu, M. Yao, and R.-J. Sun, *Preparation of carbon nanofibres through electrospinning and thermal treatment*. Polymer International, 2009. **58**: p. 1341-1349.
128. Guo, Q., X. Zhou, Z. Li, S. Chen, A. Seema, A. Greiner, and H. Hou, *Supercapacitors based on hybrid carbon nanofibers containing multiwalled carbon nanotubes*. Journal of Materials Chemistry, 2008. **19**: p. 2810-2816.
129. Toprakci, O., H.A.K. Toprakci, L.W. Ji, G.J. Xu, Z. Lin, and X.W. Zhang, *Carbon nanotube-loaded electrospun LiFePO_4 /carbon composite nanofibers as stable and binder-free cathodes for rechargeable lithium-ion batteries*. ACS Applied Materials & Interfaces, 2012. **4**(3): p. 1273-1280.
130. Toprakci, O., L.W. Ji, Z. Lin, H.A.K. Toprakci, and X.W. Zhang, *Fabrication and electrochemical characteristics of electrospun LiFePO_4 /carbon composite fibers for lithium-ion batteries*. Journal of Power Sources, 2011. **196**(18): p. 7692-7699.
131. Lee, S.H., M. Jung, J.S. Im, K.Y. Sheem, and Y.S. Lee, *Preparation and characterization of electrospun LiFePO_4 /carbon complex improving rate*

- performance at high C-rate*. Research on Chemical Intermediates, 2010. **36**(6-7): p. 591-602.
132. Von Hagen, R., H. Lorrmann, K.C. Moller, and S. Mathur, *Electrospun $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4/\text{C}$ nanofiber composites as self-supporting cathodes in Li-ion batteries*. Advanced Energy Materials, 2012. **2**(5): p. 553-559.
 133. Lou, X.W., L.A. Archer, and Z.C. Yang, *Hollow Micro-/Nanostructures: Synthesis and Applications*. Advanced Materials, 2008. **20**(21): p. 3987-4019.
 134. Su, L.W., Y. Jing, and Z. Zhou, *Li ion battery materials with core-shell nanostructures*. Nanoscale, 2011. **3**(10): p. 3967-3983.
 135. Zhang, X.W., L.W. Ji, O. Toprakci, Y.Z. Liang, and M. Alcoutlabi, *Electrospun nanofiber-based anodes, cathodes, and separators for advanced lithium-ion batteries*. Polymer Reviews, 2011. **51**(3): p. 239-264.
 136. Sathiya, M., A.S. Prakash, K. Ramesha, J.M. Tarascon, and A.K. Shukla, *V_2O_5 -anchored carbon nanotubes for enhanced electrochemical energy storage*. Journal of the American Chemical Society, 2011. **133**(40): p. 16291-16299.
 137. Hu, Y.-S., X. Liu, J.-O. Müller, R. Schlögl, J. Maier, and D.S. Su, *Synthesis and electrode performance of nanostructured V_2O_5 by using a carbon tube-in-tube as a nanoreactor and an efficient mixed-conducting network*. Angewandte Chemie International Edition, 2009. **48**(1): p. 210-214.
 138. Dominko, R., M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, J.M. Goupil, S. Pejovnik, and J. Jamnik, *Porous olivine composites synthesized by sol-gel technique*. Journal of Power Sources, 2006. **153**: p. 274-280.
 139. Lim, J., D. Kim, V. Mathew, D. Ahn, J. Kang, S.W. Kang, and J. Kim, *Plate-type LiFePO_4 nanocrystals by low temperature polyol-assisted solvothermal reaction and its electrochemical properties*. Journal of Alloys and Compounds, 2011. **509**(31): p. 8130-8135.

140. Lee, J.-K., G.-P. Kim, I.K. Song, and S.-H. Baeck, *Electrodeposition of mesoporous V_2O_5 with enhanced lithium-ion intercalation property*. Electrochemistry Communications, 2009. **11**: p. 1571-1574.
141. Kim, K.H., D.K. Roh, I.K. Song, B.C. Lee, and S.H. Baeck, *Enhanced performance as a lithium-ion battery cathode of electrodeposited V_2O_5 thin films by e-beam irradiation*. Journal of Solid State Electrochemistry, 2010. **14**(10): p. 1801-1805.
142. Macias, M., A. Chacko, J.P. Ferraris, and K.J. Balkus Jr., *Electrospun mesoporous metal oxide fibers*. Microporous and Mesoporous Materials, 2005. **86**: p. 1-13.
143. Yu, D., C. Chen, S. Xie, Y. Liu, K. Park, X. Zhou, Q. Zhang, J. Li, and G. Cao, *Mesoporous vanadium pentoxide nanofibers with significantly enhanced Li-ion storage properties by electrospinning*. Energy & Environmental Science, 2010. **4**: p. 858-861.
144. Wang, S., Z. Lu, D. Wang, C. Li, C. Chen, and Y. Yin, *Porous monodisperse V_2O_5 microspheres as cathode materials for lithium-ion batteries*. Journal of Materials Chemistry, 2011. **21**: p. 6365-6369.
145. Glushenkov, A., M. Hassan, V. Stukachev, Z. Guo, H. Liu, G. Kuvshinov, and Y. Chen, *Growth of V_2O_5 nanorods from ball-milled powders and their performance in cathodes and anodes of lithium-ion batteries*. Journal of Solid State Electrochemistry, 2010. **14**(10): p. 1841-1846.
146. Reddy, C.V.S., S. S. A. Wicker, J. Edwin H. Walker, Q.L. Williams, and R.R. Kalluru, *Vanadium oxide nanorods for Li-ion battery applications*. Journal of The Electrochemical Society, 2008. **155**(8): p. A599-A602.
147. Cheah, Y.L., T. Toh, G. Wee, and M. Srinivasan. *Olivine nanofibrous cathodes for lithium ion batteries*. in *Materials Research Society (MRS)*. 2010. USA.

148. Li, D. and Y. Xia, *Electrospinning of nanofibers: Reinventing the wheel?* Advanced Materials, 2004. **16**(14): p. 1151-1170.
149. Thavasi, V., G. Singh, and S. Ramakrishna, *Electrospun nanofibers in energy and environmental applications*. Energy & Environmental Science, 2008. **1**: p. 205-221.
150. Kumar, A., R. Jose, K. Fujihara, J. Wang, and S. Ramakrishna, *Structural and optical properties of electrospun TiO₂ nanofibers*. Chemistry of Materials, 2007. **19**(26): p. 6536-6542.
151. Gu, Y.X., D.R. Chen, and M.L. Jiao, *Synthesis and electrochemical properties of nanostructured LiCoO₂ fibers as cathode materials for lithium-ion batteries*. Journal of Physical Chemistry B, 2005. **109**(38): p. 17901-17906.
152. Teo, W.E. and S. Ramakrishna, *Electrospun fibre bundle made of aligned nanofibres over two fixed points*. Nanotechnology, 2005. **16**: p. 1878-1884.
153. Teo, W.E. and S. Ramakrishna, *A review on electrospinning design and nanofibre assemblies*. Nanotechnology, 2006. **17**: p. R89-R106.
154. Yang, Z.L., C. Cao, F.F. Liu, D.R. Chen, and X.L. Jiao, *Core-shell Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂/Li(Ni_{1/2}Mn_{1/2})O₂ fibers: Synthesis, characterization and electrochemical properties*. Solid State Ionics, 2010. **181**(15-16): p. 678-683.
155. Gu, Y.X., D.R. Chen, X.L. Jiao, and F.F. Liu, *LiCoO₂-MgO coaxial fibers: Co-electrospun fabrication, characterization and electrochemical properties*. Journal of Materials Chemistry, 2007. **17**(18): p. 1769-1776.
156. Shao, C.L., N. Yu, Y.C. Liu, and R.X. Mu, *Preparation of LiCoO₂ nanofibers by electrospinning technique*. Journal of Physics and Chemistry of Solids, 2006. **67**(7): p. 1423-1426.

157. Zhan, S.H., Y. Li, and H.B. Yu, *LiCoO₂ hollow nanofibers by co-electrospinning sol-gel precursor*. Journal of Dispersion Science and Technology, 2008. **29**(5): p. 702-705.
158. Zhan, S.H., Y. Li, and H.B. Yu, *Sol-gel co-electrospun LiNiO₂ hollow nanofibers*. Journal of Dispersion Science and Technology, 2008. **29**(6): p. 823-826.
159. Ding, Y.H., P. Zhang, Z.L. Long, Y. Jiang, and D.S. Gao, *The morphology, structure and electrochemical properties of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ prepared by electrospun method*. Journal of Alloys and Compounds, 2008. **462**(1-2): p. 340-342.
160. Ding, Y.H., P. Zhang, Z.L. Long, Y. Jiang, and F. Xu, *Morphology and electrochemical properties of Al doped LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ nanofibers prepared by electrospinning*. Journal of Alloys and Compounds, 2009. **487**(1-2): p. 507-510.
161. Kuo, J.C., S.C. Lee, K.C. Hsu, S.J. Lw, B.Y. Chou, and Y.S. Fu, *Fabrication of LiNi_{0.5+d}Mn_{0.5-d}O₂ nanofibers by electrospinning*. Materials Letters, 2008. **62**(30): p. 4594-4596.
162. Dror, Y., W. Salalha, R.L. Khalfin, Y. Cohen, A.L. Yarin, and E. Zussman, *Carbon nanotubes embedded in oriented polymer nanofibers by electrospinning*. Langmuir, 2003. **19**(17): p. 7012-7020.
163. Manuel, J., P. Raghavan, C. Shin, M.Y. Heo, J.H. Ahn, J.P. Noh, G.B. Cho, H.S. Ryu, and H.J. Ahn, *Electrosprayed polyaniline as cathode material for lithium secondary batteries*. Materials Research Bulletin, 2010. **45**(3): p. 265-268.
164. Kim, C., K.S. Yang, M. Kojima, K. Yoshida, Y.J. Kim, Y.A. Kim, and M. Endo, *Fabrication of electrospinning-derived carbon nanofiber webs for the anode material of lithium-ion secondary batteries*. Advanced Materials, 2006. **16**: p. 2393-2397.

165. Kim, C., K.-S. Yang, and W.-J. Lee, *The use of carbon nanofibre electrodes prepared by electrospinning for electrochemical supercapacitors*. *Electrochemical and Solid-State Letters*, 2004. **7**(11): p. A397-A399.
166. Sharma, Y., N. Sharma, G.V.S. Rao, and B.V.R. Chowdari, *Li-storage and cyclability of urea combustion derived ZnFe_2O_4 as anode for Li-ion batteries*. *Electrochimica Acta*, 2008. **53**(5): p. 2380-2385.
167. Santiago, E.I., A.V.C. Andrade, C.O. Paiva-Santos, and L.O.S. Bulhoes, *Structural and electrochemical properties of LiCoO_2 prepared by combustion synthesis*. *Solid State Ionics*, 2003. **158**(1-2): p. 91-102.
168. Julien, C., M.A. Camacho-Lopez, T. Mohan, S. Chitra, P. Kalyani, and S. Gopukumar, *Combustion synthesis and characterization of substituted lithium cobalt oxides in lithium batteries*. *Solid State Ionics*, 2000. **135**(1-4): p. 241-248.
169. Chitra, S., P. Kalyani, T. Mohan, R. Gangadharan, B. Yebka, S. Castro-Garcia, M. Massot, C. Julien, and M. Eddrief, *Characterization and electrochemical studies of LiMn_2O_4 materials prepared by combustion method*. *Journal of Electroceramics*, 1999. **3**(4): p. 433-441.
170. Yang, W.S., G. Zhang, J.Y. Xie, L.L. Yang, and Q.G. Liu, *A combustion method to prepare spinel phase LiMn_2O_4 cathode materials for lithium-ion batteries*. *Journal of Power Sources*, 1999. **81**: p. 412-415.
171. Si, Y.C., L.F. Jiao, H.T. Yuan, H.X. Li, and Y.M. Wang, *Structural and electrochemical properties of LiV_3O_8 prepared by combustion synthesis*. *Journal of Alloys and Compounds*, 2009. **486**(1-2): p. 400-405.
172. Prakash, I., N. Nallamuthu, P. Muralidharan, M. Venkateswarlu, and N. Satyanarayana, *Synthesis of nanocrystalline CoFe_2O_4 using citrate-urea assisted combustion process for lithium battery anode*, in *Nsti Nanotech 2008, Vol 1*,

Technical Proceedings - Materials, Fabrication, Particles, and Characterization,

M. Laudon and B. Romanowicz, Editors. 2008. p. 725-728.

173. Doeff, M.M., J.J. Chen, T.E. Conry, R.G. Wang, J. Wilcox, and A. Aumentado, *Combustion synthesis of nanoparticulate $\text{LiMg}_x\text{Mn}_{1-x}\text{PO}_4$ ($x=0, 0.1, 0.2$) carbon composites*. Journal of Materials Research, 2010. **25**(8): p. 1460-1468.
174. Recham, N., L. Dupont, M. Courty, K. Djellab, D. Larcher, M. Armand, and J.M. Tarascon, *Ionothermal synthesis of tailor-made LiFePO_4 powders for Li-Ion battery applications*. Chemistry of Materials, 2009. **21**(6): p. 1096-1107.
175. Recham, N., M. Armand, and J.-M. Tarascon, *Novel low temperature approaches for the eco-efficient synthesis of electrode materials for secondary Li-ion batteries*. Comptes Rendus Chimie, 2010. **13**: p. 106-116.
176. Muraliganth, T. and A. Manthiram, *Understanding the shifts in the redox potentials of olivine $\text{LiM}_{1-y}\text{M}_y\text{PO}_4$ ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{and Mg}$) solid solution cathodes*. Journal of Physical Chemistry C, 2010. **114**(36): p. 15530-15540.
177. Oh, S.M., S.W. Oh, C.S. Yoon, B. Scrosati, K. Amine, and Y.K. Sun, *High-performance carbon- LiMnPO_4 nanocomposite cathode for lithium batteries*. Advanced Functional Materials, 2010. **20**(19): p. 3260-3265.
178. Tang, M., W.C. Carter, and Y.M. Chiang, *Electrochemically driven phase transitions in insertion electrodes or lithium-ion batteries: Examples in lithium metal phosphate olivines*, in *Annual Review of Materials Research*. 2010. p. 501-529.
179. Yazami, R., A. Martinet, and Y. Reynier, *Some thermodynamics and kinetics aspects of the graphite-lithium negative electrode for lithium-ion batteries*, in *New carbon based materials for electrochemical energy storage systems: Batteries, supercapacitors and fuel cells*. 2006. p. 245-258.

180. Cheah, Y.L., R. Von Hagen, V. Aravindan, R. Fiz, S. Mathur, and S. Madhavi, *High-rate and elevated temperature performance of electrospun V_2O_5 nanofibers carbon-coated by plasma enhanced chemical vapour deposition*. Nano Energy, 2012.
181. Rietveld, H., *Line profiles of neutron powder-diffraction peaks for structure refinement*. Acta Crystallographica, 1967. **22**(1): p. 151-152.
182. Rietveld, H., *A profile refinement method for nuclear and magnetic structures*. Journal of Applied Crystallography, 1969. **2**(2): p. 65-71.
183. Cheary, R.W. and A. Coelho, *A fundamental parameters approach to X-ray line-profile fitting*. Journal of Applied Crystallography, 1992. **25**(2): p. 109-121.
184. Zhang, S.S., K. Xu, and T.R. Jow, *Electrochemical impedance study on the low temperature of Li-ion batteries*. Electrochimica Acta, 2004. **49**(7): p. 1057-1061.
185. Aravindan, V., K. Karthikeyan, K.S. Kang, W.S. Yoon, W.S. Kim, and Y.S. Lee, *Influence of carbon towards improved lithium storage properties of Li_2MnSiO_4 cathodes*. Journal of Materials Chemistry, 2011. **2011**(21).
186. Reynier, Y., R. Yazami, B. Fultz, and I. Barsukov, *Evolution of lithiation thermodynamics with the graphitization of carbons*. Journal of Power Sources, 2007. **165**: p. 552-558.
187. Reynier, Y.F., R. Yazami, and B. Fultz, *Thermodynamics of lithium Intercalation into graphites and disordered carbons*. Journal of The Electrochemical Society, 2004. **151**(3): p. A422-A426.
188. Maccario, M., L. Croguennec, F.L. Cras, and C. Delmas, *Electrochemical performances in temperature for a C-containing $LiFePO_4$ composite synthesized at high temperature*. Journal of Power Sources, 2008. **183**: p. 411-417.
189. Baek, D.H., J.K. Kim, Y.J. Shin, G.S. Chauhan, J.H. Ahn, and K.W. Kim, *Effect of firing temperature on the electrochemical performance of $LiMn_{0.4}Fe_{0.6}PO_4/C$*

- materials prepared by mechanical activation*. Journal of Power Sources, 2009. **189**(1): p. 59-65.
190. Wu, C.Z. and Y. Xie, *Promising vanadium oxide and hydroxide nanostructures: from energy storage to energy saving*. Energy & Environmental Science, 2010. **3**(9): p. 1191-1206.
 191. Kim, C., B.T.N. Ngoc, K.S. Yang, M. Kojima, Y.A. Kim, Y.J. Kim, M. Endo, and S.C. Yang, *Self-sustained thin webs consisting of porous carbon nanofibers for supercapacitors via the electrospinning of polyacrylonitrile solutions containing zinc chloride*. Advanced Materials, 2007. **19**: p. 2341-2346.
 192. Nie, Z.X., C.Y. Ouyang, J.Z. Chen, Z.Y. Zhong, Y.L. Du, D.S. Liu, S.Q. Shi, and M.S. Lei, *First principles study of Jahn-Teller effects in Li_xMnPO_4* . Solid State Communications, 2010. **150**(1-2): p. 40-44.
 193. Liu, X., C. Huang, J. Qiu, and Y. Wang, *The effect of thermal annealing and laser irradiation on the microstructure of vanadium oxide nanotubes*. Applied Surface Science, 2006. **253**: p. 2747-2751.
 194. Cocciantelli, J.M., J.P. Doumerc, M. Pouchard, M. Broussely, and J. Labat, *Crystal chemistry of electrochemically inserted $\text{Li}_x\text{V}_2\text{O}_5$* . Journal of Power Sources, 1991. **34**(2): p. 103-111.
 195. Chernova, N.A., M. Roppolo, A.C. Dillon, and M.S. Whittingham, *Layered vanadium and molybdenum oxides: batteries and electrochromics*. Journal of Materials Chemistry, 2009. **19**(17): p. 2526-2552.
 196. Whittingham, M.S., *Inorganic nanomaterials for batteries*. Dalton Transactions, 2008(40): p. 5424-5431.
 197. Cheah, Y.L., V. Aravindan, and M. Srinivasan, *Improved elevated temperature performance of Al-intercalated V_2O_5 electrospun nanofibers for lithium-ion batteries*. ACS Applied Materials & Interfaces, 2012. **4**(6): p. 3270-3277.

198. Wagner, C.D., A.V. Naumkin, A. Kraut-Vass, J.W. Allison, C.J. Powell, and J. John R. Rumble, *NIST X-ray photoelectron spectroscopy database* 2003.
199. Luo, D., G. Li, C. Yu, L. Yang, J. Zheng, X. Guan, and L. Li, *Low-concentration donor-doped LiCoO₂ as a high performance cathode material for Li-ion batteries to operate between -10.4 and 45.4 °C*. Journal of Materials Chemistry, 2012. **22**: p. 22233-22241.
200. Wang, J.L., Z.H. Li, J. Yang, J.J. Tang, W.B. Nie, G.T. Lei, and Q.Z. Xiao, *Effect of Al-doping on the electrochemical properties of a three-dimensionally porous lithium manganese oxide for lithium-ion batteries*. Electrochimica Acta, 2012. **75**: p. 115-122.
201. Kakuda, T., K. Uematsu, K. Toda, and M. Sato, *Electrochemical performance of Al-doped LiMn₂O₄ prepared by different methods in solid-state reaction*. Journal of Power Sources, 2007. **167**(2): p. 499-503.
202. Suzuki, S., M. Hibino, and M. Miyayama, *High rate lithium intercalation properties of V₂O₅/carbon/ceramic-filler composites*. Journal of Power Sources, 2003. **124**: p. 513-517.
203. Guerra, E.M., K.J. Ciuffi, and H.P. Oliveira, *V₂O₅ xerogel-poly(ethylene oxide) hybrid material: Synthesis, characterization, and electrochemical properties*. Journal of Solid State Chemistry, 2006. **179**(12): p. 3814-3823.
204. Aravindan, V., C. Wong, M.V. Reddy, G.V.S. Rao, B.V.R. Chowdari, and S. Madhavi, *Carbon coated nano-LiTi₂(PO₄)₃ electrodes for non-aqueous hybrid supercapacitors*. Physical Chemistry Chemical Physics, 2012. **14**(16): p. 5808-5814.
205. Zaghbi, K., A. Mauger, and C.M. Julien, *Overview of olivines in lithium batteries for green transportation and energy storage*. Journal of Solid State Electrochemistry, 2012. **16**(3): p. 835-845.

206. Aravindan, V., Y.L. Cheah, C.L. Wong, and S. Madhavi, *Effect of LiBOB additive on the electrochemical performance of LiCoPO₄*. Journal of The Electrochemical Society, 2012.
207. Taniguchi, I., N.L.D. The, and B. Shao, *Synthesis and electrochemical characterization of LiCo_xMn_{1-x}PO₄/C nanocomposites*. Electrochimica Acta, 2011. **56**(22): p. 7680-7685.
208. Olivetti, E.A., K.C. Avery, I. Taniguchi, D.R. Sadoway, and A.M. Mayes, *Electrochemical characterization of vanadium oxide nanostructured electrode*. Journal of The Electrochemical Society, 2008. **155**(7): p. A488-A493.
209. Wang, Y. and G. Cao, *Synthesis and enhanced intercalation properties of nanostructured vanadium oxides*. Chemistry of Materials, 2006. **18**(12): p. 2787-2804.
210. Swider-Lyons, K.E., C.T. Love, and D.R. Rolison, *Improved lithium capacity of defective V₂O₅ materials*. Solid State Ionics, 2002. **152-153**: p. 99-104.
211. Kakinuma, K., T. Arisaka, and H. Yamamura, *Thermal expansion and electrical conductivity of perovskite oxide (Ln_{1-x}Sr_x)CoO_{3-d} (Ln=La, Nd and Sm)*. Journal of the Ceramic Society of Japan, 2004. **112**(6): p. 342-346.
212. Qin, W., Z.H. Chen, P.Y. Huang, and Y.H. Zhuang, *Crystal lattice expansion of nanocrystalline materials*. Journal of Alloys and Compounds, 1999. **292**: p. 230-232.
213. Sengar, S.K., B.R. Mehta, and Govind, *Size and alloying induced changes in lattice constant, core, and valence band binding energy in Pd-Ag, Pd, and Ag nanoparticles: Effect of in-flight sintering temperature*. Journal of Applied Physics, 2012. **112**(014307): p. 1-8.

214. Jiang, X.G., C.Y. Li, Y. Chi, and J.H. Yan, *TG-FTIR study on urea-formaldehyde resin residue during pyrolysis and combustion*. Journal of Hazardous Materials, 2010. **173**(1-3): p. 205-210.
215. Madhurambal, G., M. Mariappan, and S.C. Mojumdar, *Thermal, UV and FTIR spectral studies of urea-thiourea zinc chloride single crystal*. Journal of Thermal Analysis and Calorimetry, 2010. **100**(3): p. 763-768.
216. Madhurambal, G., M. Mariappan, and S.C. Mojumdar, *TG-DTA, UV and FTIR spectroscopic studies of urea-thiourea mixed crystal*. Journal of Thermal Analysis and Calorimetry, 2010. **100**(3): p. 853-856.
217. Shaju, K.M., G.V.S. Rao, and B.V.R. Chowdari, *Li-ion kinetics and polarization effect on the electrochemical performance of $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$* . Electrochimica Acta, 2004. **49**(9-10): p. 1565-1576.
218. Cui, C.J., G.M. Wu, H.Y. Yang, S.F. She, J. Shen, B. Zhou, and Z.H. Zhang, *A new high-performance cathode material for rechargeable lithium-ion batteries Polypyrrole/vanadium oxide nanotubes*. Electrochimica Acta, 2010. **55**(28): p. 8870-8875.
219. Pyun, S.I. and J.S. Bae, *The ac impedance study of electrochemical lithium intercalation into porous vanadium oxide electrode*. Electrochimica Acta, 1996. **41**(6): p. 919-925.
220. Semenenko, D.A., T.L. Kulova, A.M. Skundin, D.M. Itkis, E.A. Pomerantseva, E.A. Goodilin, and Y.D. Tretyakov, *Impedance spectroscopy study of lithium ion diffusion in a new cathode material based on vanadium pentoxide*. Mendeleev Communications, 2010. **20**: p. 12-14.
221. Zhuang, Q.C., T. Wei, L.L. Du, Y.L. Cui, L. Fang, and S.G. Sun, *An electrochemical impedance spectroscopic study of the electronic and ionic*

- transport properties of spinel LiMn_2O_4* . Journal of Physical Chemistry C, 2010. **114**(18): p. 8614-8621.
222. Armstrong, G., J. Canales, A.R. Armstrong, and P.G. Bruce, *The synthesis and lithium intercalation electrochemistry of $\text{VO}_2(\text{B})$ ultra-thin nanowires*. Journal of Power Sources, 2008. **178**(2): p. 723-728.
223. Tanguy, F., J. Gaubicher, P. Soudan, N. Bourgeon-Martin, V. Mauchamp, and D. Guyomard, *Propagation of surface-assisted side reactions, A main cause for capacity fading of vanadium oxide nanograins*. Electrochemical and Solid-State Letters, 2007. **10**(8): p. A184-A188.
224. Imamura, D. and M. Miyayama, *Characterization of magnesium-intercalated V_2O_5 /carbon composites*. Solid State Ionics, 2003. **161**(1-2): p. 173-180.
225. Kittaka, S., S. Takahara, T. Yamaguchi, and M.C.B. Funel, *Interlayer water molecules in vanadium pentoxide hydrate. 8. Dynamic properties by quasi-elastic neutron scattering*. Langmuir, 2005. **21**(4): p. 1389-1397.
226. Sakunthala, A., M.V. Reddy, S. Selvasekarapandian, B.V.R. Chowdari, and P.C. Selvin, *Energy storage studies of bare and doped vanadium pentoxide, $(\text{V}_{1.95}\text{M}_{0.05})\text{O}_5$, $\text{M} = \text{Nb, Ta}$, for lithium ion batteries*. Energy & Environmental Science, 2011. **4**(5): p. 1712-1725.
227. Yao, T., Y. Oka, and N. Yamamoto, *Layered structures of hydrated vanadium oxides.1. Alkali-metal intercalates $\text{A}_{0.3}\text{V}_2\text{O}_5 \cdot \text{NH}_2\text{O}$ ($\text{A} = \text{Na, K, Rb, Cs AND NH}_4$)*. Journal of Materials Chemistry, 1992. **2**(3): p. 331-336.
228. Yao, T., Y. Oka, and N. Yamamoto, *Layered structures of hydrated vanadium oxides .2. Vanadyl intercalates $(\text{VO})_x\text{V}_2\text{O}_5 \cdot \text{NH}_2\text{O}$* . Journal of Materials Chemistry, 1992. **2**(3): p. 337-340.

229. Liu, H., Z. Bi, X.-G. Sun, R.R. Unocic, M.P. Paranthaman, S. Dai, and G.M. Brown, *Mesoporous TiO_2 -B microspheres wit superior rate performance for lithium ion batteries*. *Advanced Materials*, 2011. **23**: p. 3450-3454.
230. Franger, S., C. Bourbon, and F.L. Cras, *Optimized lithium iron phosphate for high-rate electrochemical applications*. *Journal of The Electrochemical Society*, 2004. **151**(7): p. A1024-A1027.
231. Amine, R., H.H. Sun, H.J. Sun, and J. Prakash, *Improved electrochemical performance of NH_4AlF_4 -coated LiCoO_2 cycled over 4.5 V*. *Electrochemical and Solid-State Letters*, 2010. **13**(8): p. A101-A104.
232. Eftekhari, A., *Surface modification of thin-film based LiCoPO_4 5 V cathode with metal oxide*. *Journal of The Electrochemical Society*, 2004. **151**(9): p. A1456-A1460.
233. Kim, Y.J., J. Cho, T.-J. Kim, and B. Park, *Suppression of cobalt dissolution from the LiCoO_2 cathodes with various metal-oxide coatings*. *Journal of The Electrochemical Society*, 2003. **150**(12): p. A1723-A1725.
234. Chen, Y.C., J.M. Chen, C.H. Hsu, J.F. Lee, J.W. Yeh, and H.C. Shih, *In-situ synchrotron X-ray absorption studies of $\text{LiMn}_{0.25}\text{Fe}_{0.75}\text{PO}_4$ as a cathode material for lithium ion batteries*. *Solid State Ionics*, 2009. **180**(20-22): p. 1215-1219.
235. Deb, A. and E.J. Cairns, *In situ X-ray absorption spectroscopy - A probe of cathode materials for Li-ion cells*. *Fluid Phase Equilibria*, 2006. **241**(1-2): p. 4-19.
236. Haas, O., A. Deb, E.J. Cairns, and A. Wokaun, *Synchrotron X-ray absorption study of LiFePO_4 electrodes*. *Journal of The Electrochemical Society*, 2005. **152**(1): p. A191-A196.
237. Jensen, K., M. Christensen, C. Tyrsted, and B.B. Iversen, *Real-time synchrotron powder X-ray diffraction study of the antisite defect formation during sub- and*

- supercritical synthesis of LiFePO_4 and $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ nanoparticles*. Journal of Applied Crystallography, 2011. **44**: p. 287-294.
238. Morcrette, M., Y. Chabre, G. Vaughan, G. Amatucci, J.B. Leriche, S. Patoux, C. Masquelier, and J.M. Tarascon, *In situ X-ray diffraction techniques as a powerful tool to study battery electrode materials*. Electrochimica Acta, 2002. **47**(19): p. 3137-3149.
 239. Patoux, S. and C. Masquelier, *Lithium insertion into titanium phosphates, silicates, and sulfates*. Chemistry of Materials, 2002. **14**(12): p. 5057-5068.
 240. Rhodes, K.J., R. Meisner, M. Kirkham, N. Dudney, and C. Daniel, *In situ XRD of thin film tin electrodes for lithium ion batteries*. Journal of The Electrochemical Society, 2012. **159**(3): p. A294-A299.
 241. Trease, N.M., L.N. Zhou, H.J. Chang, B.Y.X. Zhu, and C.P. Grey, *In situ NMR of lithium ion batteries: Bulk susceptibility effects and practical considerations*. Solid State Nuclear Magnetic Resonance, 2012. **42**: p. 62-70.
 242. Hamou, R.F., P.U. Biedermann, A. Erbe, and M. Rohwerder, *Numerical analysis of Debye screening effect in electrode surface potential mapping by scanning electrochemical potential microscopy*. Electrochemistry Communications, 2010. **12**(10): p. 1391-1394.
 243. Hamou, R.F., P.U. Biedermann, A. Erbe, and M. Rohwerder, *Numerical simulation of probing the electric double layer by scanning electrochemical potential microscopy*. Electrochimica Acta, 2010. **55**(18): p. 5210-5222.
 244. Hurth, C., C.Z. Li, and A.J. Bard, *Direct probing of electrical double layers by scanning electrochemical potential microscopy*. Journal of Physical Chemistry C, 2007. **111**(12): p. 4620-4627.

Appendix A: List of abbreviations

1D	one-dimensional
3D	three-dimensional
Al ³⁺	aluminium ions
BET	Brunauer-Emmett-Teller (isotherm)
BuLi	butyllithium
Co	cobalt
CNT	carbon nanotubes
CT	charge transfer
CV	cyclic voltammetric studies / cyclic voltammetry
DEC	diethyl carbonate
DMC	dimethyl carbonate
EC	ethylene carbonate
EDS	energy dispersive spectroscopy
EIS	electrochemical impedance spectroscopy
EMI-TFSI	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
ETMS	electrochemical thermodynamic measurement studies
FE-SEM	field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy

HEV(s)	hybrid electric vehicles
ICP	inductively-coupled plasma (analyses)
Li^+	lithium ions
LIB(s)	lithium ion battery (ies)
LiBOB	lithium bis (oxalato) borate
LiCoO_2	lithium cobalt oxide
LiCoPO_4 (LCP)	lithium cobalt phosphate
LiFePO_4 (LFP)	lithium iron phosphate
LiMnPO_4 (LMP)	lithium manganese phosphate
LiNiPO_4 (LNP)	lithium nickel phosphate
LiPF_6	lithium hexafluorophosphate
OCV	open circuit voltage
PANI	polyaniline
PC	propylene carbonate
PEG	polyethylene glycol
Ppy	polypyrrole
PVP	poly(vinylpyrrolidinone)
SEI	solid electrolyte interface
SEM	scanning electron microscope / microscopy

TEM	transmission electron microscope /microscopy
TGA	thermogravimetric analysis
V ₂ O ₅	vanadium pentoxide
VNF	vanadium pentoxide nanofibers
VUC	urea combustion synthesized vanadium pentoxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Appendix B: List of publications

As first author

1. Cheah, Y.L., R. von Hagen, V. Aravindan, R. Fiz, S. Mathur, and S. Madhavi, *High-rate and elevated temperature performance of electrospun V_2O_5 nanofibers carbon-coated by plasma enhanced chemical vapour deposition*. Nano Energy, 2012.
2. Cheah, Y.L., V. Aravindan, and M. Srinivasan, *Improved elevated temperature performance of Al-intercalated V_2O_5 electrospun nanofibers for lithium-ion batteries*. ACS Applied Materials & Interfaces, 2012. **4**(6): p. 3270-3277.
3. Cheah, Y.L., V. Aravindan, and M. Srinivasan, *Electrochemical lithium insertion behavior of combustion synthesized V_2O_5 cathodes for lithium-ion batteries*. Journal of The Electrochemical Society, 2012. **159**(3): p. A273-A280.
4. Cheah, Y.L., N. Gupta, S.S. Pramana, V. Aravindan, G. Wee, and M. Srinivasan, *Morphology, structure and electrochemical properties of single phase electrospun vanadium pentoxide nanofibers for lithium ion batteries*. Journal of Power Sources, 2011. **196**: p. 6465-6472.
5. Cheah, Y.L., T. Toh, G. Wee, and M. Srinivasan. *Olivine nanofibrous cathodes for lithium ion batteries*. in *Materials Research Society (MRS) Spring 2010*, Proceedings. USA.

In collaboration

1. Aravindan, V., Y.L. Cheah, G. Wee, B.V.R. Chowdari, and S. Madhavi, *Fabrication of high energy density hybrid supercapacitors using electrospun V_2O_5 nanofibers with self-supported carbon nanotube network*. ChemPlusChem, 2012.
2. Aravindan, V., Y.L. Cheah, C.L. Wong, and S. Madhavi, *Effect of LiBOB additive on the electrochemical performance of $LiCoPO_4$* . Journal of The Electrochemical Society, 2012.
3. Chen, J.S., Y.L. Cheah, Y.T. Chen, N. Jayaprakash, M. Srinivasan, Y.H. Yang, and X.W. Lou, *SnO_2 nanoparticles with controlled carbon nanocoating as high capacity anode materials for lithium-ion batteries*. Journal of Physical Chemistry C, 2010.
4. Chen, J.S., Y.L. Tan, C.M. Li, Y.L. Cheah, D. Luan, S. Madhavi, F.Y.C. Boey, L.A. Archer, and X.W. Lou, *Constructing hierarchical spheres from large ultrathin anatase TiO_2 nanosheets with nearly 100% exposed (001) facets for fast reversible lithium storage*. Journal of American Chemical Society, 2010.
5. Wee, G., H.Z. Soh, Y.L. Cheah, S.G. Mhaisalkar, and M. Srinivasan, *Synthesis and electrochemical properties of electrospun V_2O_5 nanofibers as supercapacitor electrodes*. Journal of Materials Chemistry, 2010. **20**: p. 6720-6725.

Note:

All works have been published in the above journals and authors are permitted to reproduce this work in dissertation, with permission from the respective editors and copyrights acts of respective journals. The author of this thesis also acknowledges the permission from other individual authors.