Unveiling the fundamental properties of sulphate based cathodes for next generation lithium ion batteries

Muthiah, Aravind

2018

Muthiah, A. (2018). Unveiling the fundamental properties of sulphate based cathodes for next generation lithium ion batteries. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/73346>

<https://doi.org/10.32657/10356/73346>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**UNVEILING THE FUNDAMENTAL PROPERTIES OF
SULPHATE BASED CATHODES FOR NEXT GENERATION
LITHIUM ION BATTERIES**

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**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU**

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OF SULPHATE BASED CATHODES FOR NEXT
GENERATION LITHIUM ION BATTERIES**

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

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

25 January 2018

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Date

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Abstract

Lithium ion batteries lie at the heart of many of the portable electronics and automobiles in the modern world. By 2025 they will be responsible for storing energy equivalent to 12 times the energy released by the nuclear explosion at Hiroshima during the second World War. Thus, in addition to the high energy density capability of lithium ion batteries, safety assumes special significance. $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M=Fe, Co, Mn, Ni) class of sulphate based cathodes promise to meet both these criteria. High energy density on account of their higher operating voltage owing to the inductive effect of the sulphate group. Safety, due to the thermal stability offered by the covalent S-O bonds preventing oxygen release at high operating potentials.

This thesis enabled an understanding of the electrochemical mechanism in $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode through the x-ray absorption spectroscopy technique. Subsequently, this knowledge was instrumental in unveiling the reversible electrochemical activity of the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}(\text{SO}_4)_2$ analogues at 4.85 V and 5.02 V *vs.* Li, respectively. The redox mechanism was enabled through a combination of high energy ball milling to modify the cathode material and adoption of a novel composition of an electrolyte with sebaconitrile solvent. The study also investigated for the first time the synthesis of new solid solution series of bi-metallic sulphates and their structural, thermal, moisture sensitivity and magnetic properties. The maturity and commercial viability of the $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode was evaluated by assembling an all iron full-cell and demonstrating its electrochemical stability. Finally, a techno-economic comparison of this full-cell with respect to the commercial cathode and anode chemistries was made, to place some perspective on the utility of this class of sulphate based cathodes.

Acknowledgements

As a result of this PhD study, in addition to my research findings, I realise I have ‘found’ a bit more about my own self. And for this I owe an immense debt of gratitude to the following people for their eternal lessons;

Prof Madhavi Srinivasan for her clarity in expectations, patience with failure and decisive approach;

Prof Subodh Mhaisalkar for his vision, strength in execution, faith in people and fervent support to help them fulfil their potential;

Prof Gopinathan Sankar for his honesty and undying passion for science;

Prof John Hanna for his simplicity and frankness of opinion;

Dr. Mark Copley for his practicality and being a mentor as well as a friend;

Dr. Timothy Hyde for his meticulous attention to detail;

Dr. Sarah Ball for her humility, organisation and sense of purpose;

Dr. Tom Baikie for his patience with teaching and ability to put people at ease;

Dr. Vanchiappan Aravindan for his steadfast pursuit without being distracted;

Dr. Mani Ulaganathan for his cheerfulness and strength under duress;

Dr. Shubha Nageswaran for her discipline and sense of planning;

Dr. Arun Nagasubramanian and Dr. Iulius Markovits for their display of expertise without pretension and support without seeking return;

Dr. Vivek Nair and Dr. Wong Chui Ling for their enthusiastic approach to ideas;

Dr. Rohit Satish for his willingness to dive to the depths in search of knowledge;

Dr. Vidhi Patel for her selflessness and genuine friendship;

Shen Nan for the confidence in his approach;

Eldho, Phuong, Peter and Rodney for their maturity and responsibility;

Fan Yanliang for her sincerity in emotion and strong will;

Brother for his love for family and tireless demeanour;

Mother for her balance in strong words and loving support;

Father for inspiring me to meditate;

And God for all of the above and all the rest.

Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	v
Table Captions	xi
Figure Captions	xiii
Abbreviations	xxi
1 Introduction.....	1
1.1 Background and Significance.....	2
1.2 Problem Statement	2
1.3 Objectives and Scope	6
1.4 Dissertation Overview	7
1.5 Findings and Outcomes	9
1.6 References	10
2 Literature Review.....	13
2.1 Lithium Ion Batteries	14
2.1.1 Background	16
2.1.2 Working	17
2.2 Current Status and Applications of Lithium Ion Batteries	18

2.3	Cathode Materials for Lithium Ion Batteries	20
2.3.1	Current Status of Research.....	20
2.3.2	Commercial Cathode Materials	23
2.3.3	Polyanionic cathode materials	24
2.4	Sulphate Based Cathode Materials.....	29
2.5	Electrolytes for High Voltage Cathodes.....	35
2.6	Conclusion.....	39
2.7	References	39
3	Experimental Methodology	45
3.1	Synthesis.....	46
3.1.1	High Energy Ball Milling	46
3.1.2	Solid State Synthesis.....	47
3.2	Material Characterisation	49
3.2.1	X-ray Diffraction (XRD)	49
3.2.2	X-ray Absorption Spectroscopy (XAS)	50
3.2.3	Scanning Electron Microscopy (SEM)	53
3.2.4	Electron Dispersive X-Ray(EDX) Spectroscopy	54
3.2.5	X-ray Photoelectron Spectroscopy (XPS)	55
3.2.6	Nuclear Magnetic Resonance(NMR) Spectroscopy	56
3.2.7	Thermal Analysis	57
3.2.8	SQUID Magnetometry	58
3.2.9	Three Electrode Cyclic Voltammetry	60
3.3	Device Characterisation	61
3.3.1	Electrochemical Cell Assembly	61
3.3.2	Cyclic Voltammetry (CV).....	63
3.3.3	Galvanostatic Cycling (GCD).....	64
3.3.4	Electrochemical Impedance Spectroscopy (EIS).....	65
3.4	References	66

4	Lithium Iron Sulphate Cathode – Study of the Mechanism and Effect of Binders and Carbon Additives	71
4.1	Introduction	72
4.2	Experimental Methods	73
4.2.1	Synthesis	73
4.2.2	Electrochemical Testing.....	74
4.2.3	X-ray Absorption Spectroscopy (XAS)	75
4.3	Results and Discussion.....	75
4.3.1	Structural study by X-Ray Diffraction (XRD) Analysis.....	75
4.3.2	Electrochemical Characterisation	77
4.3.3	XAS Analysis.....	77
4.3.4	Cycling Performance of Different Binders	85
4.3.5	Cycling Performance of Different Carbon Additives	88
4.3.6	Scanning Electron Microscopy	89
4.3.7	Thermal Analysis	89
4.3.8	Electrochemical Analysis.....	90
4.4	Conclusion.....	94
4.5	References	94
5	Fundamental Properties of Bi-metallic Sulphates $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2 = \text{Co, Mn, Ni}$).....	99
5.1	Introduction	100
5.2	Experimental Methods	101
5.2.1	Synthesis	101
5.2.2	Structural Analysis.....	101
5.2.3	Thermal Analysis	102
5.2.4	Moisture Sensitivity Analysis	102
5.2.5	Nuclear Magnetic Resonance Spectroscopy	102
5.2.6	SQUID Magnetometry	103

5.3	Results and Discussion.....	103
5.3.1	Structural Analysis.....	103
5.3.2	Thermal Stability	109
5.3.3	Sensitivity to Moisture	115
5.3.4	⁷ Li NMR Analysis.....	121
5.3.5	SQUID Magnetic Measurements	124
5.4	Conclusion.....	131
5.5	References	131
6	Unveiling the Electrochemical Activity of High Voltage Sulphates	137
6.1	Introduction	138
6.2	Experimental Methods	139
6.2.1	Three electrode Setup	139
6.2.2	Electrolyte Preparation.....	139
6.2.3	Electrode Preparation, Assembly and Testing	139
6.2.4	XAS and XPS Analysis	140
6.3	Results and Discussion.....	141
6.3.1	Electrochemical Analysis.....	141
6.3.2	Understanding the Mechanism of Li ₂ Mn(SO ₄) ₂	148
6.4	Conclusion.....	154
6.5	References	155
7	All Iron Full-Cell – Electrochemical Performance and Economic Comparison.....	157
7.1	Introduction	158
7.2	Experimental Methods	160
7.2.1	Material Synthesis.....	160
7.2.2	Electrode Preparation.....	161
7.2.3	Cell Assembly	161

7.3	Results and Discussion.....	162
7.3.1	Electrochemical Characterisation	162
7.3.2	Cost Estimation and Comparison of All Iron Full-cell.....	165
7.4	Conclusion.....	173
7.5	References	174
8	Conclusion and Future Work	177
8.1	Perspective	178
8.2	Summary of Results	179
8.2.1	Lithium Iron Sulphate – Electrochemical mechanism and effect of additives	179
8.2.2	Synthesis of a novel solid solution series of bi-metallic sulphates and their fundamental properties	180
8.2.3	Unveiling the electrochemical activity of Mn and Co based sulphates.....	180
8.2.4	All Iron full-cell based on a sulphate cathode	181
8.3	Novel Contributions	182
8.3.1	Scientific Contribution.....	182
8.3.2	Technological significance	182
8.4	Future Work	183
8.4.1	Electrochemical analysis of bi-metallic sulphates	183
8.4.2	Analysis of magnetic properties of solid solution series	184
8.4.3	Material modification.....	184
8.4.4	Sulphates for sodium ion batteries (NIBs).....	185
8.5	Concluding Remarks	186
8.6	References	186

Table Captions

Table 2-1: Currently available battery chemistries [3]	14
Table 2-2: Current status of cathode materials [14-16]	21
Table 2-3: Characteristics of various currently used commercial cathode materials where LCO is LiCoO_2 , LMO is LiMn_2O_4 , NCA is $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, NMC is $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$, and LFP is LiFePO_4 [26]	23
Table 2-4: Pauling electronegativity of certain elements [35-37]	29
Table 2-5: Experimental and computationally calculated operational potentials	33
Table 2-6: Current status of LIB electrolytes [70]	36
Table 2-7: Additives currently used and their properties [71]	38
Table 4-1: Details of electrodes subjected to ex-situ XANES/EXAFS analysis	78
Table 4-2: Data obtained from analysis of XAS parameters based on Fe - K edge for LFS with PVDF and PAN binders	82
Table 4-3: Decrease in discharge capacity from initial charge rate for different carbon additives	93
Table 5-1: EDX measurements showing the relative percentage concentration of the respective elements	106
Table 5-2: EDX measurements showing the relative percentage concentration of the respective elements in $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}(\text{SO}_4)_2$	107
Table 5-3: EDX measurements showing the relative percentage concentration of the respective elements in $\text{Li}_2\text{Ni}_x\text{Co}_{1-x}(\text{SO}_4)_2$	109
Table 5-4: Decomposition products of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ when exposed to relative humidity of 45-50 % quantitatively determined using Reitveld refinement of XRD patterns	117
Table 5-5: Decomposition products of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ when exposed to relative humidity of 45-50 % quantitatively determined using Reitveld refinement of XRD patterns	117

Table 5-6: Decomposition products of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ when exposed to relative humidity of 45-50 % quantitatively determined using Reitveld refinement of XRD patterns	119
Table 5-7: List of peak positions from ^7Li NMR spectra.....	124
Table 5-8: Neel temperature of Ni complexes	130
Table 6-1: Binding energies of main peaks of Mn-2p XPS spectra for 3 different electrodes	151
Table 7-1: Comparison of the most popular cathodes with LFS and anodes with Fe_2O_3 [18, 20, 21]	170

Figure Captions

Figure 1-1: Lithium Battery usage by application in 2025[2]	2
Figure 1-2: Current status of positive electrode materials for LIBs [8].....	3
Figure 1-3: Fe-based polyanionic positive electrodes [15]	5
Figure 1-4: Popular high voltage cathodes and their comparison with $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of Sulphates [9, 24]	5
Figure 2-1: Comparison of different battery chemistries in terms of volumetric and gravimetric energy density [6] (where PLiON – Polymer Lithium ion).....	16
Figure 2-2: The working of LIBs [2]	17
Figure 2-3: Lithium ion battery markets in 2015(left) and 2025(right) [11]. Other applications refer to medical devices, power tools, gardening tools, e-bikes, etc.	18
Figure 2-4: Requirements of LIB applications [10].....	19
Figure 2-5: Comparison of practical energy density of batteries today with gasoline [2].....	19
Figure 2-6: Open circuit voltage in terms of orbital fields [34].....	25
Figure 2-7: Decrease in redox voltage with coordination number [34].....	26
Figure 2-8: Higher charge on the P^{5+} cation lowers the magnitude of Madelung electric field [34].....	27
Figure 2-9: Crystal field splitting of the M^{2+} cations [34]	28
Figure 2-10: Higher number of resonance forms results in a more covalent polyanion [34].....	29
Figure 2-11: Polyanionic cathodes based on Fe [17].....	30
Figure 2-12: Polymorphs of LiMSO_4F where Blue - MO_4F_2 octahedra, Green - SO_4 tetrahedra, Yellow - Lithium atoms [22]	31
Figure 2-13: (a) Structure and (b) electrochemical properties of LiFeSO_4OH phase where Green - SO_4 tetrahedra, Blue - $\text{FeO}_3(\text{OH})_3$ octahedra, Yellow - Li, Light blue - OH and Red - O [53]	31

Figure 2-14: (a) Structure and (b) charge-discharge plot of monoclinic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ where Blue - FeO_6 octahedra , Green - SO_4 tetrahedra, Yellow - Lithium [22]	32
Figure 2-15: Sulphate based cathodes in comparison to layered oxide and other polyanionic cathodes.....	33
Figure 2-16: Voltage and specific capacity of popular high voltage cathode materials for LIBs [61].....	34
Figure 2-17: Voltage compatibility requirement of different components in a cell [69].....	36
Figure 3-1: Spex 8000D Mixer Mill	47
Figure 3-2: Carbolite Tube Furnace (left) and Muffle Furnace (right).....	48
Figure 3-3: Sample spectra of Fe-K edge indicating the two major sections of a standard XAS spectrum	51
Figure 3-4: Emission of various electrons and electromagnetic waves upon interaction of electrons with matter [17].....	53
Figure 3-5: Energy contribution from electrons in different orbitals of a Lead atom [19].....	56
Figure 3-6: The relationship between magnetisation and applied magnetic field (left) and between magnetic susceptibility and temperature (right)[28].....	60
Figure 3-7: Technical drawing of a Swagelok [®] cell[29]	63
Figure 3-8: Typical EIS spectrum of a Lithium Ion Battery representing charge transfer (R_{CT}) and ohmic (R_Ω) resistances	66
Figure 4-1: XRD pattern of as synthesised monoclinic LFS powder compared to the XRD pattern reported in Reynaud et al.[1]	76
Figure 4-2: Comparison of XRD patterns of LFS with no binder, PVDF and PAN indicates that addition of fluorinated (PVDF) and non-flourinated (PAN) binders does not alter the monoclinic LFS structure	76
Figure 4-3: The first galvanostatic charge-discharge cycle of LFS showing oxidation and reduction plateaus at 3.98 V and 3.75 V vs. Li respectively. Seven points were chosen along the charge-discharge curve for ex-situ XAS testing.	77

Figure 4-4: Normalized XANES plots of the pre-edge peaks for PVDF binder are seen in 1 and 2 and for PAN in 3 and 4. In all peaks a characteristic +2 oxidation state is seen at 7112 eV and a slightly broader peak at 7114 eV representing the +3 oxidation state.....	79
Figure 4-5: XANES plots of the absorption Fe K-edge for PVDF binder are seen in 1 and 2 and for PAN in 3 and 4. The charge process (1 and 3) shows a decrease in peak intensity while the discharge process (2 and 4) shows a decrease in peak intensity.....	80
Figure 4-6: Computed first derivative plots of the XANES data for PVDF binder are seen in 1 and 2 and for PAN in 3 and 4. In 1 and 3, the rightward shift of the peak X to Y upon charging indicates an increase in oxidation state with increasing Fe-K Edge energy. In 2 and 4 the reverse phenomena of 1 and 3 are observed during discharge indicating the presence of a redox couple of Fe.....	81
Figure 4-7: Literature[1] derived crystal structure of the monoclinic LFS with FeO ₆ octahedra (brown), SO ₄ tetrahedra (yellow) and Lithium ions (green) indicating the unit cell.....	82
Figure 4-8: Changes in Fe-O bond lengths observed through first shell analysis of ex-situ XAFS data and corresponding oxidation state of Fe estimated based on bond length. Upon charging the Fe-O bond length was found to decrease from 2.09 Å to 1.98 Å, and subsequently upon discharge was found to return to a bond length of 2.11 Å when the PVDF binder was used. When PAN was used, a similar trend follows.	84
Figure 4-9: Cycling and rate performance of LFS without binder compared to performances with PVDF and PAN binders shows that at low C-rates of C/15, the cycling is consistent with high coulombic efficiency but upon moving to higher C-rates, the system with PVDF or PAN binders retains only about 29% of discharge capacity compared to the system without any binder.....	85
Figure 4-10: Comparison of CV for the 1 st and 2 nd cycles of LFS with and without binders. It shows maximum current flow for system without binder, while PVDF shows the least current flow.....	87

Figure 4-11: Electrochemical Impedance Spectroscopy of LFS with and without binders. Indicates a large charge transfer resistance, RCT for PVDF compared to that for PAN and the system with no binder. PVDF also exhibits a high double layer capacitance compared to PAN	88
Figure 4-12: SEM images of the four carbon additives used: a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene	89
Figure 4-13: TGA curves of the four carbon additives used; a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene	90
Figure 4-14: GCD curves of the four carbon additives used: a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene	91
Figure 4-15: Cycling performance of the four carbon additives used; a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene	92
Figure 4-16: Rate performance of the four carbon additives used; a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene	93
Figure 5-1: Powder XRD patterns of $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ solid solution series	104
Figure 5-2: Monoclinic structure of: Left - $\text{Li}_2\text{Mn}(\text{SO}_4)_2$, Right - $\text{Li}_2\text{Co}(\text{SO}_4)_2$. where Green – Lithium ions, Beige – MnO_6 octahedra, Magenta - CoO_6 octahedra, Yellow – SO_4 tetrahedra	104
Figure 5-3: Variation of the lattice parameters, a, b, c, β , and unit cell volume V with x in $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ active materials powders	105
Figure 5-4: XRD patterns of $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ solid solution series	107
Figure 5-5: XRD patterns of $\text{Li}_2\text{Ni}_x\text{Co}_{1-x}(\text{SO}_4)_2$ solid solution series	108
Figure 5-6: Thermal stability analysis of the prepared samples using TGA-DSC-MS	110
Figure 5-7: Thermally induced structural changes in $\text{Li}_2\text{Co}(\text{SO}_4)_2$ when heated between 550 °C and 650 °C	111
Figure 5-8: Comparison of XRD pattern of precursor to reference patterns of α - CoSO_4 (Pnma)[24] and β - CoSO_4 (Cmcm)[25]	112

Figure 5-9: Structural representations of the different polymorphs of CoSO_4 modelled using Vesta software[28] (Left - $\alpha\text{-CoSO}_4$ (Pnma) and Right - $\beta\text{-CoSO}_4$ (Cmcm)) where magenta polyhedra represent the - CoO_6 octahedra with the SO_4 units shown as yellow tetrahedral	113
Figure 5-10: Thermally induced structural changes in $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ when heated between 550 °C and 625 °C resulting in $\text{Li}_2\text{Mn}_2(\text{SO}_4)_3$ (ref. pattern [29]) and Li_2SO_4 (ref. pattern [30])	114
Figure 5-11: Thermally induced structural changes in $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ when heated between 550 °C and 650 °C	115
Figure 5-12: Moisture induced structural changes in $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ in an atmosphere of 45-50% Relative Humidity	116
Figure 5-13: Variation of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ moisture content during analysis.	118
Figure 5-14 - Graphs of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ moisture content during analysis.	120
Figure 5-15: NMR spectra (left) and isotropic shift (right) comparison of $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$	121
Figure 5-16: NMR spectra (left) and isotropic shift (right) comparison of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$, $\text{Li}_2\text{Co}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}_{0.5}\text{Co}_{0.5}(\text{SO}_4)_2$	123
Figure 5-17: NMR spectra (left) and isotropic shift (right) comparison of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$	124
Figure 5-18: Variation of M vs. H over 3 different temperatures 10,50 and 100 K	125
Figure 5-19: Field dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$, measured at 10, 50 and 100 in magnetic field of range from 0 to 50 kOe	126
Figure 5-20: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ measured under ZFC and FC conditions with a field of 1 kOe between 10 K to 300 K back to 10 K	127
Figure 5-21: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ measured under ZFC and FC conditions	127
Figure 5-22: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ measured under ZFC and FC conditions	128

Figure 5-23: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ measured under ZFC and FC conditions	129
Figure 5-24: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Co}_{0.5}\text{Ni}_{0.5}(\text{SO}_4)_2$ measured under ZFC and FC conditions	129
Figure 5-25: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ measured under ZFC and FC conditions	129
Figure 5-26: Bethe–Slater curve[40]	130
Figure 6-1: Three electrode CV evaluation of Propylene Carbonate (PC) and Sebaconitrile in the presence of a Pt reference electrode, Glassy Carbon working electrode and Lithium counter electrode	141
Figure 6-2: Three electrode CV evaluation of Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) and Sebaconitrile in the presence of a Pt reference electrode, Glassy Carbon working electrode and Lithium counter electrode	142
Figure 6-3: CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (25:25:50) vol%	144
Figure 6-4: CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (15:15:70) vol%	144
Figure 6-5: CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (5:5:90) vol%	145
Figure 6-6: Comparison of the CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ for varying concentration of sebaconitrile from 50, 70 and 90 vol%	146
Figure 6-7: CV of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (25:25:50) vol%	147
Figure 6-8: Top: Mn K-edge XANES spectra showing the Fe absorption edge of the uncharged, fully charged and fully discharged states compared to Mn references, Bottom: Computed first derivative plots of the XANES data indicating the Mn absorption edge position of the 2 different oxidation states of the references are at 6548 eV for Mn^{+2} and 6553 eV for Mn^{+3}	149
Figure 6-9: Manganese Mn-2p ex-situ XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes	151

Figure 6-10: Sulphur S-2p ex-situ XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes	152
Figure 6-11: Oxygen O-1s ex-situ XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes	153
Figure 6-12: Lithium Li-1s ex-situ XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes	154
Figure 7-1: Battery market in 2015 by technology[1]	158
Figure 7-2: GCD test of a $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ full-cell showing a specific capacity of 58 mAh.g^{-1} in an operational window of 0.4 V to 3.5 V	163
Figure 7-3: Cycling Performance of $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ full-cell over 25 cycles at C/15.....	163
Figure 7-4: Rate Performance of $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ full-cell over 55 cycles.	164
Figure 7-5: Production cost of LFP	166
Figure 7-6: Cost comparison of popular cathode materials with LFS [18]	166
Figure 7-7: Cost comparison of popular cathode materials with Fe_2O_3 [20, 21]	167
Figure 7-8: Comparison of different cathode technologies in terms of their specific capacity and operating potential	168
Figure 7-9: Comparison of different anode technologies in terms of their specific capacity and operating potential	168
Figure 7-10: Comparison of different cathode technologies in terms of specific energy density and cost per unit energy stored	169
Figure 7-11: Comparison of full-cells in terms of the electrode mass per unit energy stored.....	171
Figure 7-12: Comparison of full-cells in terms of the electrode cost per unit energy stored.....	172
Figure 8-1: A perspective of operational $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of sulphates in comparison to other popular high voltage cathode materials [6, 7]. The red stars indicate the focus of this work	178

Figure 8-2: Contribution of this work compared to other high voltage olivines	
.....	183

Abbreviations

CNT	Carbon Nano Tube
CV	Cyclic Voltammetry
DLS	Diamond Light Source
DMC	Dimethyl Carbonate
DSC	Differential Scanning Calorimetry
EC	Ethylene Carbonate
EDX	Electron Dispersive X-ray spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EV	Electric Vehicles
EXAFS	Extended X-ray Absorption Fine Structure
FC	Field Cooled
GCD	Galvanostatic Charge-Discharge
Gr	Graphite
HEV	Hybrid Electric Vehicles
LCO	LiCoO_2
LFP	LiFePO_4
LFS	$\text{Li}_2\text{Fe}(\text{SO}_4)_2$
LIB	Lithium Ion Battery
LMO	LiMn_2O_4
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$
MS	Mass Spectroscopy
MWCNT	Multi Walled Carbon Nano Tube
NCA	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
NEXAFS	Near Edge X-ray Absorption Fine Structure

NMC	$\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$
NMR	Nuclear Magnetic Resonance
PAN	Poly acrylonitrile
PC	Propylene Carbonate
PHEV	Plug-in Hybrid Electric Vehicles
PVDF	Polyvinylidene Fluoride
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscopy
SQUID	Superconducting Quantum Interference Device
SSLS	Singapore Synchrotron Light Source
SWCNT	Single Walled Carbon Nano Tube
TEM	Transmission Electron Microscope
TGA	Thermo-Gravimetric Analysis
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZFC	Zero Field Cooled

Chapter 1

Introduction

This chapter summarises the work reported in this thesis in five brief parts. The first part provides an understanding of the present landscape of the lithium battery market and the performance targets for applications over the next decade. The second section defines the challenges and gaps in current research that need to be faced in meeting the requirements of battery applications. The third section outlines the objective of this work and the key areas of focus. The fourth section provides an overview of the dissertation and summarises the primary results in each chapter. The final section details the outcomes and novelty of this work and concludes the chapter.

1.1 Background and Significance

Lithium ion battery (LIB) technology was commercialised by Exxon first in 1976 for small watches and other devices [1]. Over the past four decades it has slowly but surely seeped into every aspect of our lives from mobile phones to hearing aids to inter-continental airlines. Today it is an industry worth over 16 billion dollars and poised to hit 36 billion dollars within the next 8 years by 2025 [2]. In terms of energy, LIBs sold worldwide in 2025 alone will be responsible for storage of 215 GWh. This is equivalent to 12 times the energy contained in the nuclear explosion that destroyed Hiroshima [3]. Since more than 80% of these devices will be in automobiles or in personal gadgets, their safety becomes of paramount importance [4] while ensuring they deliver the required amount of energy. Thus, safe LIB chemistries that are capable of high energy densities are the need of the hour.

Figure 1-1: Lithium Battery usage by application in 2025[2]

1.2 Problem Statement

The energy density of an LIB is directly proportional to two quantities, the charge capacity and potential of operation of the cell [5]. Present LIBs have demonstrated operability at 3.7 V at a capacity of 180 mAh.g⁻¹ [6]. Therefore, higher potential of operation is favourable as it leads to higher energy density of

the cell. The potential of operation of a cell, however, is determined by the voltage capability of the positive electrode or cathode material of the LIB[5]. Also, in an LIB, the cathode contributes to 50% of the mass of the cell while the anode contributes to only 20%.[7] This indicates that research into cathode materials allows for greater gain in cell energy density and makes the case for a new class of cathodes that exhibit high voltages.

There are a number of cathode materials that have been evaluated so far as illustrated in Figure 1-2. The cathodes used in LIBs commercially currently are oxides based on spinel or layered oxide structures. However, all of these provide low voltages (below 4 V). With polyanionic compounds such as olivines, olivine fluorides and silicates we have the opportunity to push the operating potential beyond the 5 V mark.

Figure 1-2: Current status of positive electrode materials for LIBs [8]

The adoption of cathode materials with voltage greater than 5V brings in a whole new set of challenges at the device level and requires that the issues below be addressed [9]:

1. Stability and cyclability of cathode and anode material is maintained over battery lifetime
2. Consistent performance even at temperatures of 60°C

3. Stable electrolyte with the ability to withstand up to preferably 6V
4. Mandatory thermal stability to ensure safety and minimise thermal runaway

Fundamental research on cathodes with polyanionic groups ($(\text{PO}_4)^{3-}$, $(\text{SiO}_4)^{4-}$, $(\text{SO}_4)^{2-}$)[10-12] over the past two decades has uncovered several advantages of these materials over the oxides;

1. The polyanion utilises the inductive effect[13, 14] to allow control over the redox potential offered by the $\text{M}^n/\text{M}^{(n-1)+}$ redox couple thereby enhancing potentials in comparison to oxides.
2. They exhibit extremely stable frameworks that fulfill the requirements of cyclability and safety.
3. Any given structure allows for a diverse set of structures and flexibility toward substitution of the cation and anion.[10]

It is these advantages of polyanionic LIBs cathodes that make them the appropriate family of materials for breaching the 5 V barrier. The work on polyanionic LIBs began in the late 90s[13, 14] and has since then spawned a variety of new materials. Industrially, iron (Fe) based polyanionic LIBs have been sought after because of their relative abundance and has resulted in LiFePO_4 positive electrodes being commercialised. Figure 1-3 illustrates how this search for better Fe based cathode materials has spawned a variety of compounds. Amongst the polyanionic compounds, the highest voltage has been exhibited by sulphates and fluoro-sulphates primarily due to the the inductive effect [11, 12, 14] caused by the high electronegativity of the SO_4^{2-} group.

Figure 1-3: Fe-based polyanionic positive electrodes [15]

While the fluorosulphates have been difficult and expensive to synthesise [16-19] the rather straightforward solid state synthesis of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ with similar operating potential (3.83 V vs. Li) [15, 20-22] makes it a viable material to translate commercially. Mn, Co and Ni analogues of this class of sulphates are expected to show higher operating potentials due to the effect of the nature of their d-orbital filling [23] and have been computationally predicted [24] to show the potentials highlighted in red(*) in Figure 1-4. These are on par with other popular high voltage cathode materials albeit of lower specific capacity.

Figure 1-4: Popular high voltage cathodes and their comparison with $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of Sulphates [9, 24]

Despite, the qualities of high voltage capability and high thermal stability of these sulphate based polyanionic cathodes, they have not shown any electrochemical activity experimentally [11, 15, 24-26]. Thus, this work seeks to utilise the high voltage capability of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of sulphate based polyanionic compounds to develop Mn, Co and Ni analogues to enable sulphate based LIBs to achieve high voltages in the 5 V range.

1.3 Objectives and Scope

The aim of this work is to understand the fundamental properties and electrochemical mechanism of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of sulphates so as to enable the electrochemical activity of the high voltage Mn, Co and Ni analogues.

In order to achieve the aim listed above, the objectives and scope of this work are listed as follows:

1. Study the electrochemical operating mechanism of electrochemically active $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ and understanding the effect of binders and carbon additives on performance

- Synthesis of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$, exploration and setting up of baseline electrochemical studies to enable effective testing of analogues of $\text{Li}_2\text{M}(\text{SO}_4)_2$ in the rest of the work
- Understanding the electrochemical mechanism operating in the $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ through the novel use of X-ray absorption spectroscopy technique
- Study the effects of binder on the $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ in a half cell as previous works have always avoided its usage
- Study the effects of carbon additives on the performance of the $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode material

2. Synthesise a novel solid solution series of bi-metallic sulphates and understand their fundamental properties

- Synthesis of $\text{Li}_2\text{M}(\text{SO}_4)_2$ ($\text{M}=\text{Co}, \text{Mn}$ and Ni) and a novel solid solution series $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2=\text{Co}, \text{Mn}$ and Ni) and detailed study of their structural properties
- Thermal analysis of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ to determine their thermal limitations and study of their sensitivity and response to humidity
- Fundamental understanding of the structural properties of this class of materials through magnetic measurements and nuclear magnetic resonance spectroscopy

3. Enable the electrochemical activity of Mn and Co based sulphates

- Development of a new composition of electrolyte to extend the operational voltage window and testing its electrochemical properties
- Modification to $\text{Li}_2\text{M}(\text{SO}_4)_2$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$) cathode materials to enable their electrochemical activity in the new electrolytes
- Analysis of the mechanism of electrochemical operation in these cathodes using X-ray absorption spectroscopy in order to compare with $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ and additional technique of X-ray photo-electron spectroscopy

4. Assemble and test a full-cell based on the sulphate synthesised

- Assembly of a novel full-cell consisting of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ as a cathode and Fe_2O_3 as anode thereby forming an all Iron based lithium ion battery
- Study of the operation of the full-cell through electrochemical tests, cycling and rate performance
- Techno-economic evaluation of the novel system with traditional LIB cathodes and anodes to understand use cases and viability of commercial application

1.4 Dissertation Overview

The thesis addresses the fundamental properties of $\text{Li}_2\text{M}(\text{SO}_4)_2$ ($\text{M}=\text{Fe}, \text{Co}, \text{Mn}, \text{Ni}$) sulphate based cathodes and their significance as candidates for use in next

generation lithium ion batteries.

Chapter 1 introduces the background of lithium ion battery cathodes and the trend of research in this field is briefly explained. The limitations of existing cathode technology are highlighted, providing the rationale for this research work while outlining the objectives and scope of this work.

Chapter 2 reviews the literature concerning lithium battery cathodes and their applications. It introduces the working principle and characteristics of lithium batteries. It explains, in detail, the need for high voltage cathodes and the different factors that determine the high voltage capability of a cathode. It describes the different types of cathode materials and electrolytes tested thus far and why specifically sulphates are good candidates. The chapter finally outlines the research gaps in current sulphate based cathodes that shaped the objectives of this thesis.

Chapter 3 describes the various characterisation techniques used in this work from both the materials as well as the device perspective. Experimental procedures for the synthesis of novel materials, characterisation of materials and fabrication of electrodes for the batteries have been detailed.

Chapter 4 focuses on $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ based cathodes and provides a comprehensive study of its electrochemical properties. The mechanism of operation of the electrode is detailed through X-ray Absorption Spectroscopy studies. The electrochemical effect of binders and carbon additives on the material have also been elucidated as a step towards practical use of the material.

Chapter 5 investigates the fundamental structural, thermal and magnetic properties of the Co, Mn and Ni analogues of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of sulphates. It describes the synthesis of a novel solid solution series of these compounds and

their structural variation upon substitution. This chapter also reports the pathways of degradation of these cathode materials when exposed to humidity.

Chapter 6 uncovers the electrochemical properties of Co and Mn in this class of sulphates for the first time. Through X-ray photoelectron spectroscopy and X-ray absorption spectroscopy studies, the reversible electrochemical mechanism of these compounds is detailed. The chapter also describes the evaluation of a new combination of electrolytes required to explore the electrochemical activity of the compounds in an extended voltage window.

Chapter 7 reports a novel full-cell system consisting of positive and negative electrodes both based on Iron. The all Iron full-cell proceeds to demonstrate the functioning of the cell in a voltage window beyond 2 V with a non-carbonaceous anode. The technology and economics of the cell is then evaluated with other commercial LIB cathode and anodes.

Chapter 8 provides a general conclusion of the findings of this study and future recommendations to enable sulphate based materials to achieve acceptance as mainstream battery materials.

1.5 Findings and Outcomes

This study had the following novelties:

1. Understanding the electrochemical mechanism of a sulphate based material, $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ through X-ray Absorption Spectroscopy. The study served to benchmark the mode of operation of these class of sulphates while also investigating the effects of addition of fluorinated and non-fluorinated binders to the electrode.
2. Synthesis of a novel solid solution series of bi-metallic sulphates $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M} = \text{Co}, \text{Mn}$ and Ni) and understanding their structural, thermal and magnetic properties. These studies in addition to

the moisture sensitivity analyses aid in building awareness of the challenges to commercial application of these materials.

3. Unveiling the reversible electrochemical activity in Mn and Co through a combination of mechanical processing of the material by milling and incorporation of a novel composition of electrolyte that allows for electrochemical testing in an extended voltage window. The *ex-situ* X-ray Absorption Spectroscopy and X-ray Photoelectron Spectroscopy studies to determine the mechanism of operation were also novel in their application to these materials.
4. Assembly and testing of a novel all iron full-cell consisting of a $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode and Fe_2O_3 anode was successfully demonstrated. The techno-economic comparison of such a cell with commonly used LIB cathodes and anodes was carried out to evaluate the pros and cons of the full cell.

1.6 References

- [1] M. S. Whittingham, "Lithium Batteries and Cathode Materials," *Chemical Reviews*, vol. 104, pp. 4271-4302, 2004/10/01 2004.
- [2] C. Pillot, "The Rechargeable Battery Market and Main Trends 2015-2025," 2016.
- [3] E. Ochiai, *Hiroshima to Fukushima*: Springer, 2016.
- [4] G. Jeong, Y.-U. Kim, H. Kim, Y.-J. Kim, and H.-J. Sohn, "Prospective materials and applications for Li secondary batteries," *Energy & Environmental Science*, vol. 4, pp. 1986-2002, 2011.
- [5] A. Kraytsberg and Y. Ein - Eli, "Higher, Stronger, Better... A Review of 5 Volt Cathode Materials for Advanced Lithium - Ion Batteries," *Advanced Energy Materials*, vol. 2, pp. 922-939, 2012.
- [6] G. E. Blomgren, "The development and future of lithium ion batteries," *Journal of The Electrochemical Society*, vol. 164, pp. A5019-A5025, 2017.
- [7] A. Kraytsberg and Y. Ein-Eli, "Higher, Stronger, Better ... A Review of 5 Volt Cathode Materials for Advanced Lithium-Ion Batteries," *Advanced Energy Materials*, vol. 2, pp. 922-939, 2012.
- [8] S. B. Chikkannanavar, D. M. Bernardi, and L. Liu, "A review of blended cathode materials for use in Li-ion batteries," *Journal of Power Sources*, vol. 248, pp. 91-100, 2014.

- [9] C. Julien and A. Mauger, "Review of 5-V electrodes for Li-ion batteries: status and trends," *Ionics*, vol. 19, pp. 951-988, 2013.
- [10] C. Masquelier and L. Croguennec, "Polyanionic (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries," *Chemical Reviews*, vol. 113, pp. 6552-6591, 2013.
- [11] G. Rousse and J.-M. Tarascon, "Sulfate-Based Polyanionic Compounds for Li-Ion Batteries: Synthesis, Crystal Chemistry, and Electrochemistry Aspects," *Chemistry of Materials*, vol. 26, pp. 394-406, 2013.
- [12] P. Barpanda, "Sulfate Chemistry for High - Voltage Insertion Materials: Synthetic, Structural and Electrochemical Insights," *Israel Journal of Chemistry*, vol. 55, pp. 537-557, 2015.
- [13] A. Manthiram and J. Goodenough, "Lithium insertion into $\text{Fe}_2(\text{MO}_4)_3$ frameworks: Comparison of $\text{M} = \text{W}$ with $\text{M} = \text{Mo}$," *Journal of Solid State Chemistry*, vol. 71, pp. 349-360, 1987.
- [14] A. Manthiram and J. Goodenough, "Lithium insertion into $\text{Fe}_2(\text{SO}_4)_3$ frameworks," *Journal of Power Sources*, vol. 26, pp. 403-408, 1989.
- [15] M. Reynaud, "Design of new sulfate-based positive electrode materials for Li- and Na-ion batteries," Ph.D., Materials Science, Université de Picardie Jules Verne, 2013.
- [16] P. Barpanda, M. Ati, B. C. Melot, G. Rousse, J. N. Chotard, M. L. Doublet, *et al.*, "A 3.90 V Iron-Based Fluorosulphate Material For Lithium-Ion Batteries Crystallizing In The Triplite Structure," *Nature Materials*, vol. 10, pp. 772-779, 2011.
- [17] N. Recham, J.-N. Chotard, L. Dupont, C. Delacourt, W. Walker, M. Armand, *et al.*, "A 3.6 V Lithium-Based Fluorosulphate Insertion Positive Electrode for Lithium-Ion Batteries," *Nature Materials*, vol. 9, pp. 68-74, 2010.
- [18] M. Ati, M. T. Sougrati, N. Recham, P. Barpanda, J.-B. Leriche, M. Courty, *et al.*, "Fluorosulfate positive electrodes for Li-ion batteries made via a solid-state dry process," *Journal of The Electrochemical Society*, vol. 157, pp. A1007-A1015, 2010.
- [19] M. Ati, W. T. Walker, K. Djellab, M. Armand, N. Recham, and J.-M. Tarascon, "Fluorosulfate positive electrode materials made with polymers as reacting media," *Electrochemical and solid-state letters*, vol. 13, pp. A150-A153, 2010.
- [20] L. Lander, M. Reynaud, J. Carrasco, N. A. Katcho, C. Bellin, A. Polian, *et al.*, "Unveiling the electrochemical mechanisms of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ polymorphs by neutron diffraction and density functional theory calculations," *Physical Chemistry Chemical Physics*, vol. 18, pp. 14509-14519, 2016.
- [21] L. Lander, M. Reynaud, G. Rousse, M. T. Sougrati, C. Laberty-Robert, R. J. Messinger, *et al.*, "Synthesis and Electrochemical Performance of the Orthorhombic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ Polymorph for Li-Ion Batteries," *Chemistry of Materials*, vol. 26, pp. 4178-4189, 2014/07/22 2014.

- [22] M. Reynaud, M. Ati, B. C. Melot, M. T. Sougrati, G. Rousse, J.-N. Chotard, *et al.*, "Li₂Fe(SO₄)₂ as a 3.83 V positive electrode material," *Electrochemistry Communications*, vol. 21, pp. 77-80, 2012.
- [23] A. Gutierrez, N. A. Benedek, and A. Manthiram, "Crystal-Chemical Guide for Understanding Redox Energy Variations of M^{2+/3+} Couples in Polyanion Cathodes for Lithium-Ion Batteries," *Chemistry of Materials*, vol. 25, pp. 4010-4016, 2013.
- [24] J. M. Clark, C. Eames, M. Reynaud, G. Rousse, J.-N. Chotard, J.-M. Tarascon, *et al.*, "High voltage sulphate cathodes Li₂M(SO₄)₂ (M= Fe, Mn, Co): atomic-scale studies of lithium diffusion, surfaces and voltage trends," *Journal of Materials Chemistry A*, vol. 2, pp. 7446-7453, 2014.
- [25] L. Lander, M. Reynaud, J. Rodríguez-Carvajal, J.-M. Tarascon, and G. Rousse, "Magnetic Structures of Orthorhombic Li₂M(SO₄)₂ (M= Co, Fe) and Li_xFe(SO₄)₂ (x= 1, 1.5) Phases," *Inorganic chemistry*, vol. 55, pp. 11760-11769, 2016.
- [26] M. Reynaud, G. Rousse, J.-N. Chotard, J. Rodríguez-Carvajal, and J.-M. Tarascon, "Marinite Li₂M(SO₄)₂ (M = Co, Fe, Mn) and LiFe(SO₄)₂: Model Compounds for Super-Super-Exchange Magnetic Interactions," *Inorganic Chemistry*, vol. 52, pp. 10456-10466, 2013/09/16 2013.

Chapter 2

Literature Review

This chapter aims at developing an understanding of the current status of research on high voltage cathodes through a comprehensive review. It begins by providing a basic understanding of the working of lithium ion batteries and its applications in the current era as well as moving forward. The need for high voltage lithium batteries in the future is then highlighted. The different types of cathode materials that have made such batteries possible have then been outlined along with a detailed explanation of the various factors that determine the high voltage capability of a battery. Subsequently, the choice of sulphates for this work has been reasoned and the current status of such sulphate based cathodes has been charted. Finally, the challenges facing sulphate based high voltage cathodes has been brought out and a review of electrolytes that can be used to evaluate the viability of such cathodes has been presented.

2.1 Lithium Ion Batteries

When it comes to small scale and portable energy storage systems, battery technologies have proven to be the most effective [1-5]. Each battery technology derives its chemistry from diverse sources as seen in Table 2-1 and possesses its own intrinsic strengths and weaknesses.

Table 2-1: Currently available battery chemistries [3]

Battery	Features	Environmental Impact
Ni-MH <i>Commercial</i>	Low voltage, moderate energy density, high power density For portable and large-scale applications	Nickel is toxic and extraction is difficult. Limited Recyclable
Lead – acid <i>Commercial</i>	Poor energy density, moderate power density, low cost For stationary, large-scale, and power start-up applications	High-temperature Limited cyclability Lead is toxic but recycling is efficient
Lithium Ion <i>Commercial</i>	High energy density, High power density, good cycle life, expensive For portable and possibly large-scale applications	Some elements such as Co are depletable but others such as Fe and Mn are abundant and sustainable Lithium chemistry relatively green but needs improvement Expensive recycling
Zinc-air <i>Commercial</i>	High capacity, high energy density but limited power density Low cost technology	Mostly primary, Smelting of Zinc is not environmentally friendly, not green

	For medium to large-scale applications (except power tools)	Easily recyclable
Lithium – Organic <i>Under Research</i>	High capacity, energy density but limited power density Possibly inexpensive For medium to large-scale (except power tools)	Rechargeable Excellent carbon footprint Renewable electrodes Easy recycling
Lithium – Air <i>Under Research</i>	High energy density but poor energy efficiency and rate capability Technology amenable to a low cost For stationary, large-scale applications	Rechargeability to be proven Low carbon footprint Renewable electrodes Easy recycling
Magnesium Sulphur <i>Under Research</i>	– Predicted: high energy density, unknown power density, unknown cyclability	Magnesium and sulphur are green and recyclable Small carbon footprint
Al-CF_x <i>Under Research</i>	Predicted: moderate energy density, unknown power density	Aluminium and fluorine are green and recyclable
Proton Battery <i>Under Research</i>	Predicted: all organic, low voltage, moderate energy density, power density unknown	Green, biodegradable

However, with the world growing ever conscious of the impact of its actions and decisions on the surrounding environment, a concerted effort must be made at the very beginning, before a technology is adopted, to choose technologies which are safe, green and use materials that are feasibly recyclable. LIBs fulfil all these criteria as well exhibit high volumetric and gravimetric energy densities (Figure 2-1) which makes them highly applicable to applications requiring portability.

Figure 2-1: Comparison of different battery chemistries in terms of volumetric and gravimetric energy density [6] (where PLiON – Polymer Lithium ion)

2.1.1 Background

Lithium battery research reached technological maturity back in 1976 when Stanley Whittingham demonstrated the intercalation of Lithium in titanium disulfide [7]. The technology was eventually commercialised by Exxon [8] and marketed as button cells in 1977-79, however the technology did not take off until oxide based cathodes were introduced by Goodenough [9]. These batteries consisting of a LiCoO_2 cathode were then commercialised by Sony in 1991[3] and the chemistry used then has dominated the market over the past two decades[8]. To understand why LIB chemistry hasn't changed much all these years, a brief understanding of the complex processes in a LIB is required.

2.1.2 Working

Every battery consists of four major components: the positive electrode, negative electrode, an electrolyte and a separator to prevent the electrodes from shorting. Figure 2-2 succinctly explains the process through the charge (bottom) and discharge (top) processes with the red arrows indicating the direction of electron flow and the green arrows indicating the direction of Lithium ion transfer.

Figure 2-2: The working of LIBs [2]

During the charging process, the battery is connected to an external power source. The electrons from the source travel to the negative electrode of the battery through the external circuit. Simultaneously, internally, there is transfer of lithium ions from the positive electrode through the electrolyte in the cell to the

negative electrode through a process called intercalation. During discharge of the battery, the reverse happens with electrons externally flowing from the negative to the positive electrode thereby powering the electronic device.

Thus, for an LIB to be commercially viable, all four components of the battery need to consistently and optimally work with each other over the entire lifetime of the battery. This provides insight into why battery chemistries haven't changed much the past two decades. The next section focuses on the applications of the LIBs so far and where they are headed in the future.

2.2 Current Status and Applications of Lithium Ion Batteries

LIBs are used predominantly in three types of applications; transportation systems, portable electronic devices (3Cs – communication, computer and consumer electronics) and electrical power storage systems [10]. As of 2015, 60 GWh of LIB storage has been employed in different applications as seen in Figure 2-3. This is expected to grow by 15% every year to 215 GWh by 2025 with automotive markets commanding more than 50% of the LIB requirements.

Figure 2-3: Lithium ion battery markets in 2015(left) and 2025(right) [11]. Other applications refer to medical devices, power tools, gardening tools, e-bikes, etc.

These three broad categories of applications all require battery materials to meet six criteria; high energy density, high power, safety, long cycle life, low cost and fast charging. However, the priority each of these parameters varies according to the application as seen in Figure 2-4.

Figure 2-4: Requirements of LIB applications [10]

In the case of transport applications, the LIBs need to compete with gasoline. The difference in practical energy densities between gasoline and current state of the art batteries is illustrated in Figure 2-5.

Figure 2-5: Comparison of practical energy density of batteries today with gasoline [2]

The top two criteria for almost all the applications are high energy density and safety. Thus, the LIBs of the next generation should meet these criteria as the first priority. All these potential applications indicate the need to raise LIB energy density. In this regard, it is useful to understand that an LIB's energy density is governed by the relation [12];

$$E_{stored} = Q_{cell} \times V_{cell}$$

Where;

E_{stored} is the energy density of the battery

Q_{cell} is the charge capacity of the cell

V_{cell} is the potential of operation of the cell

Since V_{cell} is given by [12];

$$V_{cell} = \left| \frac{\mu_{Cathode}^{Li} - \mu_{Anode}^{Li}}{F} \right|$$

Where;

$\mu_{Cathode}^{Li}$ is the chemical potential of the cathode vs. Li

μ_{Anode}^{Li} is the chemical potential of the anode vs. Li

F is the Faraday constant

In the case of a carbonaceous anode $\mu_{Anode}^{Li} \sim 0$ and therefore the cathode potential dictates the voltage of the cell and in turn the energy density of the cell. In addition the cathode comprises 50% of the weight of the cell while anode only comprises 20% [12]. This signifies the importance of the cathode or positive electrode in determining the characteristics of the cell.

2.3 Cathode Materials for Lithium Ion Batteries

2.3.1 Current Status of Research

The key development in the research to commercialise LIBs was the report of a transition metal layered oxide by Goodenough in 1980 [13] which is still a robust cathode material in commercial use even today. However, in the past 3 decades, an amazingly diverse set of cathode materials have been researched and these are listed in Table 2-2.

Table 2-2: Current status of cathode materials [14-16]

Material	Crystal Structure	Remarks	Transition element M and Voltage (V vs. Li)
Layered LiMO₂	<p>Red: Li ions Blue: Transition Metal (TM) polyhedra [14]</p>	<ul style="list-style-type: none"> Limited reversible capacities at high voltages Intrinsic low rate capability for Co-free compounds 	M=Co-3.6 M=Ni _{0.5} Mn _{0.5} -3.5-4.5
Spinel LiM₂O₄	<p>Red: Li ions Blue: TM polyhedra [14]</p>	<ul style="list-style-type: none"> High voltage is out of the electrolyte window causing electrolyte decomposition and formation of unstable SEI 	M=Ni _{0.5} Mn _{1.5} -4.7 M=Cr _y Mn _{2-y} -4.5-4.9 M=Fe _{0.5} Mn _{1.5} -4.5 M=Cu _{0.5} Mn _{1.5} -4.3
Olivine LiMPO₄	<p>Blue: TM polyhedra, Yellow: P polyhedra, Red: Li ions [14]</p>	<ul style="list-style-type: none"> Low conductivity requires synthesis modifications increasing cost Low cost, long life and environmentally friendly 	M=Fe-3.5 M=Mn-4.1 M=Co-4.8 M=Ni-5.1
Borate LiMBO₃		<ul style="list-style-type: none"> Newest generation but has the poorest performance Kinetic polarisation and moisture 	M=Fe-2.8 M=Fe _{1-x} Mn _x -3-3.7 M=Co-4 [17]

	Blue: TM polyhedra, Yellow: B polyhedra, Red: Li ions [14]	sensitivity are limiting factors	
Silicate Li_2MSiO_4		<ul style="list-style-type: none"> • Significant structural instability causes fast capacity fading 	M=Fe-3.1 M=Ni-4.8 M=Mn-4.5
Fluoro/Hydroxy-phosphate $\text{Li}_2\text{MPO}_4\text{F/OH}$		<ul style="list-style-type: none"> • High volume expansion of ~8 % [17] • Difficult to extract all Li ions [19] 	Fluoro phosphate [20] M=Fe-3.0 M=V-4.24 Hydroxy phosphate [17] M=Fe-2.5 M=Mn-3.4
Sulphates $\text{Li}_2\text{M}(\text{SO}_4)_2$		<ul style="list-style-type: none"> • Mn analogue electrochemically inactive due to unknown reasons [22] • Exhibits magnetic properties 	M=Fe-3.8
Fluoro-sulphates LiMSO_4F		<ul style="list-style-type: none"> • Extremely good ionic conductivity, thermal stability, and capacity retention • Unstable due to highly hygroscopic nature 	M=Fe-3.6-3.9 Theoretical: M=Co-4.7-4.9 M=Ni-5.3

Blue: TM polyhedra, Yellow: P polyhedra, Red: Li ions [14]	• Large (10%) volume contraction upon delithiation [23]	M=
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Composites of two or more of the cathode materials mentioned above have also been researched and are called hybrid cathodes [24]. Such hybrid cathodes provide the ability to reduce capacity loss across varying operating temperatures, increase cycle life, improve thermal stability and reduce costs [25]. However, the potentials of operation have not been influenced by such blending of cathode materials and require intrinsically new chemistries.

2.3.2 Commercial Cathode Materials

Despite the array of cathode materials available, so far only five materials have been commercialised as seen in Table 2-3. These belong to the three major classes layered oxides, spinels and olivines (polyanionic).

Table 2-3: Characteristics of various currently used commercial cathode materials where LCO is LiCoO_2 , LMO is LiMn_2O_4 , NCA is $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, NMC is $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$, and LFP is LiFePO_4 [26]

Cathode Material	Midpoint Voltage vs. Li (C/20)	Specific Capacity ($\text{Ah}\cdot\text{kg}^{-1}$)	Advantages	Disadvantages	Applications
LCO	3.9	155	Commonly used Good Cycle Life Good energy	Moderate charged state thermal stability	Mainly smaller portable electronics (3C - Computers, Communication and Consumer)
LMO	4.0	100 to 120	Very good thermal stability, inexpensive, very good power	Moderate cycle life, lower energy	Higher power applications and electric motive power

NCA	3.7	180	capability Very good combination of properties (energy, power, cycle life and thermal stability)	Moderate thermal stability in charged state, sensitive to moisture	Suitable for motive power and premium electronic applications
NMC	3.8	160	Very good combination of properties (energy, power, cycle life and thermal stability)	Patent issues	Portable and high power applications including power tools and electric vehicles
LFP	3.4	160	Very good thermal stability and cycle life, good power capability	Low energy, special preparation conditions	Mainly used in high power and energy storage applications

NCA, NMC and LCO, due to their poor thermal stability are known to be susceptible to battery fires [27] while Mn based compounds such as LMO have faced issues with fading and manganese dissolution during the charge discharge process [28]. In contrast, LFP, which was first demonstrated in 1997 [29, 30], with strong P-O bonds prevents the release of oxygen [31] and is a strong contender for the safety criterion in comparison to other cathode material prospects [32, 33]. However, the drawback for LFP based systems lies in the low energy density. Raising the energy density while maintaining the intrinsic safety offered by the chemistry of the system would provide the ideal cathode material that satisfies the two-major criterion of safety and high energy density. Such an opportunity is offered by polyanionic cathodes of which olivines are a subset.

2.3.3 Polyanionic cathode materials

Polyanionic cathodes are three dimensional frameworks consisting of transition metals and polyanions $(\text{XO}_4)^n$. They have the following advantages [20];

1. Stable crystal structures providing long-term stability ensuring extensive cyclability and high safety

2. The polyanion allows the tuning of a given $M^{n+}/M^{(n-1)+}$ redox couple thereby giving rise to higher redox potential values versus Li compared to oxides
3. High versatility toward diverse anion and cation substitutions allowing for a wide variety of crystal structures

Therefore, the polyanion allows for tuning of the redox potential of the transition element and thereby the energy density of the material. Redox potential determines the voltage of a particular cathode. It is defined as the difference in energy levels between the $M^{n+/(n+1)+}$ redox couple (where M is the transition metal in the compound) and the reference Li/Li⁺ couple. The polyanion which bonds with this transition metal can form bonds of varying degree of covalency which affect the $M^{n+/(n+1)+}$ redox couple in a variety of ways. The transition metal and oxide (M-O) bond in the polyanion plays a critical role in determining this redox couple.

The covalent nature of the M-O bond causes quantum mechanical repulsion between the bonding and anti-bonding orbitals in a compound [28, 34]. This repulsion raises the anti-bonding orbital closer to the Fermi level in lithium and causes a decrease in the overall voltage (Figure 2-6). In the case of a more ionic bonding, the voltage is increased. Gutierrez *et al* [34] lists four properties that influence the redox voltage of a transition metal compound that will form the backbone of designing novel cathode materials for this work.

Figure 2-6: Open circuit voltage in terms of orbital fields [34]

2.3.3.1 Transition-Metal Coordination

The higher the coordination number of the transition metal in the compound, the greater the redox potential of the system [34]. This characteristic is illustrated in Figure 2-7 where the decrease in voltage is from tetrahedral ($-\text{SiO}_4$) to trigonal bi-pyramidal ($-\text{BO}_3$) to octahedral ($-\text{PO}_4$).

Figure 2-7: Decrease in redox voltage with coordination number [34]

2.3.3.2 Polyhedra Connectivity

The second property which alters redox potential is the Madelung field. It is the electrostatic field experienced by an ion in a crystal structure due to all other ions in the lattice. The Madelung electric field has the effect that it destabilises the transition metal and increases the redox energy [34]. This in turn means that the stronger the field is, lower is the potential with respect to Li/Li^+ . The magnitude of Madelung field felt by a cation is dependent on two parameters;

1. It is inversely proportional to the distance of the nearest neighbour.
2. The cation-cation electrostatic repulsion reduces the magnitude of the electric field. The larger the charge on either cation, higher the repulsion. This is demonstrated in Figure 2-8 with respect to cation interactions between a transition metal ion (M^{2+}) and Lithium (Li^+)/ Phosphorous (P^{5+}) ions.

In crystal structures, the parameters mentioned above are determined through the geometry of the structure, specifically based on how two polyhedra connect with each other in the structure – through edge sharing or through corner sharing. In edge sharing polyhedra the cation-cation distances are reduced and repulsion is more pronounced than in corner sharing thereby leading to lower strength of the Madelung field and increased potential [33, 34].

Figure 2-8: Higher charge on the P^{5+} cation lowers the magnitude of Madelung electric field [34]

2.3.3.3 d-Orbital Splitting

The transition metals chiefly used in cathodes are Fe, Mn, Ni and Co. These generally exhibit redox voltages for the $\text{M}^{2+/3+}$ couple in the order $\text{Fe} < \text{Mn} < \text{Co} < \text{Ni}$. This is explained by the d-orbital splitting illustrated in Figure 2-9 where (i) the green arrow shows the electron involved in charge/discharge reactions and (ii) the blue lines indicate the redox potential with respect to Li/Li^+ . Although Fe is to the right of Mn in the periodic table, it has a lower redox potential on account of the charge/discharge electron (in green) requiring excess energy for pairing. This is absent in Mn while in Co and Ni the pairing energy cost is not significant enough lower the redox voltage below Mn.[34]

It should be noted that the density of a compound which depends on the ionic character of bonds is also indicative of the redox potentials wherein higher the density of a compound, higher the redox potential. This was observed in polymorphs of LiFeSO_4OH where the layered form (3.20 g.cm^{-3}) with higher

density than the tavorite form (3.10 g.cm^{-3}) exhibits a higher potential of 3.6 V to that of 3.2 V.[34]

Figure 2-9: Crystal field splitting of the M^{2+} cations [34]

2.3.3.4 Inductive Effect

It has been emphasised that covalency of the M-O bond greatly influences the redox voltage of a compound. The inductive effect involves manipulation of this covalency by altering the electronegativity of the anion (X) in the M-O-X bond. The electron delocalisation (resonance) in the O-X bond also adds to the covalency of the O-X bond. Higher the electronegativity of X, more covalent the O-X bond and lower the covalency of the M-O bond leading to higher voltage. Similarly, as seen in Figure 2-10 higher number of resonance forms creates a more covalent polyanion, lowering the covalency of the M-O bond again leading to higher voltage. To help determine which elements would have the greatest inductive effect, the electronegativity of certain important elements is represented on the Pauling scale in Table 2-4 where the higher the value, higher the electronegative nature. Clearly F, O, N and S are the most electronegative.

Figure 2-10: Higher number of resonance forms results in a more covalent polyanion [34]

Table 2-4: Pauling electronegativity of certain elements [35-37]

Element	Pauling Electronegativity
B	2.04
C	2.55
N	3.04
O	3.44
F	3.98
Si	1.90
P	2.19
S	2.58

Looking at the list of elements, and the trend of Pauling electronegativity, maximum impact of inductive effect is felt when $X=S$ was chosen on account of its high electronegativity [20, 22, 38].

2.4 Sulphate Based Cathode Materials

Sulphates were tested as intercalation hosts in the late 80s [39, 40] and were the first systems that tapped into the inductive effect of the Sulphate group [22]. However, it was not until much later in 2009 [41], with the synthesis of electrochemically active $FeSO_4(OH)$, that the topic was revisited. It was followed

by a period of intense research [42-47] by a novel combination of sulphate with an even more electronegative fluoride group to yield a fluorosulphate of Fe operating at 3.6 V. Subsequently, a polymorph of the same fluorosulphate operating at 3.9 V [48, 49] was synthesised and demonstrated the highest operating potential for the $\text{Fe}^{2+/3+}$ redox couple for the first time. This heralded the synthesis and electrochemical testing of a diverse set of sulphate based polyanionic cathode materials as seen in Figure 2-11.

Figure 2-11: Polyanionic cathodes based on Fe [17]

The sulphate based cathodes synthesised thus far have been classified into three categories;

1. Fluorosulphates

This family of AMSO_4F compounds possesses a diverse crystal chemistry depending upon alkali metal (A) and the transition element (M) as seen in Figure 2-12. The polymorphs illustrated are Tavorite when $\text{M} = \text{Fe}$, Co , Ni , [50] triplite when $\text{M} = \text{Mn}$ [48] and sillimanite $\text{M} = \text{Zn}$ [51, 52].

Figure 2-12: Polymorphs of LiMSO₄F where Blue - MO₄F₂ octahedra, Green - SO₄ tetrahedra, Yellow - Lithium atoms [22]

2. Hydroxysulphates

The LiFeSO₄OH phase was found to reversibly uptake 0.8 Li ions at an average redox potential of 3.6 V vs Li. Figure 2-13.b. Also, LiCoSO₄OH showed electrochemical activity at 4.8 V vs Li [53] making Co the only other transition element apart from Fe to demonstrate activity.

Figure 2-13: (a) Structure and (b) electrochemical properties of LiFeSO₄OH phase where Green - SO₄ tetrahedra, Blue - FeO₃(OH)₃ octahedra, Yellow - Li, Light blue - OH and Red - O [53]

LiFeSO_4OH was found to have a lower energy density than triplite LiFeSO_4F due to a lower redox potential. Therefore, the inductive approach was further sought after to synthesise compounds that could contain 2 SO_4^{2-} polyanions [22].

3. Sulphates

The first and only material from this class to show electrochemical activity was $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ at 3.83 V vs. Li [54]. A number of other analogues (such as Co, Mn and Ni) of this class have been synthesised [17, 21, 55] but none of them have thus far shown any electrochemical activity despite its prediction by DFT calculations [56].

Figure 2-14: (a) Structure and (b) charge-discharge plot of monoclinic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ where Blue - FeO_6 octahedra , Green - SO_4 tetrahedra, Yellow - Lithium [22]

The presence of an orthorhombic polymorph of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ has also shown to be electrochemically active [57, 58] and has been studied for its magnetic properties [55, 59] with the Co and Mn analogues.

The different categories of sulphates have been compared in terms of electrochemical performance with other cathodes in Figure 2-15 to provide perspective of their electrochemical performance with respect to commercial materials.

Figure 2-15: Sulphate based cathodes in comparison to layered oxide and other polyanionic cathodes

As has been stated earlier, amongst all the above classes of sulphates, Fe has been the only transition element to demonstrate electrochemical activity apart from Co in $\text{LiCo}(\text{SO}_4)\text{OH}$ [40]. The inactivity of Mn in such sulphates has never been explained and remains a major research gap [21]. However, DFT studies have indicated the operating potential of different sulphate based cathodes as in Table 2-5.

Table 2-5: Experimental and computationally calculated operational potentials

Polyanionic Sulphates	Redox Couple	Average Potential	
		Experimental	Calculated
LiM(SO₄)F	Fe ^{2+/3+}	3.60 [47]	3.54 [60]
	Co ^{2+/3+}	-	4.73 [40]
	Ni ^{2+/3+}	-	5.16 [40]
Li₂M(SO₄)₂	Fe ^{2+/3+}	3.83 [54]	3.91 [56]
	Mn ^{2+/3+}	-	4.54 [42]
	Co ^{2+/3+}	-	5.20 [42]
LiM(SO₄)OH	Fe ^{2+/3+}	3.20 [41], 3.60 [53]	-
	Co ^{2+/3+}	4.7 [53]	5.0 [22]

The high potentials of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ Sulphate class are of special interest as they would enable offset the low capacity of the system (due to high molecular

weight) and thereby provide moderate energy densities. In terms of high voltages, the currently popular cathodes in this segment are illustrated in Figure 2-16.

Figure 2-16: Voltage and specific capacity of popular high voltage cathode materials for LIBs [61]

Among these cathodes, only LiNiPO₄ exhibits a voltage greater than 5 V but is plagued by a number of challenges such as poor electronic conductivity, low stability of the Ni²⁺/Ni³⁺ redox pair, large particle size, high operating voltage requiring alternative electrolytes and poor cyclability [62].

Therefore, there is a void in the number materials that offer voltages greater than 5 V which the Sulphates described earlier can hope to fill. However, apart from the material itself, the other aspect of high voltage operation of LIBs is the suitability of electrolytes and their safety at high voltages.

2.5 Electrolytes for High Voltage Cathodes

The review so far has focussed on energy density aspect of the two major criteria that LIBs need to cater to for applications in the future. The other criterion is that of safety. Safety of an LIB is a function of the stability of the electrode materials and electrolyte [63]. Conventional carbonate based electrolytes have been known to exhibit poor cycling performance due to release of gases resulting in cell failure [64-68]. While polyanionic cathodes address the issue of safety partially, in the realm of high voltage batteries, electrolytes play a crucial role as well.

Electrolytes are an important part of LIBs as they are responsible for diffusion of Li ions inside the cell and completing the circuit. They are in contact with the electrodes in a cell and result in reactions at the interface with the electrode that affects electrochemical behaviour. An electrolyte is chosen based on the voltage window it operates in which is the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The voltage window of the ideal electrolyte is illustrated in Figure 2-17. The lowest Fermi energy level of the anti-bonding states of the transition metal in the positive electrode or cathode and the Fermi energy level of the negative electrode or anode lie completely within the HOMO and LUMO energy levels of the electrolyte.

If the positive electrode has Fermi energy higher than the HOMO of electrolytes it results in oxidation of the electrolyte by electron transfer from the electrode. Conventional electrolytes, which usually contain a Lithium salt dissolved in an organic carbonate solvent, tend to be oxidised at about 5 V but the transition-metal ions in the positive electrode could catalyze and accelerate the decomposition of electrolytes at lower potentials, leading to rapid capacity fading [15].

Figure 2-17: Voltage compatibility requirement of different components in a cell [69]

Therefore, there is an urgent need for electrolytes with broader voltage windows that can enable the implementation of high voltage positive electrodes. This is being pursued in two ways (i) including additives to existing electrolytes and (ii) synthesis of new solvents for electrolytes. The various types of electrolytes currently available and the challenges they need to overcome to become viable high voltage electrolytes are given in Table 2-6.

Table 2-6: Current status of LIB electrolytes [70]

Solvent Class	Solvent Name	Voltage Window (V vs. Li)			Features
Carbonate	Ethyl Carbonate (EC)	5.5	Conventional	liquid	
	Dimethyl Carbonate (DMC)	5.3	electrolytes		
	Diethyl Carbonate (DEC)	5.15	Have small voltage window < 5.2 V		

Sulfone	Dimethyl Sulfone (DMS)	-	Protective layer on
	Ethyl Methyl Sulfone (EMS)	5.9	graphitic anode fails to form
	Methoxy Methyl Sulfone (MEMS)	5.6	Slow diffusion of Li ion
	Ethyl Methoxyethyl Sulfone (EMES)	5.6	High viscosity causes electrode active material to not be fully utilised
	Ethyl Methoxyethoxyethyl Sulfone (EMEES)	5.3	[61]
	Tetramethylene Sulfone or Sulfolane (TMS(SL))	5.5	
	Ethyl Sulfonyl Cyclopentane (ESCP)	5.8	
	Trifluoropropyl Methyl Sulfone (FPMS)	5.8	
Nitrile	Succinonitrile	-	Mainly used as a co-solvent
	Malononitrile	-	
	Glutaronitrile	7.3	High flash point
	Adiponitrile	6.9	Can sustain high ionic conductivity
	Pimelonitrile	7.0	
	Suberonitrile	6.8	Low cost
	Azelanitrile	-	Does not form SEI with carbon based anodes
	Sebaconitrile	7.2	
Ionic Liquids	Imidazolium	>5.5	High viscosity
	Piperidinium		Low ionic conductivity
	Pyrrolidinium		Low compatibility with graphitic anodes Poor performance at low temperature

Carbonate Derivatives	F-DMC	Advisable	Contain	a	highly
	CN-F-DMC	between	electronegative	molecular	
	CN-DMC	4.5-5 V	group like F ⁻ , -CN, -SO ₂ -		
		[70]	Strong	oxidation	
			resistance	at high voltage	
			but	poor	reduction
			resistance	at low voltage	

Additives work on the principle of assisting in forming a protective film on the cathode at the interface with the electrolyte which helps reduce the degradation of the electrolyte at high voltage. The additives are oxidised and form conductive polymers which enhance electronic conductivity thereby improving the cathode performance [15].

Table 2-7: Additives currently used and their properties [71]

Additive	Remarks
LiClO₄	Potentially explosive with organic solvents
LiBF₄	Better thermal stability Interferes with formation of SEI layer at anode Lower sensitivity towards moisture
LiPF₆	Most widely used salt Thermally unstable and decomposes to LiF/PF ₅ Easily hydrolysable
LiBC₄O₈ - LiBOB	Thermal stability up to 300°C (> 80°C of LiPF ₆ salt)
Lithium bis(oxalato)borate	Stabilises positive electrode current collector up to 5.0V versus Li ⁺ /Li Forms solutions of high conductivity Highly hydrolysable
LiPF₃(C₂F₅)₃ - LiFAP	Stable toward hydrolysis
Lithium fluoroalkylphosphates	Not easily flammable

LiN(SO₂CF₃)₂	- Stable toward hydrolysis
LiTFSI	Good thermal stability
Lithium bis (trifluoro-methyl-sulfonyl) imide	Corrodes Al current collector

2.6 Conclusion

The literature review has been instrumental in formulating the aims and objectives of this thesis. The review clearly indicates a need for high energy density and extremely safe LIBs for applications in the near future. These twin characteristics are met by LIBs utilising polyanionic cathodes particularly those based on sulphates. The fact that only iron based sulphates have shown reversible electrochemical behaviour poses many questions about conventional understanding of battery chemistry. These challenging questions thus serve as the starting point of this work.

2.7 References

- [1] H. Ibrahim, A. Ilinca, and J. Perron, "Energy storage systems—characteristics and comparisons," *Renewable and Sustainable Energy Reviews*, vol. 12, pp. 1221-1250, 2008.
- [2] M. M. Thackeray, C. Wolverton, and E. D. Isaacs, "Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries," *Energy & Environmental Science*, vol. 5, pp. 7854-7863, 2012.
- [3] M. Armand and J.-M. Tarascon, "Building better batteries," *Nature*, vol. 451, pp. 652-657, 2008.
- [4] B. Scrosati, J. Hassoun, and Y.-K. Sun, "Lithium-ion batteries. A look into the future," *Energy & Environmental Science*, vol. 4, pp. 3287-3295, 2011.
- [5] R. Marom, S. F. Amalraj, N. Leifer, D. Jacob, and D. Aurbach, "A review of advanced and practical lithium battery materials," *Journal of Materials Chemistry*, vol. 21, pp. 9938-9954, 2011.
- [6] J.-M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature*, vol. 414, pp. 359-367, 2001.
- [7] M. S. Whittingham, "Electrical energy storage and intercalation chemistry," *Science*, vol. 192, pp. 1126-1127, 1976.

- [8] M. S. Whittingham, "Lithium Batteries and Cathode Materials," *Chemical Reviews*, vol. 104, pp. 4271-4302, 2004/10/01 2004.
- [9] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, " Li_xCoO_2 ($0 < x < 1$): A new cathode material for batteries of high energy density," *Materials Research Bulletin*, vol. 15, pp. 783-789, 1980/06/01/ 1980.
- [10] G. Jeong, Y.-U. Kim, H. Kim, Y.-J. Kim, and H.-J. Sohn, "Prospective materials and applications for Li secondary batteries," *Energy & Environmental Science*, vol. 4, pp. 1986-2002, 2011.
- [11] C. Pillot, "The Rechargeable Battery Market and Main Trends 2015-2025," 2016.
- [12] A. Kraytsberg and Y. Ein - Eli, "Higher, Stronger, Better... A Review of 5 Volt Cathode Materials for Advanced Lithium - Ion Batteries," *Advanced Energy Materials*, vol. 2, pp. 922-939, 2012.
- [13] K. Mizushima, P. Jones, P. Wiseman, and J. B. Goodenough, " Li_xCoO_2 ($0 < x < 1$): A new cathode material for batteries of high energy density," *Materials Research Bulletin*, vol. 15, pp. 783-789, 1980.
- [14] B. Xu, D. Qian, Z. Wang, and Y. S. Meng, "Recent progress in cathode materials research for advanced lithium ion batteries," *Materials Science and Engineering: R: Reports*, vol. 73, pp. 51-65, 2012.
- [15] M. Hu, X. Pang, and Z. Zhou, "Recent progress in high-voltage lithium ion batteries," *Journal of Power Sources*, vol. 237, pp. 229-242, 2013.
- [16] Z. Gong and Y. Yang, "Recent advances in the research of polyanion-type cathode materials for Li-ion batteries," *Energy & Environmental Science*, vol. 4, pp. 3223-3242, 2011.
- [17] M. Reynaud, "Design of new sulfate-based positive electrode materials for Li- and Na-ion batteries," Ph.D. Doctoral Dissertation, Materials Science, Université de Picardie Jules Verne, 2013.
- [18] N. R. Khasanova, O. A. Drozhzhin, S. S. Fedotov, D. A. Storozhilova, R. V. Panin, and E. V. Antipov, "Synthesis and electrochemical performance of $\text{Li}_2\text{Co}_{1-x}\text{M}_x\text{PO}_4\text{F}$ ($\text{M} = \text{Fe}, \text{Mn}$) cathode materials," *Beilstein journal of nanotechnology*, vol. 4, pp. 860-867, 2013.
- [19] J. Yu, K. M. Rosso, J.-G. Zhang, and J. Liu, "Ab initio study of lithium transition metal fluorophosphate cathodes for rechargeable batteries," *Journal of Materials Chemistry*, vol. 21, pp. 12054-12058, 2011.
- [20] C. Masquelier and L. Croguennec, "Polyanionic (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries," *Chemical Reviews*, vol. 113, pp. 6552-6591, 2013.
- [21] M. Reynaud, M. Ati, S. Boulineau, M. T. Sougrati, B. C. Melot, G. Rousse, *et al.*, "Bimetallic Sulfates $\text{A}_2\text{M}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{A} = \text{Li}, \text{Na}$ and $\text{M} = \text{Transition Metal}$): as New Attractive Electrode Materials for Li-and Na-Ion Batteries," *ECS Transactions*, vol. 50, pp. 11-19, 2013.
- [22] G. Rousse and J.-M. Tarascon, "Sulfate-Based Polyanionic Compounds for Li-Ion Batteries: Synthesis, Crystal Chemistry, and Electrochemistry Aspects," *Chemistry of Materials*, vol. 26, pp. 394-406, 2013.

- [23] B. L. Ellis, K. Town, and L. F. Nazar, "New composite materials for lithium-ion batteries," *Electrochimica Acta*, vol. 84, pp. 145-154, 2012.
- [24] C. Wei, W. He, X. Zhang, J. Shen, and J. Ma, "Recent progress in hybrid cathode materials for lithium ion batteries," *New Journal of Chemistry*, vol. 40, pp. 2984-2999, 2016.
- [25] S. B. Chikkannanavar, D. M. Bernardi, and L. Liu, "A review of blended cathode materials for use in Li-ion batteries," *Journal of Power Sources*, vol. 248, pp. 91-100, 2014.
- [26] G. E. Blomgren, "The development and future of lithium ion batteries," *Journal of The Electrochemical Society*, vol. 164, pp. A5019-A5025, 2017.
- [27] H. J. Bang, H. Joachin, H. Yang, K. Amine, and J. Prakash, "Contribution of the structural changes of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes on the exothermic reactions in Li-ion cells," *Journal of The Electrochemical Society*, vol. 153, pp. A731-A737, 2006.
- [28] T. Muraliganth and A. Manthiram, "Understanding the Shifts in the Redox Potentials of Olivine $\text{LiM}_{1-y}\text{MyPO}_4$ (M= Fe, Mn, Co, and Mg) Solid Solution Cathodes," *The Journal of Physical Chemistry C*, vol. 114, pp. 15530-15540, 2010.
- [29] A. Padhi, K. Nanjundaswamy, and J. Goodenough, "Phospho - olivines as positive - electrode materials for rechargeable lithium batteries," *Journal of the electrochemical society*, vol. 144, pp. 1188-1194, 1997.
- [30] A. Padhi, K. Nanjundaswamy, C. Masquelier, S. Okada, and J. Goodenough, "Effect of structure on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple in iron phosphates," *Journal of the Electrochemical Society*, vol. 144, pp. 1609-1613, 1997.
- [31] K. Zaghib, A. Guerfi, P. Hovington, A. Vijh, M. Trudeau, A. Mauger, *et al.*, "Review and analysis of nanostructured olivine-based lithium rechargeable batteries: Status and trends," *Journal of Power Sources*, vol. 232, pp. 357-369, 2013/06/15/ 2013.
- [32] H. Joachin, T. D. Kaun, K. Zaghib, and J. Prakash, "Electrochemical and thermal studies of carbon-coated LiFePO_4 cathode," *Journal of the Electrochemical Society*, vol. 156, pp. A401-A406, 2009.
- [33] K. Zaghib, J. Dubé, A. Dallaire, K. Galoustov, A. Guerfi, M. Ramanathan, *et al.*, "Enhanced thermal safety and high power performance of carbon-coated LiFePO_4 olivine cathode for Li-ion batteries," *Journal of Power Sources*, vol. 219, pp. 36-44, 2012.
- [34] A. Gutierrez, N. A. Benedek, and A. Manthiram, "Crystal-Chemical Guide for Understanding Redox Energy Variations of $\text{M}^{2+}/\text{M}^{3+}$ Couples in Polyanion Cathodes for Lithium-Ion Batteries," *Chemistry of Materials*, vol. 25, pp. 4010-4016, 2013.
- [35] L. C. Allen, "Electronegativity is the average one-electron energy of the valence-shell electrons in ground-state free atoms," *Journal of the American Chemical Society*, vol. 111, pp. 9003-9014, 1989.

- [36] A. Allred, "Electronegativity values from thermochemical data," *Journal of Inorganic and nuclear chemistry*, vol. 17, pp. 215-221, 1961.
- [37] L. Pauling, *The nature of the chemical bond and the structure of molecules and crystals: an introduction to modern structural chemistry* vol. 18: Cornell University Press, 1960.
- [38] P. Barpanda, "Pursuit of sustainable iron-based sodium battery cathodes: two case studies," *Chemistry of Materials*, vol. 28, pp. 1006-1011, 2016.
- [39] A. Manthiram and J. Goodenough, "Lithium insertion into $\text{Fe}_2(\text{SO}_4)_3$ frameworks," *Journal of Power Sources*, vol. 26, pp. 403-408, 1989.
- [40] A. Manthiram and J. Goodenough, "Lithium insertion into $\text{Fe}_2(\text{MO}_4)_3$ frameworks: Comparison of $\text{M} = \text{W}$ with $\text{M} = \text{Mo}$," *Journal of Solid State Chemistry*, vol. 71, pp. 349-360, 1987.
- [41] M. Anji Reddy, V. Pralong, V. Caignaert, U. Varadaraju, and B. Raveau, "Monoclinic iron hydroxy sulphate: A new route to electrode materials," *Electrochemistry Communications*, vol. 11, pp. 1807-1810, 2009.
- [42] M. Ramzan, S. Lebègue, and R. Ahuja, "Crystal and electronic structures of lithium fluorosulphate based materials for lithium-ion batteries," *Physical Review B*, vol. 82, p. 125101, 09/03/ 2010.
- [43] M. Ati, W. T. Walker, K. Djellab, M. Armand, N. Recham, and J.-M. Tarascon, "Fluorosulfate positive electrode materials made with polymers as reacting media," *Electrochemical and solid-state letters*, vol. 13, pp. A150-A153, 2010.
- [44] M. Ati, M. T. Sougrati, N. Recham, P. Barpanda, J.-B. Leriche, M. Courty, *et al.*, "Fluorosulfate positive electrodes for Li-ion batteries made via a solid-state dry process," *Journal of The Electrochemical Society*, vol. 157, pp. A1007-A1015, 2010.
- [45] R. Tripathi, G. R. Gardiner, M. S. Islam, and L. F. Nazar, "Alkali-ion conduction paths in LiFeSO_4F and NaFeSO_4F tavorite-type cathode materials," *Chemistry of Materials*, vol. 23, pp. 2278-2284, 2011.
- [46] R. Tripathi, T. Ramesh, B. L. Ellis, and L. F. Nazar, "Scalable synthesis of tavorite LiFeSO_4F and NaFeSO_4F cathode materials," *Angewandte Chemie*, vol. 122, pp. 8920-8924, 2010.
- [47] N. Recham, J.-N. Chotard, L. Dupont, C. Delacourt, W. Walker, M. Armand, *et al.*, "A 3.6 V Lithium-Based Fluorosulphate Insertion Positive Electrode for Lithium-Ion Batteries," *Nature Materials*, vol. 9, pp. 68-74, 2010.
- [48] P. Barpanda, M. Ati, B. C. Melot, G. Rousse, J. N. Chotard, M. L. Doublet, *et al.*, "A 3.90 V Iron-Based Fluorosulphate Material For Lithium-Ion Batteries Crystallizing In The Triplite Structure," *Nature Materials*, vol. 10, pp. 772-779, 2011.
- [49] M. B. Yahia, F. Lemoigno, G. Rousse, F. Boucher, J.-M. Tarascon, and M.-L. Doublet, "Origin of the 3.6 V to 3.9 V voltage increase in the LiFeSO_4F cathodes for Li-ion batteries," *Energy & Environmental Science*, vol. 5, pp. 9584-9594, 2012.

- [50] P. Barpanda, N. Recham, J.-N. Chotard, K. Djellab, W. Walker, M. Armand, *et al.*, "Structure and electrochemical properties of novel mixed Li (Fe $1-x$ M x) SO₄F (M= Co, Ni, Mn) phases fabricated by low temperature ionothermal synthesis," *Journal of materials chemistry*, vol. 20, pp. 1659-1668, 2010.
- [51] M. Ati, B. C. Melot, G. Rousse, J. N. Chotard, P. Barpanda, and J. M. Tarascon, "Structural and Electrochemical Diversity in LiFe_{1- δ} Zn δ SO₄F Solid Solution: A Fe - Based 3.9 V Positive - Electrode Material," *Angewandte Chemie International Edition*, vol. 50, pp. 10574-10577, 2011.
- [52] R. Tripathi, G. Popov, B. L. Ellis, A. Huq, and L. Nazar, "Lithium metal fluorosulfate polymorphs as positive electrodes for Li-ion batteries: synthetic strategies and effect of cation ordering," *Energy & Environmental Science*, vol. 5, pp. 6238-6246, 2012.
- [53] C. V. Subban, M. Ati, G. I. Rousse, A. M. Abakumov, G. Van Tendeloo, R. I. Janot, *et al.*, "Preparation, Structure, and Electrochemistry of Layered Polyanionic Hydroxysulfates: LiMSO₄OH (M= Fe, Co, Mn) Electrodes for Li-Ion Batteries," *Journal of the American Chemical Society*, vol. 135, pp. 3653-3661, 2013.
- [54] M. Reynaud, M. Ati, B. C. Melot, M. T. Sougrati, G. Rousse, J.-N. Chotard, *et al.*, "Li₂Fe(SO₄)₂ as a 3.83 V positive electrode material," *Electrochemistry Communications*, vol. 21, pp. 77-80, 2012.
- [55] M. Reynaud, G. Rousse, J.-N. Chotard, J. Rodríguez-Carvajal, and J.-M. Tarascon, "Marinite Li₂M(SO₄)₂ (M = Co, Fe, Mn) and LiFe(SO₄)₂: Model Compounds for Super-Super-Exchange Magnetic Interactions," *Inorganic Chemistry*, vol. 52, pp. 10456-10466, 2013/09/16 2013.
- [56] J. M. Clark, C. Eames, M. Reynaud, G. Rousse, J.-N. Chotard, J.-M. Tarascon, *et al.*, "High voltage sulphate cathodes Li₂M(SO₄)₂ (M= Fe, Mn, Co): atomic-scale studies of lithium diffusion, surfaces and voltage trends," *Journal of Materials Chemistry A*, vol. 2, pp. 7446-7453, 2014.
- [57] L. Lander, M. Reynaud, J. Carrasco, N. A. Katcho, C. Bellin, A. Polian, *et al.*, "Unveiling the electrochemical mechanisms of Li₂Fe(SO₄)₂ polymorphs by neutron diffraction and density functional theory calculations," *Physical Chemistry Chemical Physics*, vol. 18, pp. 14509-14519, 2016.
- [58] L. Lander, M. Reynaud, G. Rousse, M. T. Sougrati, C. Laberty-Robert, R. J. Messinger, *et al.*, "Synthesis and Electrochemical Performance of the Orthorhombic Li₂Fe(SO₄)₂ Polymorph for Li-Ion Batteries," *Chemistry of Materials*, vol. 26, pp. 4178-4189, 2014/07/22 2014.
- [59] L. Lander, M. Reynaud, J. Rodríguez-Carvajal, J.-M. Tarascon, and G. Rousse, "Magnetic Structures of Orthorhombic Li₂M(SO₄)₂ (M= Co, Fe) and Li_xFe(SO₄)₂ (x= 1, 1.5) Phases," *Inorganic chemistry*, vol. 55, pp. 11760-11769, 2016.

- [60] Y. Cai, G. Chen, X. Xu, F. Du, Z. Li, X. Meng, *et al.*, "First-principles calculations on the $\text{LiMSO}_4\text{F}/\text{MSO}_4\text{F}$ ($\text{M} = \text{Fe}, \text{Co}, \text{and Ni}$) systems," *The Journal of Physical Chemistry C*, vol. 115, pp. 7032-7037, 2011.
- [61] C. Julien and A. Mauger, "Review of 5-V electrodes for Li-ion batteries: status and trends," *Ionics*, vol. 19, pp. 951-988, 2013.
- [62] S. M. Rommel, N. Schall, C. Brünig, and R. Wehrich, "Challenges in the synthesis of high voltage electrode materials for lithium-ion batteries: a review on LiNiPO_4 ," *Monatshefte für Chemie-Chemical Monthly*, vol. 145, pp. 385-404, 2014.
- [63] Y. S. Meng and M. E. Arroyo-de Dompablo, "Recent advances in first principles computational research of cathode materials for lithium-ion batteries," *Accounts of chemical research*, vol. 46, pp. 1171-1180, 2012.
- [64] A. Kajiyama, R. Masaki, T. Wakiyama, K. Matsumoto, A. Yoda, T. Inada, *et al.*, "Principal factors of carbon conductive agents that contribute to the gas formation in high-voltage cathode systems," *Journal of The Electrochemical Society*, vol. 162, pp. A1516-A1522, 2015.
- [65] L. Ma, J. Xia, and J. Dahn, "Improving the High Voltage Cycling of Li $[\text{Ni}_{0.42}\text{Mn}_{0.42}\text{Co}_{0.16}]\text{O}_2$ (NMC442)/Graphite Pouch Cells Using Electrolyte Additives," *Journal of The Electrochemical Society*, vol. 161, pp. A2250-A2254, 2014.
- [66] K. Nelson, G. d'Eon, A. Wright, L. Ma, J. Xia, and J. Dahn, "Studies of the Effect of High Voltage on the Impedance and Cycling Performance of Li $[\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}]\text{O}_2$ /Graphite Lithium-Ion Pouch Cells," *Journal of The Electrochemical Society*, vol. 162, pp. A1046-A1054, 2015.
- [67] K.-S. Lee, Y.-K. Sun, J. Noh, K. S. Song, and D.-W. Kim, "Improvement of high voltage cycling performance and thermal stability of lithium-ion cells by use of a thiophene additive," *Electrochemistry Communications*, vol. 11, pp. 1900-1903, 2009.
- [68] J. Xia, K. Nelson, Z. Lu, and J. Dahn, "Impact of electrolyte solvent and additive choices on high voltage Li-ion pouch cells," *Journal of Power Sources*, vol. 329, pp. 387-397, 2016.
- [69] W. Li, B. Song, and A. Manthiram, "High-voltage positive electrode materials for lithium-ion batteries," *Chemical Society Reviews*, vol. 46, pp. 3006-3059, 2017.
- [70] S. Tan, Y. J. Ji, Z. R. Zhang, and Y. Yang, "Recent Progress in Research on High - Voltage Electrolytes for Lithium - Ion Batteries," *ChemPhysChem*, vol. 15, pp. 1956-1969, 2014.
- [71] P. Balakrishnan, R. Ramesh, and T. Prem Kumar, "Safety mechanisms in lithium-ion batteries," *Journal of Power Sources*, vol. 155, pp. 401-414, 2006.

Chapter 3

Experimental Methodology

This chapter aims to elucidate the synthesis and characterisation techniques utilised in this work. The first section details the synthesis technique used and sheds light on the rationale for the selection of the techniques. The second section provides a brief description of the structural characterisation to understand the physical properties and thermal limits of these novel materials. The techniques include powder x-ray diffraction, electron microscopy, spectroscopy, thermal analysis and moisture sensitivity analysis. This initial characterisation aids in synthesising materials with suitable properties for electrochemical testing. The process of assembly of these materials into electrochemical cells is outlined in the third section. The final section details the electrochemical characterisation techniques; such as cyclic voltammetry, galvanostatic charge-discharge cycling, and impedance spectroscopy, used to understand the performance of the materials in lithium battery applications.

3.1 Synthesis

3.1.1 High Energy Ball Milling

The ball mill is used for grinding materials and aids in effectively increasing solid-state chemical reactivity [1]. High-Energy ball milling, a type of ball milling, has been used in the last 45 years, since the use by Benjamin and co-workers[2] for processing diverse types of materials into nano-crystalline or amorphous materials. Of the many types of high energy mills, the system used in this work is of the mixer mill type.

3.1.1.1 Principle

The mixer mill consists of two vials, containing the sample and milling balls, secured in a clamp. This vial is energetically swung back and forth. The vial appears to describe a figure-8 motion as the back-and-forth shaking motion is combined with the lateral movements of the vial [3]. The length of the swing is about the same as the internal length of the vial. With each swing, the ball collides against the sample and the vial ends, thereby simultaneously milling and mixing the sample. The amplitude and velocity of the swinging vial causes the balls to develop significant G-forces, that pulverise the toughest materials [4]. A variety of factors that affect milling are; type of mill, milling time, temperature of mill, material of sample/vial, ball to powder ratio, mill charge, environment (dry/wet) and frequency of operation [5].

3.1.1.2 Application

SPEX 8000D mixer mill was used for high energy ball milling in this work. A stainless-steel vial with stainless balls was used for the milling. The vial was vibrated with an amplitude of two inches and 875 cycles at 230V/50Hz. The balls to sample weight ratio used was 15:1. In the case of Fe based compounds, the milling was done after sealing the vials in an Ar glovebox. This was to prevent oxidation of Fe during milling. For the same reason cooling periods were allowed

while milling; every 15 mins in the case of Fe and every 1 hr in the case of Mn, Co and Ni,

Figure 3-1: Spex 8000D Mixer Mill

3.1.2 Solid State Synthesis

Solid state synthesis involves annealing of precursors in stoichiometric quantities at high temperatures causing them to react and form the required product. It is the most commonly used synthesis procedure as it requires minimal preparation and is easily scalable. First, the appropriate precursors of required purity are chosen to yield the required product. Next, they are weighed in stoichiometric quantities and are mixed either through hand grinding or ball milling (described earlier). During this process a solvent to ensure homogenisation may or may not be added. If a solvent is added, the slurry is dried after grinding. The well mixed powder is then pelletised to ensure good contact. Finally, the pellets are placed in a ceramic crucible that can withstand the temperature of the annealing and heated in the presence or absence of oxygen depending on the requirement.

3.1.2.1 Principle

Solid state synthesis is based on studies of phase diagrams of the final product and its precursors. The temperature for annealing and pressure are important parameters in determining the optimal conditions for synthesis of a product. The reaction conditions are also influenced by reactant properties such as surface area, thermodynamic free energy change and reactivity [6, 7]. As the reaction

temperature increases, diffusion of the precursors takes place over a few hours to days and react with or without the release of gases to form the desired products. The central principle for raising temperatures to enable solid state reactions is based on Tammann's rule which states that solid state materials become reactive beyond two thirds of the melting point of any of the individual constituents [8, 9].

3.1.2.2 Application

In this work, solid state, high temperature synthesis was carried out using two types of furnaces; (i) Carbolite muffle furnace in an environment open to air and (ii) Carbolite Tube furnace in an environment of inert Argon gas. The parameters of annealing consisting of heating rate (ramp rate), dwell time and temperature are optimised to form the required phase of the product. This technique was employed in synthesis of a range of novel materials of the type $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$. The Argon based tube furnace assisted the formation of oxygen and moisture sensitive compounds like $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ and forming the anhydrous phases of precursors.

Figure 3-2: Carbolite Tube Furnace (left) and Muffle Furnace (right)

3.2 Material Characterisation

3.2.1 X-ray Diffraction (XRD)

Max Von Laue first discovered the use of X-rays in studying crystalline materials [10]. The layers of a crystalline material, individually called lattice, acted as diffraction gratings for X-rays and created diffraction patterns due to interference. These patterns were then used to identify crystalline structures.

3.2.1.1 Principle

Monochromatic X-rays are collimated and directed towards the surface of the sample to be analysed. The X-rays incident on the crystalline sample are scattered by the atoms of the sample, and undergo constructive interference in accordance with Bragg's Law [11];

$$n\lambda = 2d \cdot \sin\theta \text{ -----(3.1)}$$

Where,

n is a positive integer

λ is the incident X-ray wavelength

d is the inter-planar distance between crystal lattices

θ is the diffraction angle

The random orientation of the lattices in the powdered sample generate X-rays of diverse diffraction directions. the diffracted X-rays from the sample are detected, counted and processed.

3.2.1.2 Working

X-ray diffractometers consist of three components:

1. Source: Heated filaments in cathode ray tubes produce electrons. A high voltage is applied to these electrons to accelerate them toward a target, the most common being Cu producing X-rays of wavelength $K_{\alpha} = 1.5418 \text{ \AA}$. This wavelength is characteristic of the target material used. The monochromatic X-ray thus produced is filtered by foils or additional monochromators.

2. Sample Holder: The sample holder is commonly a stationary stage which may or may not be rotated depending on the requirements of the measurement. The sample on the stage is placed so as to enable the detector to receive maximum X-rays from the sample. The critical issue is that of sample preparation where care needs to be taken to ensure that the surface of the sample is smooth and flat. The powder samples should not be excessively compacted as this could result in the development of preferred orientation in the crystals. This in turn biases the diffraction data in favour of these orientations.

3. Detector: The X-rays incident on the sample undergo diffraction as per Bragg's law. These diffracted X-rays are recorded by a detector which converts the X-ray signal to a count rate which is then plotted as intensity of counts across varying diffraction angles. This plot called a diffraction spectrum is then analysed by the user.

3.2.1.3 Application

XRD was heavily used a characterisation technique in this work. Powder samples were analysed and the resulting XRD spectra were subjected to Reitveld refinement for calculation of crystallographic parameters and estimation of compositions. Three types of XRD machines were used; Bruker D8 Advance XRD, Shimadzu XRD-6000, PANalytical X'pert XRD was used for the analysis of;

1. Newly synthesised compounds
2. Effects of thermal treatment on materials
3. Effects of humidity on materials

3.2.2 X-ray Absorption Spectroscopy (XAS)

XAS is a technique for determining the local electronic and/or geometric structure of matter. It is usually carried out at synchrotron radiation sources, which provide high intensity, tunable X-ray beams for sample analysis. This work used facilities at the Diamond Light Source, United Kingdom and the Singapore Synchrotron Light Source, Singapore.

3.2.2.1 Principle

In an X-ray absorption experiment, the sample to be analysed is bombarded with X-rays of specific energy. The atoms in the sample absorb some of these X-rays causing a core electron to be excited or ejected. This intensity of the incident beam can be compared to the intensity of the transmitted beam to yield a definite value for the absorption. This absorption value is specific to the energy of the incident X-rays [12]. By slightly changing the energy and repeating the process through an energy range, a spectrum as seen in Figure 3-3 is generated.

Figure 3-3: Sample spectra of Fe-K edge indicating the two major sections of a standard XAS spectrum

The spectrum consists of three parts:

1. Absorption Edge - The absorption is a discontinuous increase in absorption (7125 eV in Figure 3-1). Here, the energy of the incident X-ray is sufficiently high to eject, via photoelectric effect, a core electron from an atom in the sample. These absorption edges are named in accordance with the shell from which the electron is excited (K=1s; LI=2s;

- LII, LIII=2p, etc.) [13]. The absorption edge is useful in elemental identification.
2. X-ray Absorption Near Edge Structure (XANES) - This comprises the energy range within 100 eV before the absorption edge and up to 50 eV after the absorption edge. It mainly consists of two parts; (i) the pre-edge and (ii) edge. The pre-edge is the region just before the absorption edge and the edge is when a sudden jump in the absorption coefficient is absorbed. The XANES region provides information on oxidation state and geometry of the element being analysed. In many cases XANES is not analysed quantitatively [14].
 3. Extended X-ray Absorption Fine Structure (EXAFS) - The oscillations above the absorption edge, which extends up to 1000 eV or more comprises the EXAFS region. This region is sensitive to the radial distribution of electron density around the absorbing atom[13] and is used to quantitatively determine the bond length and coordination number.

3.2.2.2 Application

XAS techniques in this work were primarily used for two purposes, (i) qualitative analysis of oxidation state of the transition element in the battery material during various states of charge and discharge, (ii) quantitative estimation of bond length with nearest neighbor during cycling. All XAS measurements were conducted at a ring energy 0.7 GeV and ring current of ca 200 mA. A Si (111) crystal monochromator was used and data were collected on XAFCA[15] in Quick EXAFS transmission mode at ambient temperature under vacuum. The data was collected in a typical scan time of 180 seconds. Repetitions were made to improve the signal/noise. Reference spectra were collected using a reference metal foil for the measurement of reference materials *ca.* 5 mg of the powder reference sample was mixed with *ca.* 80 mg of Boron Nitride and pressed into a 10-mm diameter pellet and mounted onto the sample holder for measurements in transmission mode. The XANES and EXAFS data were analysed using *Athena* and *Artemis* software from the *Demeter* suite for XAS analysis [16]. In this work, the K-edges

of Iron and Manganese were recorded. Pure metallic foils were used as standards in addition to appropriate reference material powders so that the spectra obtained could be compared with each other.

3.2.3 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that utilises a focused electron beam to visualise a sample's surface topography and composition.

3.2.3.1 Principle

Figure 3-4: Emission of various electrons and electromagnetic waves upon interaction of electrons with matter [17]

As seen in Figure 3-4, an incident electron beam results in the production of a number of signals of which the SEM utilises the secondary electrons and back-scattered electron. The secondary electrons are emitted from a region very close to the surface of the sample and hence can be used to generate high resolution images of the sample surface and understand its topography. This is used

primarily for morphological studies. The back-scattered electrons come from deeper locations within the sample and their intensity is strongly related to the atomic number of the specimen. Thus, they provide information on elemental distribution.

3.2.3.2 Application

The SEM used in this work was of two types; the JEOL FESEM 6340 F and JEOL FESEM 7600F. The purpose of SEM was twofold; study of the morphology of the materials synthesised and study of various types of carbon coating additives used to enhance battery material conductivity.

3.2.4 Electron Dispersive X-Ray(EDX) Spectroscopy

EDX is an analytical technique used to characterise the elemental or chemical composition of a sample. When coupled with electron microscopes it uses an electron beam and when coupled with x-ray fluorescence spectrometers it uses an x-ray beam as a source to generate characteristic X-rays. EDX utilises the characteristic X-rays emitted by a sample to determine the composition of the sample.

3.2.4.1 Principle

The sample contains atoms with electrons in their ground or unexcited state. When an electron beam is shone on the sample, the incident beam excites an electron and ejects it from the inner shell creating an electron hole in its place. Subsequently an electron from a higher energy shell fills this hole by emitting energy equivalent to the difference between the higher and lower energy shell in the form of X-rays. The number and energy of the emitted X-rays are then measured by an energy-dispersive spectrometer. Since these X-rays are of characteristic energies, the type and intensity of the X-ray allows for determining the atomic structure of the emitting element and thereby estimate the elemental composition of the specimen [18].

3.2.4.2 Application

In this study EDX was primarily used to confirm the substitution of elements in the synthesis of novel solid solution series of $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2 = \text{Co, Mn, Ni}$). EDX analysis was carried out using the same instrument JEOL FESEM 6340 F and JEOL FESEM 7600F at 30 kV with a probe current of 13 nA at five different spots on each sample and then averaged out.

3.2.5 X-ray Photoelectron Spectroscopy (XPS)

XPS is a quantitative spectroscopic technique that is sensitive to surface phenomena. XPS spectra are obtained by shining the sample with a beam of X-rays and measuring the kinetic energy and count of electrons that are subsequently emitted. It can be used to measure elemental composition and oxidation state of the elements that exist within a material.

3.2.5.1 Principle

The governing equation for XPS studies[19] is based on a special form of photoemission which involves the emission of an electron from a core level by an X-ray photon.

$$E_b = h\nu - E_K - W$$

Where

$h\nu$ is the energy of the source radiation.

E_K is the kinetic energy of the electron measured by spectrometer

E_b is the binding energy of the electron

W is the spectrometer work function

All the quantities on the right-hand side of the equation are known or measurable and hence can be used to calculate the binding energy. The plot of this energy with the intensity of the emissions yield a characteristic spectrum such as the one in Figure 3-5. This can be used to reproduce the electronic structure of the element being analysed and serves as a fingerprinting tool.

Figure 3-5: Energy contribution from electrons in different orbitals of a Lead atom [19]

3.2.5.2 Application

XPS has been used in this work as an analytical tool to determine any change in the oxidation state of a specific element. The data specific to elements was obtained by carrying out high resolution scans in a narrow energy band around the reported binding energy of the element. An increase in binding energy implies that the net nuclear charge of the remaining electrons increases which is indicative of an increased oxidation state. This increased oxidation state leads to a chemical shift wherein the spectra shift to a higher energy. Sample preparation was of paramount importance as the battery materials are sensitive to the ultra-high vacuum conditions in the XPS system. The samples were dried and degassed in an inert environment before analysis.

3.2.6 Nuclear Magnetic Resonance(NMR) Spectroscopy

NMR spectroscopy is a powerful tool to determining molecular level structure and dynamics. Since in battery materials, Li ions are directly involved in the

electrochemistry, ^7Li solid state NMR serves as a useful tool in characterising the local structures of systems even if they are highly disordered [20].

3.2.6.1 Principle

NMR spectra are obtained by placing samples in strong magnetic field and recording the sample's response to radiofrequency radiation applied as short pulses. This radiation gives rise to magnetic fields that in turn form small perturbations in energy causing transitions [21].

3.2.6.2 Application

^7Li solid-state Nuclear Magnetic Resonance (NMR) was used to probe the local environment of the lithium within the $\text{Li}_2\text{M}(\text{SO}_4)_2$ samples. All ^7Li ($I = 3/2$) spectra were recorded on a Bruker Avance HD spectrometer (2.35 T) at a Larmor frequency (ν_0) of 38.9 MHz (ν_0 (^1H) = 100 MHz[22]). A 1.3 mm double air bearing magic angle spinning probe was utilised to give frequencies of 40 kHz. All spectra were referenced to $\text{LiCl}_{(\text{s})}$ ($\delta_{\text{iso}} = -0.77$ ppm w.r.t. 1M $\text{LiCl}_{(\text{aq})} = 0$ ppm). A saturation recovery echo sequence was employed to measure the T_1 relaxation of the systems, with variable delays ranging from 1×10^{-4} to 0.5 seconds over a temperature range of 265.1 to 315.1 K. All data was fitted to a single exponential ($f(t) = I_0 \times (1 - e^{-t/T_1})$). A prior to measurement temperature calibration was completed on samarium stannate [23].

3.2.7 Thermal Analysis

Thermo-gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were combined with Mass Spectroscopy (MS) to understand the impact of thermal treatment to a novel set of materials.

3.2.7.1 Principle

TGA works on the principle of measuring the mass of a sample as it is heated to high temperatures in a furnace. The variation of mass is then plotted with respect to the temperature of the sample. TGA indicates the thermal stability of a

materials and helps determine the decomposition limit of the material. In DSC analysis, a sample and reference are heated identically. Due to thermal processes, there might be a change in the temperature between the sample and reference and a certain amount of excess energy is supplied to maintain the same temperature. Thus, DSC measures this energy required to keep both reference and sample at same temperature while the temperature of the entire system is raised. The energy required is then plotted versus temperature to yield a DSC plot. DSC gives a detailed picture of phase transitions and indicates if a process is exothermic or endothermic.

3.2.7.2 Application

In this work, the TGA experiments were carried out on ~15 mg of powder on a TGA Q500 (TA Instruments) in a temperature range of 30-700°C at a heating rate of 10 °C.min⁻¹. The TGA experiments were carried out under either Ar or Synthetic air flow depending on the requirement. TGA-DSC-MS analyses were carried out on ~15 mg of powder samples placed in an alumina crucible, in the temperature range 20-800°C (heating rate: 10°C/min) under argon flow (50 cm³.min⁻¹) using a STA-449C Jupiter unit (Netzsch) coupled to a quadrupole mass spectrometer QMS 403 Aëlos equipped with a stainless-steel capillary and a secondary-electron multiplier detector (Channeltron).

3.2.8 SQUID Magnetometry

A magnetometer is an instrument that measures the magnetism of a material. A superconducting quantum interference (SQUID) magnetometer is a highly sensitive device used to detect the magnetic moment of a sample [24]. They are versatile instruments used to measure physical quantities that can be converted to flux such as magnetic field gradient, voltage, current, magnetic field, and magnetic susceptibility [25].

3.2.8.1 Principle

SQUIDS combine the two physical phenomena of quantized flux in a closed superconducting loop and Josephson tunneling [25]. The SQUID does not detect a sample's magnetic field directly. Instead, the sample is made to move through a set of superconducting coils. Since the sample has a magnetic moment, the motion of the sample induces an electric current in the superconducting detection coils. This detection coil is in a closed superconducting loop with the SQUID input coil. The SQUID functions as a linear current to voltage convertor and therefore converts the current induced in the detection coils to an output voltage proportional to the sample's magnetic moment. These voltage variations are then analyzed through three methods: 1) full scan – area under the voltage vs. position curve is integrated as it is proportional to the magnetic moment, 2) linear regression and 3) iterative regression methods which involve fitting of a theoretical signal to the actual signal [26].

3.2.8.2 Application

The SQUID is used to make two principal measurements of magnetism;

1. $M(H)$ – magnetisation vs. applied magnetic field (at constant temperature)
2. $M(T)$ – magnetisation vs. temperature (constant applied magnetic field)

These measurement techniques help to distinguish between the five major types of magnetism observed in materials; para-, dia-, ferro-, antiferro- and ferrimagnetism. The M vs. H plot helps to distinguish between the five forms of magnetism while the M vs. T plot helps determine the ferro-, antiferro – and paramagnetism as seen in Figure 3-6 [27].

Figure 3-6: The relationship between magnetisation and applied magnetic field (left) and between magnetic susceptibility and temperature (right)[28]

3.2.9 Three Electrode Cyclic Voltammetry

Three-electrode electrochemical cells are used in the electrochemical characterisation of electrolytes.

3.2.9.1 Principle

Voltammetry experiments involve measuring of current through a system as the voltage is varied. This is primarily used to investigate the half-cell reactivity of an analyte. The voltammetry experiments involve at least two electrodes; the working electrode and counter electrode. The working electrode, is used to apply the desired potential in a defined way, thereby enabling charge transfer to and from the electrolyte. The counter electrode must have a known potential so as to gauge the potential of the working electrode. In addition, it should balance the charge removed or added by the working electrode. Here, as an electrode counters the effects of the working electrode, it is difficult to maintain a constant potential. In order to solve this issue, a third electrode is introduced to the system that supplies the necessary charge to balance the system. The only role of this electrode is to act as a reference in measuring and controlling the potential of the working electrode. This electrode called the reference electrode does not pass any current. The counter electrode however passes all the current required to balance

the working electrode and in order to achieve this current, can often swing to extreme potentials. At these extremes, it either oxidises or reduces the electrolyte and the corresponding currents are then recorded to provide voltammogram or voltammetry curve. When this is repeated in a cyclic fashion mimicking the charge and discharge of a battery it results in a cyclic voltammetry curve obtained through a three-electrode setup.

3.2.9.2 Application

In this work, the three-electrode setup was used to determine the stability window of novel electrolyte combinations. A setup consisting of Platinum (Pt) as reference electrode, Glassy Carbon as working electrode and Li as Counter Electrode was assembled inside an MBRAUN Ar filled glovebox with H₂O and O₂ levels less than 0.1 ppm. The electrodes were arranged in a specially made glass vessel which held the electrolyte. 500 μ L of the electrolyte was used for every test performed and tests were repeated twice each to ensure consistency of the result. The electrodes were connected through a port in the glovebox to a portable Biologic SP-200 Potentiostat placed outside the glovebox. The tests were carried out at 25 mV.s⁻¹ between 6 V and 0 V vs. Li.

3.3 Device Characterisation

3.3.1 Electrochemical Cell Assembly

3.3.1.1 Coin Cells

The positive electrodes were prepared by using a combination of active material, Super P Carbon and polyvinylidene fluoride (PVDF – Kynar) binder with the masses in the ratio 75%, 19% and 6% respectively. The three components were ground thoroughly in N-methyl-2-pyrrolidone solvent for 15 mins and then coated over an Aluminum foil by the doctor blading method. The thickness of the coating was between 30-40 μ m and then the coated foil was dried in a convection oven overnight at 80 °C. The foil was then flattened in a roller press

and electrodes of diameter 12 mm were punched from this sheet. Subsequently, half cells were assembled using CR2016 coin-type cell inside an argon filled glove box (MBraun). A porous glass fiber (Whatman Cat. No. 1825–047, UK) was used as the separator and filled with 100-130 μL electrolyte solution of 1 M LiPF_6 in ethylene carbonate (EC)/di-methyl carbonate (DMC) (1:1 v/v, Merck KGaA, Germany). Lithium metal foil was used as the negative electrode and a corrugated aluminium sheet welded onto a current collector was used to complete the cell. The coin cell was then sealed and set aside a few hours before testing.

3.3.1.2 Swagelok[®] Cells

The high voltage cathode was prepared by first ball milling the active material with Super P Carbon in an inert atmosphere in a ratio of 80:20 wt% for three periods of 12 minutes, each separated by 10 mins. The carbon coated cathode was then manually ground with either 6% PVDF (Kynar-battery grade) or 6% poly acrylonitrile (Sigma Aldrich) binder. The finely mixed powder was directly placed in a Swagelok[®] cell as positive working electrode and lithium foil as the counter electrode. The loading of the active material was 8 mg.cm^{-2} . Two pieces of porous glass microfibre (Whatman Cat. No. 1825–047, UK) were used as the separator and 250 μL electrolyte solution of 1M LiClO_4 – propylene carbonate (PC) was used to soak the separator. This assembled cell as shown in Figure 3-7 was then subjected to electrochemical testing.

Figure 3-7: Technical drawing of a Swagelok[®] cell[29]

3.3.2 Cyclic Voltammetry (CV)

CV is a potentiodynamic electrochemical measurement. It is widely used to study a variety of redox reactions, determine reaction product stability, investigate the presence of intermediates during reactions,[30] kinetics of electron transfer,[31] and the reversibility of a reaction [32].

3.3.2.1 Principle

In CV experiments, the working electrode potential is linearly ramped versus time in cyclical phases. The potential is measured between the working electrode and the reference electrode, while the current is measured between the working electrode and the counter electrode. In coin cell testing, often the counter and reference electrode are the same. The working electrode potential is linearly ramped to a set potential after which it is ramped in the opposite direction to the other set potential of the initially defined potential window. The voltammogram

is generated by plotting the current at the working electrode versus the applied voltage.

3.3.2.2 Application

In this study, the CV was used to determine the voltage stability window of a novel electrolyte combination through a three-electrode setup. It was also used to demonstrate reversibility in a novel cathode for lithium batteries, CV experiments were carried out using the Solartron 1256E where the voltage window varied in the range from 3.2 V to 5.6 V (vs. Li) based on the material being tested.

3.3.3 Galvanostatic Cycling (GCD)

Galvanostatic charge discharge is a constant current electrochemical test used to replicate the charge and discharge process of a battery in the laboratory.

3.3.3.1 Principle

GCD consists of applying a constant current across an electrochemical cell to charge and discharge the working electrode. It is typically done after the potential window of redox activity is established through CV tests. GCD profiles are valuable in providing direct access to the chemical potential within the electrodes and understanding the thermodynamics of the system [33]. The straightforward connection between a GCD voltage curve and the Gibbs free allows for understanding the occurrence and characteristic of phase transformations during charge and discharge processes of lithium ion batteries. The GCD profile for batteries can be divided into different categories based on the slope of the profile.

If the profile exhibits a smooth slope, the electrode host material will tend to form a solid solution with Li. If, the profile exhibits a plateau, it indicates a first order phase transformation caused by Li insertion. If there are multiple steps in the voltage profile, it indicates an intermediary phase which is energetically stable, often caused by ordering of Li ions and vacancies [33].

3.3.3.2 Application

The GCD tests in this work were carried out with the purpose of establishing the discharge capacity of the cathode materials and its variation across many cycles. These tests were predominantly done at low currents of C/15 in a voltage window of 3.2 to 4.2 V vs. Li on a Neware Battery Testing system. The tests were also used to understand the performance of the cathode materials at high charge and discharge rates of up to 8C/15. These were classified as rate performance tests that help understand the roadblocks to be overcome in the path to the commercialisation of these materials.

3.3.4 Electrochemical Impedance Spectroscopy (EIS)

EIS is a technique to elucidate the electrochemical processes and especially understand the kinetics of Li intercalation/deintercalation processes in a Lib. It aids in characterisation of the electrical properties of materials and their interfaces with electrically conducting electrolytes. It also enables a qualitative evaluation of charge-transfer and diffusion-controlled reactions between cells of different charge states, different ages and those of different materials.

3.3.4.1 Principle

EIS measurement involves application of a single frequency voltage or current to a system and monitoring of the corresponding amplitude and phase shift. The real and imaginary resistances of the resulting output are calculated through a fast fourier transform(FFT) function. The analysis of a typical EIS spectra for a half cell lithium battery consists of three segments as seen in Figure 3-8. The sloping straight line in the low frequency region is indicative of the lithium diffusion kinetics, and is denoted as the Warburg element in the equivalent circuit [29]. The semicircle in the middle to low frequency region relates to the charge transfer (CT) and the interfacial capacitance across the interface of the electrode and electrolyte. The diameter of this circle gives the charge transfer resistance (R_{CT}). The point at which the semicircle begins in the high frequency region gives the ohmic resistance (R_{Ω}) of the electrochemical setup being tested.

Figure 3-8: Typical EIS spectrum of a Lithium Ion Battery representing charge transfer (R_{CT}) and ohmic (R_{Ω}) resistances

3.3.4.2 Application

In this work, EIS studies were carried out with the purpose of understanding the effects of additives on cathode materials in terms of the resistance offered. The experiments were performed using a Solartron 1256 E by applying an AC current of amplitude 10 mV over the frequency range from 1mHz to 100 kHz at open circuit potential, at room temperature. The data was represented as Nyquist plots Z'' vs. Z' which were compiled and analysed using Zplot and Zview software (Version 2.2, Scribner Associates Inc., USA).

3.4 References

- [1] L. Takacs, "Self-sustaining reactions induced by ball milling," *Progress in Materials Science*, vol. 47, pp. 355-414, 2002/01/01/ 2002.

- [2] E. G. Araújo, R. M. L. Neto, M. F. Pillis, and F. Filho, "High energy ball mill processing," in *Materials science forum*, 2003, pp. 128-133.
- [3] C. C. Koch, "The synthesis and structure of nanocrystalline materials produced by mechanical attrition: A review," *Nanostructured Materials*, vol. 2, pp. 109-129, 1993/03/01/ 1993.
- [4] "Operating Manual 8000D Mixer/Mill," S. SamplePrep, Ed., ed, 2003.
- [5] P. Baláž, "High-Energy Milling," in *Mechanochemistry in Nanoscience and Minerals Engineering*, ed Berlin, Heidelberg: Springer Berlin Heidelberg, 2008, pp. 103-132.
- [6] P. Hagenmuller, *Preparative methods in solid state chemistry*: Elsevier, 2012.
- [7] A. R. West, *Solid state chemistry and its applications*: John Wiley & Sons, 2007.
- [8] G. Tammann, "Lehrbuch der Metallkunde Verlag Voss," ed: Berlin, 1929.
- [9] R. Merkle and J. Maier, "On the Tammann–Rule," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 631, pp. 1163-1166, 2005.
- [10] M. Eckert, "Max von Laue and the discovery of X-ray diffraction in 1912," *Annalen der Physik*, vol. 524, pp. A83-A85, 2012.
- [11] W. H. Bragg and W. L. Bragg, "The Reflection of X-rays by Crystals," *Proceedings of the Royal Society of London. Series A*, vol. 88, pp. 428-438, 1913.
- [12] S. Calvin, *XAFS for Everyone*: CRC press, 2013.
- [13] J. E. Penner-Hahn, "X-ray absorption spectroscopy in coordination chemistry," *Coordination Chemistry Reviews*, vol. 190, pp. 1101-1123, 1999.
- [14] J. E. Penner - Hahn, "X - ray Absorption Spectroscopy," *eLS*, 2005.
- [15] Y. Du, Y. Zhu, S. Xi, P. Yang, H. O. Moser, M. B. Breese, *et al.*, "XAFCA: A New XAFS Beamline for Catalysis Research," *Journal of Synchrotron Radiation*, vol. 22, pp. 839-843, 2015.
- [16] B. Ravel and M. Newville, "ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy using Ifeffit," *Journal of Synchrotron Radiation*, vol. 12, pp. 537-541, 2005.

- [17] JEOL. (2009). *Scanning electron microscope A to Z: Basic knowledge for using the SEM*.
- [18] J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. E. Lyman, E. Lifshin, *et al.*, "The SEM and Its Modes of Operation," in *Scanning Electron Microscopy and X-ray Microanalysis: Third Edition*, J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. E. Lyman, E. Lifshin, *et al.*, Eds., ed Boston, MA: Springer US, 2003.
- [19] J. F. Watts and J. Wolstenholme, "Electron Spectroscopy: Some Basic Concepts," in *An Introduction to Surface Analysis by XPS and AES*, ed: John Wiley & Sons, Ltd, 2005, pp. 1-15.
- [20] C. P. Grey and N. Dupré, "NMR Studies of Cathode Materials for Lithium-Ion Rechargeable Batteries," *Chemical Reviews*, vol. 104, pp. 4493-4512, 2004/10/01 2004.
- [21] D. C. Apperley, R. K. Harris, and P. Hodgkinson, *Solid-State NMR: Basic Principles and Practice*: Momentum Press, 2012.
- [22] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, and P. Granger, "NMR nomenclature: nuclear spin properties and conventions for chemical shifts. IUPAC Recommendations 2001. International Union of Pure and Applied Chemistry. Physical Chemistry Division. Commission on Molecular Structure and Spectroscopy," *Magnetic Resonance in Chemistry*, vol. 40, pp. 489-505, 2002.
- [23] T. F. Kemp, G. Balakrishnan, K. J. Pike, M. E. Smith, and R. Dupree, "Thermometers for low temperature Magic Angle Spinning NMR," *Journal of Magnetic Resonance*, vol. 204, pp. 169-172, 2010/05/01/ 2010.
- [24] A. D. Hibbs, R. E. Sager, S. Kumar, J. E. McArthur, A. L. Singaas, K. G. Jensen, *et al.*, "A SQUID - based ac susceptometer," *Review of Scientific Instruments*, vol. 65, pp. 2644-2652, 1994.
- [25] J. Clarke and A. I. Braginski, *The SQUID Handbook: Applications of SQUIDs and SQUID Systems*: John Wiley & Sons, 2006.
- [26] M. McElfresh, "Fundamentals of Magnetism and Magnetic Measurements," Quantum Design, San Diego 1994.
- [27] C. M. Julien, A. Ait-Salah, A. Mauger, and F. Gendron, "Magnetic properties of lithium intercalation compounds," *Ionics*, vol. 12, pp. 21-32, 2006/05/01 2006.
- [28] (7 Aug 2017). *Comparison of magnetic behaviour (magnetization and susceptibility) of various kinds of magnetic materials versus temperature*. Available: http://nptel.ac.in/courses/113104005/lecture31/31_4.htm

- [29] M. Reynaud, "Design of new sulfate-based positive electrode materials for Li- and Na-ion batteries," Ph.D., Materials Science, Université de Picardie Jules Verne, 2013.
- [30] R. S. Nicholson, "Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics," *Analytical Chemistry*, vol. 37, pp. 1351-1355, 1965/10/01 1965.
- [31] S. H. DuVall and R. L. McCreery, "Control of Catechol and Hydroquinone Electron-Transfer Kinetics on Native and Modified Glassy Carbon Electrodes," *Analytical Chemistry*, vol. 71, pp. 4594-4602, 1999/10/01 1999.
- [32] D. H. Evans, K. M. O'Connell, R. A. Petersen, and M. J. Kelly, "Cyclic voltammetry," ed: ACS Publications, 1983.
- [33] A. Van der Ven, J. Bhattacharya, and A. A. Belak, "Understanding Li Diffusion in Li-Intercalation Compounds," *Accounts of chemical research*, vol. 46, pp. 1216-1225, 2012.

Chapter 4

Lithium Iron Sulphate Cathode – Study of the Mechanism and Effect of Binders and Carbon Additives

Li₂Fe(SO₄)₂ is thus far the only compound in this class of Li₂M(SO₄)₂ based sulphates to have been shown to be electrochemically active. With the objective of moving towards the commercialisation of Fe-based high voltage cathode Li₂Fe(SO₄)₂, the effect of fluorinated binder (polyvinylidene fluoride - PVDF) and non-fluorinated binder (polyacrylonitrile - PAN) was evaluated. First, the redox mechanism involved in the cycling of Li₂Fe(SO₄)₂ cathode in the presence of these two binders was investigated through ex-situ X-ray Absorption Spectroscopy (XAS) studies which can directly determine oxidation state changes of the Fe ion during the charge-discharge process. Secondly, the effects of the binders on the cycling and rate performance were evaluated. Finally, since polyanionic systems such as sulphates suffer from low electronic conductivity, the effect of four carbon based additives in improving conductivity of Li₂Fe(SO₄)₂ active material was investigated. This section therefore provides a comprehensive account of the electrochemical performance of Li₂Fe(SO₄)₂ and the challenges to overcome prior to its commercial use in lithium ion batteries.

4.1 Introduction

The sulphate - $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ (Lithium Iron Sulphate (LFS)) has been synthesised earlier[1] and demonstrated consistent cycling in a Swagelok[®] Cell in the absence of a binder. Mossbauer spectroscopy studies[2] have shed light on the oxidation state changes in the presence of carbon additives and the effect of ball milling. However, the process of oxidation of Fe ions during de-intercalation and reduction during intercalation of Lithium ions in the presence of fluorinated and non-fluorinated binders has not been evaluated. Hence, in this work, we investigate the redox reaction of the Fe ion during the charge-discharge process using *ex-situ* X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption spectroscopy (EXAFS) to monitor oxidation state changes and corresponding bond length changes through direct measurements at the Fe K-edge. The shape and edge position of the XANES spectrum is determined by various parameters, in particular the local structural environment of the element of interest (in this case the transition metal ion Fe), ligand type, geometry, coordination number and oxidation state [3]. Furthermore, as this technique is element-specific and the intense X-ray beam can penetrate the battery electrode, it enables the observation and deep understanding of the system which is vital for understanding the battery performance. Here we investigate the electronic and geometric structure of sulphate based cathode material LFS at different states of charge and discharge using X-ray absorption spectroscopy (XAS) at the Fe-K edge. This helps us to determine how structural changes influence the electrochemical behaviour of LFS in the presence of a binder.

A previous study[1] had indicated that fluorinated salt in electrolyte reacts with the electrode and had suggested the possibility of fluorinated binder (PVDF) reacting detrimentally with the electrode as well. Hence, it is of critical importance to evaluate the effect of PVDF binder on the LFS system to determine the cycling stability of the material. This study also compares PVDF with a non-fluorinated binder poly acrylonitrile (PAN) to look for differences in

performance. Finally, this chapter looks into the effects of carbon-based additives on the electrochemical performance of the active material. The additives were evaluated using microscopy and electrochemical testing in order to determine the most suitable additive.

4.2 Experimental Methods

4.2.1 Synthesis

Anhydrous FeSO_4 and Li_2SO_4 were used to synthesis monoclinic LFS. The anhydrous FeSO_4 was firstly obtained by heating green coloured $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma Aldrich) in a tube furnace under argon flow for 2 hours at 350 °C at a heating rate of 2.5 °C.min⁻¹. Anhydrous Li_2SO_4 was obtained by heating white coloured $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Sigma Aldrich) in a tube furnace under argon flow for 1 hour at 200 °C at a heating rate of 2.5 °C.min⁻¹. The anhydrous precursors were then mixed with a few drops of ethanol and placed in ball mill vials sealed in argon. They were then ball-milled in a SPEX 8000M high energy ball mill for two periods of 18 minutes each separated by 10 mins to prevent oxidation of Fe^{2+} to Fe^{3+} . The powder was then pressed into a pellet at a force of 8 kN after which it was heated to 350 °C for 12 hours with a 2.5 °C.min⁻¹ ramp rate in a tube furnace under argon flow.

The resulting ivory white coloured LFS powder was analysed for phase purity using *Match!* v3.1 phase identification software from powder diffraction data obtained on a PANalytical X'pert X-Ray Diffractometer at settings of 40 kV and 30 mA. Data were collected between 10 and 80 °2 θ at a scan rate of 0.019 °min⁻¹. The synthesised compound and anhydrous precursors were all stored in Ar filled glovebox to prevent moisture reabsorption. The carbon coating on the active materials for improving the conductivity was carried out using the *SPEX* high energy ball milling process. Finally, all the carbon coated samples were

stored in an argon filled glovebox at <0.1 ppm O_2 and <0.1 H_2O ppm prior to use in the electrochemical analysis.

4.2.2 Electrochemical Testing

The electrochemical tests were carried out in a half-cell configuration using Swagelok[®] cell architecture. The important characteristics such as cycling and rate performances of the prepared cells were compared with the results obtained earlier [11]. To obtain the structural changes during the charge-discharge process, CR2016 coin cells were fabricated and charged to different voltages. The electrodes from the cells were then subjected to *ex-situ* XAS analysis.

4.2.2.1 Electrodes for Swagelok[®] Cell

The high voltage cathode was prepared by first ball milling LFS with Super P Carbon in an inert atmosphere in a ratio of 80:20 wt% for three periods of 12 minutes, each separated by 10 mins. The carbon coated LFS powder was then manually ground with either 6% PVDF (Kynar-battery grade) or 6% PAN (Sigma Aldrich) binder. The finely mixed powder was directly placed in a Swagelok[®] cell as positive working electrode and lithium foil as the counter electrode. The loading of the active material was 8 mg.cm^{-2} . Two pieces of porous glass microfibre (Whatman Cat. No. 1825–047, UK) were used as the separator and soaked in an electrolyte of 1M $LiClO_4$ in propylene carbonate (PC). This assembled cell was then subjected to cyclic voltammetry and galvanostatic charge-discharge (GCD) tests.

4.2.2.2 Coin Cells for *ex-situ* XAS analysis

A conventional electrode was fabricated by preparing a slurry that was coated on an aluminium foil using doctor blade technique. The slurry consisted of LFS ball milled with Super P Carbon (as described in the previous section) and PVDF or PAN binder (6 wt.%) with N-Methyl-2-pyrrolidone (Sigma Aldrich) as the solvent. The prepared composite electrode was used as a working electrode and unlike the Swagelok[®] Cell, the loading of the active material here was about 5

mg.cm⁻². The electrode, electrolyte and separator were the same as that used for the Swagelok[®] cell. These components were assembled in CR2016 coin-type cells in an argon filled glovebox (MBRAUN). These cells were subjected to GCD cycling at different current rates from 3.2 V to 4.2 V *vs.* Li; importantly, the cells were stopped at different charge-discharge potentials for *ex-situ* XAS analysis.

4.2.3 X-ray Absorption Spectroscopy (XAS)

The coated Al-foil electrodes were sealed between two pieces of kapton tape to prevent moisture and oxygen from affecting the charged state of the electrodes. The electrodes along with the representative iron sulphate reference standards were measured at the XAFCA beamline [4] of the Singapore Synchrotron Light Source. All XAS measurements were conducted at a ring energy 0.7 GeV and ring current of circa 200 mA. A Si (111) crystal monochromator was used and data were collected on XAFCA in Quick EXAFS transmission mode at ambient temperature under vacuum. Fe K-edge data was collected in the range of 6992 and 7911 eV in a typical scan time of 180 seconds. Repetitions were made to improve the signal/noise. Reference spectra were collected using a Fe metal foil for the measurement of reference materials circa 5 mg of the powder reference sample was mixed with 80 mg of Boron Nitride and pressed into a 10 mm diameter pellet and mounted onto the sample holder for measurements in transmission mode. The Fe K-edge XANES and EXAFS data were analysed using *Athena* and *Artemis* software from the *Demeter* suite for XAS analysis [5].

4.3 Results and Discussion

4.3.1 Structural study by X-Ray Diffraction (XRD) Analysis

The as-synthesised ivory white coloured powder was analysed using powder XRD and the assigned diffraction pattern of the monoclinic LFS, was found to closely match the XRD pattern obtained from earlier studies[1](Figure 4-1).

Figure 4-1: XRD pattern of as synthesised monoclinic LFS powder compared to the XRD pattern reported in Reynaud *et al.*[1]

Subsequently, this powder was subjected to high energy ball milling with Super P carbon. The carbon coated sample was used for electrochemical investigations in both Swagelok[®] Cell and conventional coin cell fabrications. The carbon coated LFS was manually ground with PVDF and PAN binders for XRD analysis (Figure 4-2). It was noted that the addition of either binder did not cause any structural modification in comparison to the purely carbon coated LFS devoid of binder.

Figure 4-2: Comparison of XRD patterns of LFS with no binder, PVDF and PAN indicates that addition of fluorinated (PVDF) and non-fluorinated (PAN) binders does not alter the monoclinic LFS structure

4.3.2 Electrochemical Characterisation

The Swagelok[®] cell was tested electrochemically through GCD tests with the ball-milled powder as the working and Li foil as counter electrode. The GCD in Figure 4-3 indicates the discharge capacity of 58 mAh g⁻¹ at a current density of 0.1 C rate. This value is nearly 60% of the theoretical capacity (102 mAh.g⁻¹) of the LFS system. The plateaus of intercalation of Li ions were observed at a redox potential of 3.9 V *vs.* Li for the charging process and 3.7 V *vs.* Li for the discharge process. This is significantly larger considering the most favoured polyanionic cathode material, LiFePO₄ operates at 3.5 V *vs.* Li.[6]

Figure 4-3: The first galvanostatic charge-discharge cycle of LFS showing oxidation and reduction plateaus at 3.98 V and 3.75 V *vs.* Li respectively. Seven points were chosen along the charge-discharge curve for ex-situ XAS testing.

4.3.3 XAS Analysis

Various cut-off potentials were selected along the charge-discharge cycle as shown in Table 4-1 and Figure 4-3 to represent various stages of the charge and discharge process which will enable understanding of the structural changes in

the sulphate electrode material. *Ex-situ* XAS studies were conducted on the electrodes at the Fe-K edge.

Table 4-1: Details of electrodes subjected to ex-situ XANES/EXAFS analysis

Electrode	Electrode State	Potential
		(w.r.t. Li) (V)
A	Fresh electrode, open circuit potential	3.3
B	Charged, before redox potential	3.9
C	Charged, after redox potential	4.1
D	Completely Charged	4.2
E	Discharged, before redox potential	3.8
F	Discharged, after redox potential	3.7
G	Fully Discharged	3.2

4.3.3.1 XANES Analysis

The XANES studies consists of the analysis of two regions, the pre-edge and the absorption edge. The position of the pre-edge has been frequently used in the determination of redox states of Fe in the Fe K-edge analysis of numerous earth materials.[7] The pre-edge, located around 15–20 eV before the Fe absorption K-edge[8], reveals a peak (Figure 4-4) around 7112 eV representing a 1s to 3d electron transition.[9] Comparing the 7112 eV peak to similar peak energy of LiFePO_4 [10] it is clear that the initial oxidation state is +2. Upon charging, the pre-edge peak shifts towards higher energy of 7114 eV indicating the formation of a higher oxidation state. [9, 11, 12] Again, comparing this energy to literature¹⁹, it reflects same pre-edge peak energy as the Fe(+3) in FePO_4 indicating a +3 oxidation state. It was also seen that the pre-edge intensity was weak throughout the charge-discharge process indicating Fe atoms predominantly occupy the FeO_6 octahedral site.[13-15] However, the relationship between pre-edge intensity and coordination number at the Fe site has been found to not be applicable when the complex shows strong distortions due to the type of ligation or optimal

geometries.[16] This necessitates the need for EXAFS studies to confirm the correlation here.

Figure 4-4: Normalized XANES plots of the pre-edge peaks for PVDF binder are seen in 1 and 2 and for PAN in 3 and 4. In all peaks a characteristic +2 oxidation state is seen at 7112 eV and a slightly broader peak at 7114 eV representing the +3 oxidation state

Analysis of the main absorption edge peak (Figure 4-5) shows a notable drop in intensity while charging and an increase in intensity during discharge. This has been attributed to changing structural disorder around the Fe atoms. The lowering intensity and broadening of the peak indicates an increase in the structural disorder.[17] In both the binders, the intensity was found to have an offset when comparing the initial 3.3 V charge state to the final 3.2 V discharge state. This indicates the creation of irreversible disorder in the first cycle although the majority of the structure returns to its ordered state as shown by nearly similar intensities and peak profiles between the initial state and completely discharged state.

Figure 4-5: XANES plots of the absorption Fe K-edge for PVDF binder are seen in 1 and 2 and for PAN in 3 and 4. The charge process (1 and 3) shows a decrease in peak intensity while the discharge process (2 and 4) shows an increase in peak intensity.

To ascertain the change in oxidation state, a derivative of the Fe K-edge spectra was computed, shown in Figure 4-6. It was observed that the derivative peak X shifted towards higher energy from by 2.2 eV to Y (7120.2 eV to 7122.4 eV) for PVDF and by 2.2 eV to Y (7120.7 eV to 7123.1 eV) for PAN as shown in Table 2. confirming the change in oxidation state of Fe ion. Such a shift corresponds to local change of LFS to a reduced state.[18] To further analyse the structure of the system during the charge-discharge process, EXAFS analysis was conducted.

Figure 4-6: Computed first derivative plots of the XANES data for PVDF binder are seen in 1 and 2 and for PAN in 3 and 4. In 1 and 3, the rightward shift of the peak X to Y upon charging indicates an increase in oxidation state with increasing Fe-K Edge energy. In 2 and 4 the reverse phenomena of 1 and 3 are observed during discharge indicating the presence of a redox couple of Fe.

4.3.3.2 EXAFS Analysis

More quantitative structural changes were investigated via a first shell analysis of the EXAFS data to determine the correlation between the atomic distances of Fe with its nearest neighbour – oxygen and disorder with the charge and discharge cycles. The typical LFS crystal structure modelled using Vesta software[19] is shown in Figure 4-7. In particular, the representation of the various coordination environments of iron and sulphur highlighting the FeO_6 octahedron is indicated.

Figure 4-7: Literature[1] derived crystal structure of the monoclinic LFS with FeO_6 octahedra (brown), SO_4 tetrahedra (yellow) and Lithium ions (green) indicating the unit cell.

Table 4-2: Data obtained from analysis of XAS parameters based on Fe - K edge for LFS with PVDF and PAN binders

	Electrode	CN	σ^2 ($\text{\AA}^2$)	R ($\text{\AA}$)	R- factor	Edge Position (eV)	Bond Valence Sum
	FeSO_4 - Fe^{+2} Std.	6.00	0.008	2.10	0.005	7123.8	2.25
	$\text{Fe}_2(\text{SO}_4)_3$ - Fe^{+3} Std.	6.13	0.006	1.98	0.021	7127.4	3.28
PVDF	A	5.56	0.013	2.09	0.042	7120.2	2.26
	B	5.49	0.012	2.12	0.058	7120.9	
	C	6.50	0.010	2.06	0.033	7120.9	
	D	5.30	0.016	1.98	0.063	7122.4	3.32
	E	5.04	0.017	1.97	0.068	7122.4	
	F	5.73	0.019	2.09	0.098	7121.1	
	G	5.22	0.014	2.11	0.047	7120.8	2.14
PAN	A	5.85	0.011	2.10	0.062	7120.7	2.22
	B	6.14	0.017	2.10	0.056	7120.7	
	C	8.03	0.009	1.99	0.035	7121.3	
	D	7.17	0.010	1.98	0.042	7123.1	3.30
	E	9.01	0.007	1.99	0.036	7121.2	
	F	6.66	0.013	2.04	0.042	7120.9	
	G	5.94	0.012	2.11	0.066	7120.5	2.18

CN – Coordination Number

σ^2 – EXAFS Debye–Waller factor or Disorder Factor

R - Bond distance

R-factor – Goodness of fit

Edge position – From the first derivative marked in Figure 3

Bond Valence Sum is given by [20, 21];

$$BVS_i = \sum_{j=1}^n \exp \left[\frac{(R_0 - R)}{B} \right]$$

Where

i – Binding site (Fe)

R_0 – Empirically determined constant;

for Fe(II)-O, $R_0=1.734$ and Fe(III)-O, $R_0=1.759$ [20, 22, 23]

B – 0.37, Empirically determined constant [20]

n - coordination number of binding site i

The bond-valence model has been reported as a reliable way to use structural data to validate assumed oxidation states [24]. Here the bond valence sum (BVS), calculated using a coordination number of 6 (Table 4-2), were compared to those of LFS and $\text{LiFe}(\text{SO}_4)_2$ reported from magnetic and nuclear measurements by Reynaud *et. al.*[25] The +2 oxidation state of LFS compared favourably with a value of 2.26 for PVDF and 2.22 for PAN in comparison to the reported 2.22 [25]. While LFS showed a discrepancy with 3.32 for PVDF and 3.30 for PAN in comparison to the reported 2.93 [25]. However, the BVS values for PAN and PVDF were found to compare favourably with the +3 oxidation state reference, $\text{Fe}_2(\text{SO}_4)_3$ of BVS value 3.28. Next, the Fe-O bond lengths in Table 4-2 were plotted along with the charge-discharge cycle as a function of time (Figure 4-8).

Figure 4-8: Changes in Fe-O bond lengths observed through first shell analysis of *ex-situ* XAFS data and corresponding oxidation state of Fe estimated based on bond length. Upon charging the Fe-O bond length was found to decrease from 2.09 Å to 1.98 Å, and subsequently upon discharge was found to return to a bond length of 2.11 Å when the PVDF binder was used. When PAN was used, a similar trend follows.

It was observed that the Fe-O bond length maintains its value between 2.09 Å and 2.12 Å during the charging process from 3.3 V to 3.9 V vs. Li. Beyond 3.9 V the de-intercalation of Li from LFS begins and a large reduction in the Fe-O bond length is observed from 2.12 Å to 1.98 Å at the point of maximum charge. This is indicative of Fe moving from 2+ oxidation state to 3+ in accordance with Fe-O bond lengths for Fe^{2+} reference at 2.10 Å and for Fe^{3+} reference at 1.98 Å (Table 4-2). These values reflect Fe-O bond length variation with oxidation state observed previously [26]. Subsequently, upon discharge, the Fe-O bond length increased when the intercalation process began and returned to 2.11 Å, slightly greater than its initial state. This indicates that the local structure is restored after the first cycle of charge and discharge as Fe cycles through an oxidation state of Fe^{2+} to Fe^{3+} and back to Fe^{2+} .

4.3.4 Cycling Performance of Different Binders

Here, we have evaluated the performance of the high voltage LFS electrode using conventional cell testing methods where the electrode was prepared using 6 wt% of PVDF or PAN binder by manual grinding with active material. Importantly, the obtained results were compared with the existing results[1] in terms of cycling and rate performance.

Figure 4-9: Cycling and rate performance of LFS without binder compared to performances with PVDF and PAN binders shows that at low C-rates of C/15, the cycling is consistent with high coulombic efficiency but upon moving to higher C-rates, the system with PVDF or PAN binders retains only about 29% of discharge capacity compared to the system without any binder.

Figure 4-9 shows the cycling performance over 25 cycles at a C-rate of C/15 followed by another 55 cycles at increased C-rates. For the very first time, long term cycle life was tested for such a class of sulphates in both the cell fabrication methods, with and without PVDF binder. The cycle life tested for the cell is illustrated in Figure 4-9 and shows consistent cycling performance at low C-rate of C/15 (1C= 2.475 mA) for systems with and without binder. The obtained

results showed a long cycle life (of 25 cycles) than the previous report (10 cycles) [1]. The observed retention in capacity was about 92% over the 25 cycles for system without binder; whereas it was 85% for the cell assembled with binder (both PAN and PVDF). This was repeated over multiple times and all indicated consistency in results.

At a high C-Rate (8C/15) the cell fabricated with binder showed a discharge capacity about 61% lower than the cell without binder at the same C-rate. This was primarily attributed to the addition of the binder, which has an insulating nature, encapsulating the carbon coated LFS. It needs to be noted that this decrease in performance was observed for both binders, indicating that a fluorinated binder has no advantage or disadvantage compared to a non-fluorinated binder, with respect to sulphate materials. This indicates that the binder plays a crucial role in performance at high currents. Finally, it was noted that upon reducing the current to the original C-rate (C/15), the loss in discharge capacity was less than 10 mAh.g⁻¹ in both systems indicating that the binder did not cause any structural modification of the LFS active material.

Cyclic Voltammetry studies were carried out at 0.05 mV.s⁻¹ in a voltage range of 3.2 V to 4.2 V with respect to a Li metal anode. Figure 4-10 shows the result across 2 cycles. There were two distinct peaks, indicating the Fe^{2+/3+} redox couple at 3.65 V and 4.1 V respectively. Two redox couple peaks seem to exist in the region between 3.7 V and 3.9 V as well. These 2 peaks have been attributed to poor elasticity of the precursor phases of LFS thereby resulting in intermediate phases that act as a buffer [27]. The result of interest from this study, however, is with respect to the current involved for the three different systems in the process. The highest current was seen in the case when no binder was used while least current is seen in the case where PVDF was used. This indicates higher resistance of the PVDF binder.

Figure 4-10: Comparison of CV for the 1st and 2nd cycles of LFS with and without binders. It shows maximum current flow for system without binder, while PVDF shows the least current flow

This in turn was corroborated by electrochemical impedance spectroscopy (EIS) studies (Figure 4-11), which indicate a high charge transfer resistance, R_{CT} for PVDF that inhibits electron flow [28, 29]. This resistance was magnified at higher C-rates explaining why the PVDF caused such low capacity at high currents. However, PAN showed similar resistance to that of a system without binder. Hence it needs further investigation as to why it caused low capacities at high C-rate. Thus, this detailed study on effect of binders in retarding performance of LFS at high C-rates will allow for greater research into novel binders more suited to sulphates.

Figure 4-11: Electrochemical Impedance Spectroscopy of LFS with and without binders. Indicates a large charge transfer resistance, R_{CT} for PVDF compared to that for PAN and the system with no binder. PVDF also exhibits a high double layer capacitance compared to PAN

4.3.5 Cycling Performance of Different Carbon Additives

After understanding the behaviour of LFS in the presence of binders, the effects of carbon additives which are used to improve electronic conductivity of the poorly electronically conduction sulphates were studied. Four different carbon

additives were used; Super P Carbon (Timcal), Multi Walled Carbon Nanotubes (MWCNT) (Nanocyl NC7000), Single Walled Carbon Nanotubes (SWCNT) (Nanocyl NC1100) and Graphene.

4.3.6 Scanning Electron Microscopy

These above four additives were chosen to represent the gradual transition from amorphous spherical particles of Super P carbon to crystalline graphene with a transition through CNTs of varying diameters (Figure 4-12).

Figure 4-12: SEM images of the four carbon additives used: a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene

4.3.7 Thermal Analysis

The active material was ball milled with each of the carbon additives in the ratio of 80:20 (wt%). The four samples were then subjected to TGA tests to observe

the thermal behaviour when heated in a furnace with air flow. The sample with SWCNT additive showed the earliest combustion indicated by the weight loss initiating at 300 °C (Figure 4-13). MWCNT, Super P carbon and graphene showed increasing temperatures of combustion. Although the Super P carbon started combustion after SWCNT, it undergoes rapid combustion to show similar weight loss as the SWCNT based system by 600 °C.

Figure 4-13: TGA curves of the four carbon additives used; a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene

4.3.8 Electrochemical Analysis

Next, the LFS sample was subjected to GCD test to observe its electrochemical behaviour in the presence of each of the four additives. It was noted that the samples with increasingly crystalline additives, showed discharge curves with increasingly pronounced steps as seen in Figure 4-14. This could be attributed to the differing conductivity of the additives. The rapid electron flow in the highly crystalline additives but sluggish electron flow in the active material could result in an accumulation of electrons and therefore ions thereby leading to the

formation of intermediate species. However, such steps are not seen in the charge cycle and requires further study.

Figure 4-14: GCD curves of the four carbon additives used: a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene

Finally, the four samples were subjected to rate performance studies at a C-rate of C/15, to observe cycling performance up to 50 cycles. Figure 4-15 showed that the least loss of discharge capacity was observed after 50 cycles compared to the 1st cycle, when the MWCNT additive was used. For both MWCNT and SWCNT additives, there was an initial increase in discharge capacity up to the first 10 cycles. Thereafter, it was followed by consistent decrease in the discharge capacity. However, in the case of Super P carbon and graphene, the discharge capacity consistently decreased right from the first cycle. While all the additives showed consistent discharge capacity while cycling, the SWCNT showed a sudden drop in efficiency after 25-30 cycles and a steeper decrease in discharge

capacity. This, in turn, means that charging capacity suddenly drops thereby indicating a bottleneck in Li ion intercalation over 25 cycles when SWCNT additive is used.

Figure 4-15: Cycling performance of the four carbon additives used; a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene

Similarly, rate performance studies were carried out on the additives to understand how the kinetics of intercalation are affected by use of differently conducting additives. All the rate performance tests were done after 50 cycles at C/15 rate. The C-rate was varied every 11 cycles from $C^* = C/15$ to $8C^*$. Figure 4-16 details the effect of the various additives on the performance of LFS. All the additives showed a similar profile of the magnitude of discharge capacity in terms of variation with C-rate. However, the variation in efficiency was found to be the most for the SWCNT additive. The efficiency was found to be lowest at C^* while there was a greater than 10% improvement in efficiency with increased C-rates. Table 4-3 shows the percentage decrease of the discharge capacity at various rates

compared to the initial C-rate of C^* . The SWCNT was found to exhibit the least drop in capacity at each rate. However, graphene was found to be surprisingly poorer than even Super P carbon indicating that the conductivity was not a key factor in improving rate performance. This effect of additives requires further studies which it is hope will be pursued in the future.

Figure 4-16: Rate performance of the four carbon additives used; a) Super P carbon, b) MWCNT, c) SWCNT, d) graphene

Table 4-3: Decrease in discharge capacity from initial charge rate for different carbon additives

Charge Rate	Discharge Capacity decrease (%)			
	Super P	MWCNT	SWCNT	Graphene
$C^*=C/15$				
C^*	-	-	-	-
$2C^*$	8%	5%	2%	14%
$4C^*$	16%	15%	10%	26%
$8C^*$	22%	26%	20%	37%
C^*	7%	7%	2%	17%

4.4 Conclusion

Monoclinic LFS was successfully synthesised and a detailed study of its electrochemical mechanism in the presence of fluorinated and non-fluorinated binders, during the charge and discharge processes, was analysed using XAS. This is the first time, such *ex-situ* XAS analysis of LFS cathode has been carried out. Subsequently, cycling and rate performance studies were also conducted on this class of sulphates to study its interaction with binders - PVDF and PAN - as well as 4 types of carbon additives; a) Super P carbon, b) MWCNT, c) SWCNT, and graphene. Again, this was the first time that the extended cycling performance (50 cycles) of such sulphate based electrodes was studied. It was determined that at low C-rate (C/15) the binder has no effect on the consistency of the cycling performance of the electrode. However, at high C-rate, the cell with binder showed low discharge capacity and requires further improvement for achieving better performance. Regarding the carbon additives, it was observed that LFS with SWCNT additive showed poor cycling performance while with MWCNTs, it showed the most consistency.

4.5 References

- [1] M. Reynaud, M. Ati, B. C. Melot, M. T. Sougrati, G. Rousse, J.-N. Chotard, *et al.*, "Li₂Fe(SO₄)₂ as a 3.83 V positive electrode material," *Electrochemistry Communications*, vol. 21, pp. 77-80, 2012.
- [2] M. Reynaud, "Design of new sulfate-based positive electrode materials for Li- and Na-ion batteries," Ph.D. Doctoral Dissertation, Materials Science, Université de Picardie Jules Verne, 2013.
- [3] T. Okumura, Y. Yamaguchi, and H. Kobayashi, "X-ray Absorption Near-Edge Structures of LiMn₂O₄ and LiNi_{0.5}Mn_{1.5}O₄ Spinel Oxides for Lithium-Ion Batteries: First-Principles Calculation Study," *Physical Chemistry Chemical Physics*, 2016.
- [4] Y. Du, Y. Zhu, S. Xi, P. Yang, H. O. Moser, M. B. Breese, *et al.*, "XAFCA: A New XAFS Beamline for Catalysis Research," *Journal of Synchrotron Radiation*, vol. 22, pp. 839-843, 2015.

- [5] B. Ravel and M. Newville, "ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy using Ifeffit," *Journal of Synchrotron Radiation*, vol. 12, pp. 537-541, 2005.
- [6] B. Scrosati and J. Garche, "Lithium batteries: Status, prospects and future," *Journal of Power Sources*, vol. 195, pp. 2419-2430, 2010.
- [7] M. Wilke, F. Farges, P.-E. Petit, G. E. Brown, and F. Martin, "Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study," *American Mineralogist*, vol. 86, pp. 714-730, 2001.
- [8] G. A. Waychunas, M. J. Apter, and G. E. Brown, "X-ray K-edge absorption spectra of Fe minerals and model compounds: near-edge structure," *Physics and Chemistry of Minerals*, vol. 10, pp. 1-9, 1983.
- [9] A. Deb, U. Bergmann, E. J. Cairns, and S. P. Cramer, "Structural investigations of LiFePO₄ electrodes by Fe X-ray absorption spectroscopy," *The Journal of Physical Chemistry B*, vol. 108, pp. 7046-7051, 2004.
- [10] A. A. M. Prince, S. Mylswamy, T. S. Chan, R. S. Liu, B. Hannoyer, M. Jean, *et al.*, "Investigation of Fe valence in LiFePO₄ by Mössbauer and XANES spectroscopic techniques," *Solid State Communications*, vol. 132, pp. 455-458, 2004/11/01/ 2004.
- [11] E. White and H. McKinsty, "Chemical effect on X-ray absorption-edge fine structure," in *Advances in X-ray Analysis*, ed: Springer, 1966, pp. 376-392.
- [12] U. Srivastava and H. Nigam, "X-ray absorption edge spectrometry (XAES) as applied to coordination chemistry," *Coordination Chemistry Reviews*, vol. 9, pp. 275-310, 1973.
- [13] O. Haas, A. Deb, E. Cairns, and A. Wokaun, "Synchrotron X-ray absorption study of LiFePO₄ electrodes," *Journal of the Electrochemical Society*, vol. 152, pp. A191-A196, 2005.
- [14] A. Manceau, A. I. Gorshkov, and V. A. Drits, "Structural chemistry of Mn, Fe, Co, and Ni in manganese hydrous oxides; Part I, information from XANES spectroscopy," *American Mineralogist*, vol. 77, pp. 1133-1143, 1992.
- [15] M. Belli, A. Scafati, A. Bianconi, S. Mobilio, L. Palladino, A. Reale, *et al.*, "X-ray absorption near edge structures (XANES) in simple and complex Mn compounds," *Solid State Communications*, vol. 35, pp. 355-361, 1980.

- [16] T. E. Westre, P. Kennepohl, J. G. DeWitt, B. Hedman, K. O. Hodgson, and E. I. Solomon, "A multiplet analysis of Fe K-edge $1s \rightarrow 3d$ pre-edge features of iron complexes," *Journal of the American Chemical Society*, vol. 119, pp. 6297-6314, 1997.
- [17] T. Zhao, X.-J. Zhang, X. Li, and S.-G. Lu, "Crystallinity dependence of electrochemical properties for LiFePO_4 ," *Rare Metals*, vol. 34, pp. 334-337, May 01 2015.
- [18] K. Inoue, S. Fujieda, K. Shinoda, S. Suzuki, and Y. Waseda, "Chemical state of iron of LiFePO_4 during charge-discharge cycles studied by in-situ x-ray absorption spectroscopy," *Materials transactions*, vol. 51, pp. 2220-2224, 2010.
- [19] K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *Journal of Applied Crystallography*, vol. 44, pp. 1272-1276, 2011.
- [20] I. Brown and D. Altermatt, "Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database," *Acta Crystallographica Section B: Structural Science*, vol. 41, pp. 244-247, 1985.
- [21] I. t. Brown and R. Shannon, "Empirical bond-strength-bond-length curves for oxides," *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, vol. 29, pp. 266-282, 1973.
- [22] S. M. Kanowitz and G. J. Palenik, "Bond Valence Sums in Coordination Chemistry Using Oxidation-State-Independent R_0 Values. A Simple Method for Calculating the Oxidation State of Iron in Fe-O Complexes," *Inorganic Chemistry*, vol. 37, pp. 2086-2088, 1998/04/20 1998.
- [23] H. H. Thorp, "Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes," *Inorganic Chemistry*, vol. 31, pp. 1585-1588, 1992.
- [24] H. Zheng, K. M. Langner, G. P. Shields, J. Hou, M. Kowiel, F. H. Allen, *et al.*, "Data mining of iron(II) and iron(III) bond-valence parameters, and their relevance for macromolecular crystallography," *Acta Crystallographica. Section D, Structural Biology*, vol. 73, pp. 316-325, 2017.
- [25] M. Reynaud, G. Rousse, J.-N. Chotard, J. Rodríguez-Carvajal, and J.-M. Tarascon, "Marinite $\text{Li}_2\text{M}(\text{SO}_4)_2$ ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}$) and $\text{LiFe}(\text{SO}_4)_2$: Model Compounds for Super-Super-Exchange Magnetic Interactions," *Inorganic Chemistry*, vol. 52, pp. 10456-10466, 2013/09/16 2013.

- [26] Z. Y. Wu, S. Gota, F. Jollet, M. Pollak, M. Gautier-Soyer, and C. R. Natoli, "Characterization of Iron Oxides by X-Ray Absorption at the Oxygen K Edge using a Full Multiple-Scattering Approach," *Physical Review B*, vol. 55, pp. 2570-2577, 01/15/ 1997.
- [27] L. Lander, M. Reynaud, G. Rousse, M. T. Sougrati, C. Laberty-Robert, R. J. Messinger, *et al.*, "Synthesis and Electrochemical Performance of the Orthorhombic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ Polymorph for Li-Ion Batteries," *Chemistry of Materials*, vol. 26, pp. 4178-4189, 2014/07/22 2014.
- [28] A. Jossen, "Fundamentals of battery dynamics," *Journal of Power Sources*, vol. 154, pp. 530-538, 2006.
- [29] D. Aurbach, "Review of selected electrode–solution interactions which determine the performance of Li and Li ion batteries," *Journal of Power Sources*, vol. 89, pp. 206-218, 2000.

Chapter 5

Fundamental Properties of Bi-metallic Sulphates

$\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2 = \text{Co, Mn, Ni}$)

A novel solid solution series of bi-metallic sulphates $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2 = \text{Co, Mn, Ni}$ and $x=0$ to 1) was synthesised using a combination of high energy ball milling and annealing in a completely solid state process. These substituted sulphates were analysed to determine their structural, thermal, magnetic and moisture sensitivity properties. The structural analysis describes the transition between different crystal systems upon substitution. The thermal analysis of the end members of the solid solutions series details the decomposition pathway of the material at high temperature. Since sulphates are known to be sensitive to moisture, this sensitivity was characterised by determining the hydration mechanism. This played a crucial role in the handling of these sulphate based electrode materials during cell fabrication. Finally, the magnetic properties of the materials were investigated using solid state ^7Li NMR and SQUID magnetometry.

5.1 Introduction

Lithium iron phosphate (LiFePO_4) is a positive electrode material that allows for safe handling and operation [1, 2]. Its discovery heralded research into polyanionic electrode materials as viable systems for lithium ion batteries. This has resulted in intensive research in these types of compounds over the past two decades[3]. One of the major issues with these compounds is the additional weight of the polyanionic group[3] that reduces the specific capacity of the system. This directly affects the energy density of the system. Since the energy density is linearly linked with the operating potential of the cathode material, it is important to increase the operating potential window of such a compound for further enhancement in the cell characteristics. In turn, the operational potential window of any battery material is mainly based on the redox reaction involved in the compounds during the cell operation. The redox potential in polyanionic systems is governed primarily by the iono-covalency of the M-O bond (M - transition metal), where the higher the ionicity of the bond, greater is the system's redox potential[4]. The O-ion component of the XO_4^{n-} ($\text{X} = \text{P, S, W, Si}$) polyanionic group is subjected to an inductive effect, based on the electronegative character of the X ion [5, 6]. A higher electronegativity results in a higher redox potential, and this has prompted the intense research of sulphate based lithium electrode materials [4, 7, 8].

Among the sulphate based positive electrode materials the sulphates synthesised through solid state reactions have shown highest the redox potentials for Fe at 3.83 V (*vs.* Li) [9], second only to the ionothermally synthesised fluorosulphate analogue that shows 3.90 V (*vs.* Li) [10]. This was followed by synthesis of the Co, Mn and Ni based compounds [11, 12]. Previous reports[9, 11, 13-16] have purely focused on Fe based sulphates as they have been unable to uncover the electrochemical activity of other transition elements except Co in LiCoSO_4OH at 4.8 V *vs* Li [17]. However, the atomistic modelling/Density Functional Theory (DFT) techniques of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of sulphates have predicted the redox

potential to be 5.2 V vs. Li for Co and 4.54 V vs. Li for Mn [18]. Co activity is outside the voltage window of conventional electrolytes and hence has not been tested earlier, however Mn which lies well within the voltage window was found to be electrochemically inactive [4]. The Mn dissolution from the crystal lattice in the Mn based compounds has been pointed to as the major issue for its inactivity [19]. Substitution with Co would alleviate such a Mn dissolution issue. Hence, in this work, the main focus was on developing a novel solid-solution series of $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2 = \text{Co, Mn, Ni}$ and $x=0$ to 1) high voltage cathodes and detailing their structural, thermal, magnetic and moisture sensitivity properties.

5.2 Experimental Methods

5.2.1 Synthesis

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (99%), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, used to prepare the anhydrous phases, were purchased from Sigma Aldrich. Anhydrous phases were prepared by heating the compound in an Ar atmosphere in a tube furnace for 1 hr. $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was dehydrated at 200 °C, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ at 300 °C and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ at 350 °C. To prepare a pure phase of $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ ($x=0$ to 1), stoichiometric ratios of CoSO_4 , MnSO_4 and Li_2SO_4 were subjected to a solid-state synthesis procedure reported earlier[9]. The given mol fraction/percentage of the precursors were mixed with few drops of absolute ethanol and subjected to high energy ball milling in a SPEX 8000M system for 24 min in air. The resultant powder was then collected and pressed into a 20 mm diameter pellet at a pressure of 8 kN followed by annealing the pellet at 450 °C for 12 hrs with a temperature ramping of 5 °C.min⁻¹ in a box furnace.

5.2.2 Structural Analysis

Structural characteristics of the as-synthesised samples were analysed using an X'Pert Powder Panalytical X-Ray Diffraction (XRD) analyzer, equipped with Cu-K α radiation operated at 40 kV and 30 mA. The data was recorded over the

range of 2θ from 10° to 80° at $1.147^\circ\text{min}^{-1}$. Elemental analysis was carried out using Energy Dispersive X-ray (EDX) spectroscopy using a Field Emission Scanning Electron Microscope (FESEM; Jeol 6340F, Japan).

5.2.3 Thermal Analysis

The as prepared samples were subjected to thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to determine the thermal stability of the compounds. Thermal studies were also coupled with Mass Spectroscopy (MS) to analyse the evolution of the gas species with respect to the heating temperature. The TGA and MS experiments were carried out under Ar flow ($50\text{ ml}\cdot\text{min}^{-1}$) with $\sim 15\text{-}20\text{ mg}$ of powder samples over the temperature range from ambient temperature to 800°C , at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

5.2.4 Moisture Sensitivity Analysis

Synthesised samples were exposed to a humid atmosphere for a prolonged period to determine the effect of atmospheric moisture on the structural stability. The samples were placed in a controlled humidity chamber with a controlled relative humidity of 45-60% over a period of 36 days. Subsequently, XRD tests were conducted on the sample to track the extent of degradation.

5.2.5 Nuclear Magnetic Resonance Spectroscopy

All ^7Li ($I = 3/2$) spectra were recorded on a Bruker Advance HD spectrometer (2.35 T) at a Larmor frequency (ν_0) of 38.9 MHz ($\nu_0(^1\text{H}) = 100\text{ MHz}$ [20]). A 1.3 mm double air bearing magic angle spinning probe was utilised to give frequencies of 40 kHz. All spectra were referenced to $\text{LiCl}_{(\text{s})}$ ($\delta_{\text{iso}} = -0.77\text{ ppm}$ w.r.t. $1\text{M LiCl}_{(\text{aq})} = 0\text{ ppm}$). A saturation recovery echo sequence was employed to measure the T_1 relaxation of the systems, with variable delays ranging from 1×10^{-4} to 0.5 seconds over a temperature range of 265.1 to 315.1 K. All data was fitted to a single exponential ($f(t) = I_0 \times (1 - e^{-t/T_1})$). A prior to measurement temperature calibration was completed on samarium stannate [21].

5.2.6 SQUID Magnetometry

A superconducting quantum interference device (SQUID) was used to carry out magnetic measurements. A Quantum Design MPMS-XL SQUID magnetometer was used for the tests in the temperature range 10–300 K. Irreversibility of the dependence of magnetisation(M) on the applied magnetic field(H) was determined using zero field cooled (ZFC) and field cooled tests (FC) [22]. ZFC measurement was made by first cooling the sample to 10 K at $H=0$. Once the readings had stabilised, a magnetic field of 1 kOe was applied and the magnetisation was measured as a function of temperature up to 300 K. Subsequently, the FC data was collected by cooling the sample back to 10 K at the same applied of 1 kOe. These set of data comprised the magnetisation(M) vs. temperature(T) plots. The M vs. H plots were determined by varying the applied magnetic field(H) at three different temperatures; 10 K, 50 K and 100 K.

5.3 Results and Discussion

5.3.1 Structural Analysis

5.3.1.1 $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$

Figure 5-1 shows the XRD patterns of the $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ samples. The entire series showed the single phase monoclinic crystal structure, and there was no evidence of the presence of orthorhombic polymorph as the synthesis temperature exceeded 400 °C [16]. A shift towards larger diffraction angles is observed with increasing Co substitution (mole fraction x varying from 0 to 1) in the final composition of the synthesised powders. This indicates a reduction in cell volume as plotted in Figure 5-3. This trend is expected due to the substitution of the larger Mn^{2+} ion (Ionic Radius = 0.75 Å)[23] by the smaller Co^{2+} ion (Ionic Radius = 0.65 Å)[23] in the presence of high spin ligand SO_4^{2-} . Thus, the linear reduction in cell parameters with increasing Co substitution in the synthesis is also indicated in the Figure 2. Since, all the three parameters a , b and c obtained from this study show the similar trend, the variation in the crystal structure properties could be considered isotropic.

Figure 5-1: Powder XRD patterns of $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ solid solution series

Figure 5-2: Monoclinic structure of: Left - $\text{Li}_2\text{Mn}(\text{SO}_4)_2$, Right - $\text{Li}_2\text{Co}(\text{SO}_4)_2$, where Green – Lithium ions, Beige – MnO_6 octahedra, Magenta - CoO_6 octahedra, Yellow – SO_4 tetrahedra

Figure 5-3: Variation of the lattice parameters, a , b , c , β , and unit cell volume V with x in $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ active materials powders

In addition to XRD analysis, the successful substitution and nominal compositions of the samples were confirmed by Energy-dispersive X-ray spectroscopy (EDX) measurements (Table 5-1). The substitution was consistent and in accordance with the stoichiometry used during synthesis process.

Table 5-1: EDX measurements showing the relative percentage concentration of the respective elements

Sample	Co %	Mn %	Experimental Ratio Co: Mn	Theoretical Ratio Co: Mn
$\text{Li}_2\text{Mn}(\text{SO}_4)_2$	-	20.1	0:1	0:1
$\text{Li}_2\text{Co}_{0.1}\text{Mn}_{0.9}(\text{SO}_4)_2$	2.3	18.5	1:8	1:9
$\text{Li}_2\text{Co}_{0.3}\text{Mn}_{0.7}(\text{SO}_4)_2$	6.6	14.4	3:6.6	3:7
$\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$	10.6	10.5	1:1	1:1
$\text{Li}_2\text{Co}_{0.7}\text{Mn}_{0.3}(\text{SO}_4)_2$	15.2	6.1	7.5:3	7:3
$\text{Li}_2\text{Co}_{0.9}\text{Mn}_{0.1}(\text{SO}_4)_2$	18.8	2.1	9:1	9:1
$\text{Li}_2\text{Co}(\text{SO}_4)_2$	21.0	-	1:0	1:0

5.3.1.2 $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}(\text{SO}_4)_2$

XRD patterns of the as prepared $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ samples are shown in Figure 5-4. The series shows the single phase monoclinic crystal structure and from $x = 0$ to 0.5 and orthorhombic from $x = 0.5$ to 1. At $x=0.5$ we see the initial stages of growth of an orthorhombic phase indicated by the presence of a peak just before the diffraction angle at 15° . Thus, at $x=0.5$ we have a 2- phase product. In addition to XRD analysis, the successful substitution and nominal compositions of the samples were confirmed by Energy-dispersive X-ray spectroscopy (EDX) measurements (Table 5-2). The substitution was consistent and in accordance with the stoichiometry used during synthesis process.

Figure 5-4: XRD patterns of $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}(\text{SO}_4)_2$ solid solution seriesTable 5-2: EDX measurements showing the relative percentage concentration of the respective elements in $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}(\text{SO}_4)_2$

Sample	Ni %	Mn %	Experimental	Theoretical
			Ratio	Ratio
			Ni: Mn	Ni: Mn
$\text{Li}_2\text{Mn}(\text{SO}_4)_2$	-	20.1	0:1	0:1
$\text{Li}_2\text{Ni}_{0.1}\text{Mn}_{0.9}(\text{SO}_4)_2$	1.9	18.4	1:9.7	1:9
$\text{Li}_2\text{Ni}_{0.3}\text{Mn}_{0.7}(\text{SO}_4)_2$	21.5	54.4	3:7.6	3:7
$\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$	5.2	5.5	1:1	1:1
$\text{Li}_2\text{Ni}_{0.7}\text{Mn}_{0.3}(\text{SO}_4)_2$	15.2	6.1	6.7:3	7:3
$\text{Li}_2\text{Ni}_{0.9}\text{Mn}_{0.1}(\text{SO}_4)_2$	15.9	7.1	9.3:1	9:1
$\text{Li}_2\text{Ni}(\text{SO}_4)_2$	20.5	-	1:0	1:0

5.3.1.3 $\text{Li}_2\text{Ni}_x\text{Co}_{1-x}(\text{SO}_4)_2$

XRD patterns of the as prepared $\text{Li}_2\text{Ni}_x\text{Co}_{1-x}(\text{SO}_4)_2$ samples are shown in Figure 5-5. The series shows the single phase monoclinic crystal structure and from $x = 0$ to 0.5 and orthorhombic from $x = 0.5$ to 1. At $x=0.5$ we see the initial stages of growth of an orthorhombic phase indicated by the presence of a peak just before the diffraction angle at 15° . Thus, at $x=0.5$ we have a 2- phase product. In addition to XRD analysis, the successful substitution and nominal compositions of the samples were confirmed by Energy-dispersive X-ray spectroscopy (EDX) measurements (Table 5-3). The substitution was consistent and in accordance with the stoichiometry used during synthesis process.

Figure 5-5: XRD patterns of $\text{Li}_2\text{Ni}_x\text{Co}_{1-x}(\text{SO}_4)_2$ solid solution series

Table 5-3: EDX measurements showing the relative percentage concentration of the respective elements in $\text{Li}_2\text{Ni}_x\text{Co}_{1-x}(\text{SO}_4)_2$

Sample	Ni %	Co %	Experimental Ratio Ni: Co	Theoretical Ratio Ni: Co
$\text{Li}_2\text{Co}(\text{SO}_4)_2$	-	21.0	0:1	0:1
$\text{Li}_2\text{Ni}_{0.1}\text{Co}_{0.9}(\text{SO}_4)_2$	2.0	18.9	1:9.5	1:9
$\text{Li}_2\text{Ni}_{0.3}\text{Co}_{0.7}(\text{SO}_4)_2$	6.0	14.8	3:7.4	3:7
$\text{Li}_2\text{Ni}_{0.5}\text{Co}_{0.5}(\text{SO}_4)_2$	9.9	10.5	1:1.1	1:1
$\text{Li}_2\text{Ni}_{0.7}\text{Co}_{0.3}(\text{SO}_4)_2$	14.3	6.5	6.6:3	7:3
$\text{Li}_2\text{Ni}_{0.9}\text{Co}_{0.1}(\text{SO}_4)_2$	18.7	2.2	8.5:1	9:1
$\text{Li}_2\text{Ni}(\text{SO}_4)_2$	20.5	-	1:0	1:0

5.3.2 Thermal Stability

Previous work[16] on this class of bi-metallic sulphates focused on the thermal stability below 500 °C. In for the very first time, high temperature tolerance (>500 °C) of such class of materials was investigated which gives clear visibility about thermal stability of the samples. These obtained results were in a much higher range than the previously reported work [16].

The as prepared $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$, and $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ samples were subjected to simultaneous TGA, DSC and MS tests. The obtained results are shown in Figure 5-6 and are found to be similar for all three materials, and can possibly be attributed to their similar crystal structures. The TGA curve of all the samples showed a weight loss only after 650, 700 and 750 °C for $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$, and $\text{Li}_2\text{Mn}(\text{SO}_4)_2$, respectively. This indicates that higher Mn concentration in the system prevents decomposition products from being released at lower temperatures.

Figure 5-6: Thermal stability analysis of the prepared samples using TGA-DSC-MS

The DSC curve showed three peaks between 550 °C and 650 °C in all three systems; however, the coupled MS did not reveal any release of gas in this temperature range and thus a phase change of the materials was suspected. In order to investigate this, further, a sample of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ was chosen as a representative crystal structure and subjected to in-situ XRD under a reduced pressure. During the in-situ XRD study, an amorphous phase was obtained beyond 450 °C specifically when heated under a reduced pressure. Hence to avoid the formation of an amorphous phase, a traditional setup of ex-situ XRD was used. Here the sample was first heated in a box furnace, cooled to room temperature and then finally subjected to powder XRD. The heating was carried out in stages of 25 °C as per the critical range indicated in the DSC pattern from 550 °C to 650 °C. The resulting XRD pattern showed the evolution of multiple phases as seen in Figure 5-7.

Figure 5-7: Thermally induced structural changes in $\text{Li}_2\text{Co}(\text{SO}_4)_2$ when heated between 550 °C and 650 °C

The XRD pattern of the phase finally formed at 650 °C was subjected to Rietveld refinement and yielded the formation of two phases, anhydrous Li_2SO_4 and $\alpha\text{-CoSO}_4$. In Figure 5-8, comparison of the XRD pattern of the anhydrous CoSO_4 precursor with the reference patterns of α and $\beta\text{-CoSO}_4$ obtained from literature[24, 25] shows that the precursor is $\beta\text{-CoSO}_4$.

Figure 5-8: Comparison of XRD pattern of precursor to reference patterns of α -CoSO₄ (*Pnma*)[24] and β -CoSO₄ (*Cmcm*)[25]

The α -CoSO₄ (space group *Pnma*) is structurally different from the β -CoSO₄ (space group *Cmcm*) as shown in Figure 5-9. α -CoSO₄ is isostructural to chalcocyanite [24] and is the more stable of the two polymorphs at temperatures above 432 °C [26]. Therefore, it is proposed that while β -CoSO₄ reacts with Li₂SO₄ to form Li₂Co(SO₄)₂ at lower temperatures, at high temperature (550 °C) more stable α -CoSO₄ is formed which does not recombine with the Li₂SO₄ upon cooling to reform Li₂Co(SO₄)₂. It was also noted from literature that at 575 °C Li₂SO₄ also undergoes a transformation from monoclinic to cubic structure [27]. The resulting reaction is detailed below.

Thus, the degradation of Li₂Co(SO₄)₂ occurs at a much lower temperature than indicated by the TGA curve.

Figure 5-9: Structural representations of the different polymorphs of CoSO_4 modelled using Vesta software[28] (Left - $\alpha\text{-CoSO}_4$ ($Pnma$) and Right - $\beta\text{-CoSO}_4$ ($Cmcm$)) where magenta polyhedra represent the CoO_6 octahedra with the SO_4 units shown as yellow tetrahedral

The $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ sample on the other hand showed a different mechanism when subjected to temperatures between 550 °C and 625 °C. Here, the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ decomposes into $\text{Li}_2\text{Mn}_2(\text{SO}_4)_3$ and Li_2SO_4 as indicated in Figure 5-10 . This mechanism, like in the decomposition of $\text{Li}_2\text{Co}(\text{SO}_4)_2$, does not involve any gas evolution and therefore the mass remains constant as indicated in the TGA plot in Figure 5-6. Reactions 5.3 and 5.4 detail the mechanism of decomposition.

Figure 5-10: Thermally induced structural changes in $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ when heated between 550 °C and 625 °C resulting in $\text{Li}_2\text{Mn}_2(\text{SO}_4)_3$ (ref. pattern [29]) and Li_2SO_4 (ref. pattern [30])

Finally, the $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ end member was analysed in the same temperature range as the Co and Mn analogues. It was found that beyond 550 °C the sample was again unstable and underwent decomposition with the evolution of SO_2 gas. Analysis of the XRD patterns as seen in Figure 5-11 and refinement of the products across the different stages of heating showed that the likely mechanism of decomposition was as shown in reactions 5.5 and 5.6.

Figure 5-11: Thermally induced structural changes in $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ when heated between 550 °C and 650 °C

Thus, it was seen that the end members of the solid solution series are thermally stable only below 550 °C. Since the other members of the solid solution series are isostructural and show similar DSC patterns, this maximum temperature of stability is applicable to the other materials as well.

5.3.3 Sensitivity to Moisture

Sulphates are generally soluble in water[4] and are susceptible to moisture during the various stages of materials synthesis, transport and battery fabrication. Thus, this segment focuses on understanding the mechanism of degradation of the parent sulphates; $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}(\text{SO}_4)_2$. The samples were placed in a container with relative humidity levels between 45 – 50 % to mimic real world situations. The analysis using powder XRD tests showed extensive degradation of the material within 36 days (Figure 5-12).

Figure 5-12: Moisture induced structural changes in $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ in an atmosphere of 45-50% Relative Humidity

Table 5-4: Decomposition products of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ when exposed to relative humidity of 45-50 % quantitatively determined using Reitveld refinement of XRD patterns

Compound	Percentage Weight Composition	
	after exposure to humidity	
	0 days	36 days
$\text{Li}_2\text{Co}(\text{SO}_4)_2$	100 %	-
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-	39 %
$\text{CoSO}_4 \cdot \text{H}_2\text{O}$	-	16 %
$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	-	45 %

The initially synthesised $\text{Li}_2\text{Co}(\text{SO}_4)_2$ was completely reduced to its hydrated precursors phases. This indicates stringent anhydrous protocols need to be adopted while handling sulphate based materials. The predominant degradation products were $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ while a significant proportion of monohydrate of CoSO_4 indicates an intermediate stage before complete hydration. Therefore, the mechanism of hydration using a previous study[31] on $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ dehydration is prospected to be as follows:

In the case of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$, the most stable hydrated form, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was formed along with $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ as seen in Table 5-5.

Table 5-5: Decomposition products of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ when exposed to relative humidity of 45-50 % quantitatively determined using Reitveld refinement of XRD patterns

Compound	Percentage Weight Composition	
	after exposure to humidity	
	0 days	36 days
$\text{Li}_2\text{Mn}(\text{SO}_4)_2$	100%	17 %
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-	33 %
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	-	50 %

Earlier reports [32, 33] have shown the presence of tetra, penta- and heptahydrated manganese sulphate. The reason that these higher states of hydration have not formed like in the case of the Co analogue can be attributed to the conditions of exposure to humidity. The temperature and relative humidity were maintained at 20-25 °C and 45-50 % respectively. It has been noted that for pentahydrates to form lower temperatures of nearly 15 °C and 98 % humidity is required [34]. Therefore, at lower temperatures and higher humidity, perhaps the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ could decompose to form higher hydrates as well. But in normal atmospheric conditions, the monohydrate is the most favoured state as shown in Table 5-5. Hence, the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ absorbs far less water per unit mass when compared to $\text{Li}_2\text{Co}(\text{SO}_4)_2$ which can hold more water molecules owing to a favoured hexahydrate state of the $\text{Co}(\text{SO}_4)$.

Figure 5-13: Variation of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ moisture content during analysis.

The rate of absorption of water as seen in Figure 5-13 was calculated to be consistent at 0.2 wt% per day over 68 days. The total moisture content was of two different types, water of hydration and adsorbed water. The total moisture absorbed continued rising even after touching 14% on day 68. It was observed that the water of hydration consistently increased and was the major component of the two at 85-88 % of the total moisture absorbed. Since the water of hydration is directly linked to the decomposition products as seen in Reaction 5.9, this indicates that the decomposition is at a constant rate and does not slow down with increasing absorbed moisture content. Also, theoretically the maximum moisture of hydration that can be taken up by complete degradation of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ is 13.9 % of the mass of the dry $\text{Li}_2\text{Mn}(\text{SO}_4)_2$, meaning that the water of hydration is nearing saturation in this system after 68 days.

In the case of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$, the most stable hydrated form, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ was formed along with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ as seen in Table 5-6.

Table 5-6: Decomposition products of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ when exposed to relative humidity of 45-50 % quantitatively determined using Reitveld refinement of XRD patterns

Compound	Percentage Weight Composition	
	after exposure to humidity	
	0 days	36 days
$\text{Li}_2\text{Ni}(\text{SO}_4)_2$	100%	13 %
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-	12%
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	-	33 %
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	-	42 %

An earlier report [35] has shown the decomposition of hepta-hydrated nickel sulphate to pass through various intermediary stages of hydration namely – hex,

tetra, and mono hydrate phases. Reactions 5.10 and 5.11 do indicate this as the refinement of the XRD patterns did not show the presence of the entire set of intermediary products except the mono and hexa-hydrate phase. It is possible that these hydrates were in small quantities and hence not readily distinguishable through XRD.

Figure 5-14 - Graphs of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ moisture content during analysis.

The rate of absorption of water as seen in Figure 5-14 was seemed to reach saturation after 42 days. It was observed that the water of hydration on day 42 was 73 % of the total moisture absorbed. Since the water of hydration is directly linked to the decomposition products as seen in Reaction 5.10, this indicates that the decomposition rate slows down with increasing absorbed moisture content. Also, theoretically, the maximum moisture of hydration that can be taken up by complete degradation of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ is 54.3 % of the mass of the dry $\text{Li}_2\text{Ni}(\text{SO}_4)_2$. This is nearly 4 times that of the theoretical maximum of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$. It was correspondingly observed that the hydration moisture content was 18% for $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ compared to only 7 % for $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ on day 42. The higher rate

of hydration and higher moisture content is primarily attributed to the mechanism of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ hydration as seen in Reaction 5.11, where the formation of a heptahydrate allows for increased moisture absorption.

5.3.4 ^7Li NMR Analysis

The ^7Li NMR studies were used to probe the Li atom and understand its environment in the parent as well as substituted sulphates. Six samples were analysed; the three parent sulphates $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$, $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ and three mixed sulphates $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}_{0.55}\text{Ni}_{0.5}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}_{0.5}\text{Ni}_{0.5}(\text{SO}_4)_2$.

5.3.4.1 $\text{Li}_2\text{Co}_x\text{Mn}_{1-x}(\text{SO}_4)_2$

The NMR spectra of the end members and the central member of this solid solution series is seen in Figure 5-15. The monoclinic structure of this series (Figure 5-1) consists of a single site for the two Li ions in the compound. Ideally this single site is represented by a single peak in the ^7Li NMR spectra. This was seen in $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ (peak 1) at a δ_{iso} at 26.5 ppm. However, there was an additional peak observed having nearly zero shift at -1.1 ppm. The same peak shows no variation with temperature in the isotropic shift plot in Figure 5-1. This indicates that the impurity is diamagnetic and hence the peak was attributed to Li_2SO_4 impurity in the compound [36]. Li_2SO_4 being a precursor used in the synthesis of the compound. However, this impurity was not visible in the XRD spectrum and hence is thought to exist in small quantities in the sample.

Figure 5-15: NMR spectra (left) and isotropic shift (right) comparison of $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$

Analysis of the $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ ^7Li NMR spectrum shows three peaks. The high intensity peak (peak 2) shows a shift comparable to $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ (peak 1) at 25.2 ppm. This indicates that the preferred site of occupancy for Li is similar to the Mn only environment observed in the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$. In addition, peaks 1 and 3 are seen at 188.8 ppm and -54.4 ppm. This indicates that the Li ion is capable of existing in a total of three different environments in $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$. Such multiple sites affect the intercalation and deintercalation of the Li ions in the electrode. This is because the Li ion sites might not be in the expected pathway as seen in Figure 5-2.

In the case of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ a broad peak is seen at 93.5 ppm. The broadness of the peak is indicative of disorder. This requires a deconvolution of the peak to fully understand the spectrum and has been proposed for future investigation. In the isotropic shift plots of all the peaks (except the peak attributed to Li_2SO_4), a linear relationship is observed between the shift and the inverse of the temperature. This shows paramagnetic character of the series and is further validated in the section on SQUID measurements.

5.3.4.2 $\text{Li}_2\text{Co}_x\text{Ni}_{1-x}(\text{SO}_4)_2$

The NMR spectra of the end members and the central member of this solid solution series is seen in Figure 5-16. $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ has been shown to have an orthorhombic structure through the XRD analysis earlier. Such orthorhombic structures have two Li sites and this was confirmed by the presence of two peaks in the ^7Li NMR spectra. The peaks at 25 ppm (peak 1) and -20 ppm (peak 2) are sharp indicating a very ordered structure of the compound. Between these two peaks is the presence of a very low intensity peak at -1 ppm. This nearly overlaps with the Li_2SO_4 peak earlier seen with $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ indicating the presence of the same impurity. The isotropic shift plots of the major peaks of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ both are gently sloping and linear versus inverse temperature indicating a milder paramagnetic character compared to the strongly sloping isotropic shift of $\text{Li}_2\text{Co}(\text{SO}_4)_2$.

Figure 5-16: NMR spectra (left) and isotropic shift (right) comparison of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$, $\text{Li}_2\text{Co}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}_{0.5}\text{Co}_{0.5}(\text{SO}_4)_2$

In the case of the $\text{Li}_2\text{Ni}_{0.5}\text{Co}_{0.5}(\text{SO}_4)_2$ ^7Li NMR spectrum, the analysis reveals a broad peak that shows significantly high slope in the isotropic shift plot. This is indicative of the broad peak consisting of a number of smaller peaks and again requires further study.

5.3.4.3 $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}(\text{SO}_4)_2$

The NMR spectra of the end members and the central member of this solid solution series is seen in Figure 5-17. Since the $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ and $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ spectra have been discussed in the previous two subsections, the focus will be on the $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ ^7Li NMR spectrum here. Five peaks were observed at 52.5 ppm, 42 ppm, 25.8 ppm, 9.5 ppm and -18.2 ppm. Peak 3 overlaps with the peak 1 of both $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}(\text{SO}_4)_2$. However, this is of lower intensity compared to peak 5 which nearly overlaps with peak 2 of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$. This indicates that the sites that Li occupies in the mixed sulphate is comparable to the site it occupies in $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ and not $\text{Li}_2\text{Mn}(\text{SO}_4)_2$. All these peaks (except $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ peak 2) display a positive slope and therefore a predominant paramagnetic character. The list of peak positions of all the sample analysed are summarised in Table 5-7.

Figure 5-17: NMR spectra (left) and isotropic shift (right) comparison of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$

Table 5-7: List of peak positions from ^7Li NMR spectra

Sample	Peak Position (ppm)				
	1	2	3	4	5
$\text{Li}_2\text{Co}(\text{SO}_4)_2$	93.5	-	-	-	-
$\text{Li}_2\text{Mn}(\text{SO}_4)_2$	26.5	-1.1	-	-	-
$\text{Li}_2\text{Ni}(\text{SO}_4)_2$	25.0	-20.0	-	-	-
$\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$	188.8	25.2	-54.4	-	-
$\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$	52.5	42.0	25.8	9.5	-18.2
$\text{Li}_2\text{Co}_{0.5}\text{Ni}_{0.5}(\text{SO}_4)_2$	9.7	-	-	-	-

In order to investigate the paramagnetic characteristics of these compounds, the samples were then subjected to magnetic measurements using a SQUID system.

5.3.5 SQUID Magnetic Measurements

5.3.5.1 M vs. H

The M vs. H plots (Figure 5-18) at all three temperatures (10, 50 and 100 K) were found to be linear for all samples except $\text{Li}_2\text{Ni}(\text{SO}_4)_2$. These linear, reversible plots passing through the origin indicate that the samples are paramagnetic. [37] The slope of the plots gives the magnetic susceptibility, χ , of the material. Figure 5-18 shows that χ generically decreases with increasing temperature for the different samples. Across the temperatures tested, $\text{Li}_2\text{Co}(\text{SO}_4)_2$, $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ were found to have the highest susceptibilities. At 10 K $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ was the highest, at 50 K $\text{Li}_2\text{Co}(\text{SO}_4)_2$ and at 100 K $\text{Li}_2\text{Mn}(\text{SO}_4)_2$. This in turn indicates all the samples with Ni content had a lower magnetic susceptibility. The susceptibility follows the Curie-Weiss law in this

paramagnetic region[38]. Subsequently, if the material becomes ordered, it behaves in a complex way and thus for a given field strength, can have multiple values. Paramagnetism can have different origins and this is determined by analysing the temperature dependence of magnetic susceptibility χ vs. T . These results are detailed in the next section.

Figure 5-18: Variation of M vs. H over 3 different temperatures 10,50 and 100 K

The M vs. H plot of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ (Figure 5-19) is unique in comparison to the other samples. Here the magnetisation is not a linear function of the magnetic field from 0-5 K. This is attributed to the existence of a ferromagnetic impurity [39]. The M vs. H plot is initially curved between 0 to 5 kOe and then is subsequently linear. This indicates that the ferromagnetic impurity is a second phase as opposed to a solid solution with $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ [40].

Figure 5-19: Field dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$, measured at 10, 50 and 100 in magnetic field of range from 0 to 50 kOe

5.3.5.2 χ vs T

Macroscopic magnetic properties of the six samples were analysed through χ vs T plots. For the samples $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ in Figure 5-20 and Figure 5-21 the ZFC and FC curves show a complete overlap in the region from 10 – 300 K at 1 kOe applied magnetic field. This is in contrast to the samples containing Ni which all show a cusp (Figure 5-23, Figure 5-24, Figure 5-25) at their respective Neel temperatures.

Figure 5-20: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ measured under ZFC and FC conditions with a field of 1 kOe between 10 K to 300 K back to 10 K

Figure 5-21: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ measured under ZFC and FC conditions

The Curie-Weiss equation was used to determine the Curie temperature (T_C) for $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$. They were found to be negative indicating the presence of a paramagnetic to antiferromagnetic transition. In practice, this transition temperature between paramagnetic and antiferromagnetic phases occurs at a positive temperature T_N known as the Neel temperature.[38] A study reported earlier [12] indicated that for $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ the T_N occurs at 6 K. Since this is below the testing range of 10-300 K for the analysis above, it explains the absence of the cusp in the plot.

In the case of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ the ZFC and FC curves have a huge separation indicating a spin glass behaviour. Spin glasses are defined as magnetic systems with quenched disorder where there is a competition between ferro- and antiferromagnetic interactions. This could be due to a high disorder in the system which was also corroborated by the broad peak in the ^7Li spectra seen in Figure 5-15. This phenomenon however requires further study as an earlier report [12] showed purely antiferromagnetic behaviour of the same material.

Figure 5-22: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ measured under ZFC and FC conditions

For all the samples containing Ni, the χ vs. T plots show a maximum at a certain critical temperature Neel temperature T_N . The sample is paramagnetic above T_N and antiferromagnetic below it.[40] Above the T_N , the material obeys the Curie–Weiss law but with a negative value of T_C . Both T_N and T_C divide the temperature scale into two regions: a magnetically ordered region below the critical temperature and a paramagnetic region above the critical temperature that is disordered [40]. The T_N of 28.5 K (Figure 5-23) for $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ agrees well with the literature reported value of 28 K [41]. When Ni is substituted with Mn and Co, the T_N was found to be 25 (Figure 5-25) and 22 K (Figure 5-24), respectively. All these temperatures have been reported in Table 5-8.

Figure 5-23: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Ni}(\text{SO}_4)_2$ measured under ZFC and FC conditions

Figure 5-24: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Co}_{0.5}\text{Ni}_{0.5}(\text{SO}_4)_2$ measured under ZFC and FC conditions

Figure 5-25: Temperature dependence of the magnetic susceptibility (χ) of $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$ measured under ZFC and FC conditions

Table 5-8: Neel temperature of Ni complexes

Sample	T_N (K)	
	This Work	Literature
$\text{Li}_2\text{Mn}(\text{SO}_4)_2$	-	-
$\text{Li}_2\text{Ni}(\text{SO}_4)_2$	28.5	28
$\text{Li}_2\text{Co}(\text{SO}_4)_2$	-	7
$\text{Li}_{0.5}\text{Mn}_{0.5}\text{Co}_{0.5}(\text{SO}_4)_2$	-	6
$\text{Li}_{0.5}\text{Ni}_{0.5}\text{Co}_{0.5}(\text{SO}_4)_2$	22	-
$\text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{0.5}(\text{SO}_4)_2$	25	-

The lowering in the T_N is due to the exchange interactions of the three different elements seen in Figure 5-26.

Figure 5-26: Bethe-Slater curve[40]

The Co being far more ferromagnetic has a higher effect on the T_N and lowers the value than Mn which is antiferromagnetic. However, deeper study of the substituted compounds is required to clearly articulate their magnetic properties and reason for variation.

5.4 Conclusion

A novel solid solution series of $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($x = 0$ to 1 , $\text{M}^1, \text{M}^2 = \text{Mn, Co}$ and Ni) was successfully synthesised and the structural characteristics were confirmed using powder X-ray diffraction. Representative samples of the series were subjected to thermal stability and moisture sensitivity tests. It was found that this class of sulphates was found to be stable up to 550°C after which the materials decompose into their constituent components with three different reaction mechanisms for each of the three parent sulphates $\text{Li}_2\text{M}(\text{SO}_4)_2$ ($\text{M} = \text{Co, Mn, Ni}$). The moisture sensitivity analysis yielded a pronounced impact of atmospheric moisture on the chemical stability of the material. Approximately, 90% of the original phase was degraded with hydrated sulphates identified as the major crystalline decomposition products during the handling of these materials. The moisture sensitivity of these materials makes it particularly challenging to realise the practical applications of such sulphate based battery electrode materials. Finally, the NMR of the materials were successfully carried out to probe and understand the local environment of within the $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ samples. The SQUID studies complemented the NMR analysis by providing the first exploration of the effect of the substituted compounds on the magnetic properties of this class of sulphates.

5.5 References

- [1] A. Padhi, K. Nanjundaswamy, and J. Goodenough, "Phospho - olivines as positive - electrode materials for rechargeable lithium batteries," *Journal of the electrochemical society*, vol. 144, pp. 1188-1194, 1997.
- [2] M. Hu, X. Pang, and Z. Zhou, "Recent progress in high-voltage lithium ion batteries," *Journal of Power Sources*, vol. 237, pp. 229-242, 2013.
- [3] C. Masquelier and L. Croguennec, "Polyanionic (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries," *Chemical Reviews*, vol. 113, pp. 6552-6591, 2013.

- [4] G. Rousse and J.-M. Tarascon, "Sulfate-Based Polyanionic Compounds for Li-Ion Batteries: Synthesis, Crystal Chemistry, and Electrochemistry Aspects," *Chemistry of Materials*, vol. 26, pp. 394-406, 2013.
- [5] A. Gutierrez, N. A. Benedek, and A. Manthiram, "Crystal-Chemical Guide for Understanding Redox Energy Variations of $M^{2+/3+}$ Couples in Polyanion Cathodes for Lithium-Ion Batteries," *Chemistry of Materials*, vol. 25, pp. 4010-4016, 2013.
- [6] A. Manthiram, "Materials challenges and opportunities of lithium ion batteries," *The Journal of Physical Chemistry Letters*, vol. 2, pp. 176-184, 2011.
- [7] P. Barpanda, "Sulfate Chemistry for High - Voltage Insertion Materials: Synthetic, Structural and Electrochemical Insights," *Israel Journal of Chemistry*, vol. 55, pp. 537-557, 2015.
- [8] D. Dwibedi and P. Barpanda, "Designing Novel Sulphate-based Ceramic Materials as Insertion Host Compounds for Secondary Batteries," *Transactions of the Indian Ceramic Society*, vol. 74, pp. 191-194, 2015/10/02 2015.
- [9] M. Reynaud, M. Ati, B. C. Melot, M. T. Sougrati, G. Rousse, J.-N. Chotard, *et al.*, " $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ as a 3.83 V positive electrode material," *Electrochemistry Communications*, vol. 21, pp. 77-80, 2012.
- [10] P. Barpanda, M. Ati, B. C. Melot, G. Rousse, J. N. Chotard, M. L. Doublet, *et al.*, "A 3.90 V Iron-Based Fluorosulphate Material For Lithium-Ion Batteries Crystallizing In The Triplite Structure," *Nature Materials*, vol. 10, pp. 772-779, 2011.
- [11] M. Reynaud, M. Ati, S. Boulineau, M. T. Sougrati, B. C. Melot, G. Rousse, *et al.*, "Bimetallic Sulfates $\text{A}_2\text{M}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ (A= Li, Na and M= Transition Metal): as New Attractive Electrode Materials for Li-and Na-Ion Batteries," *ECS Transactions*, vol. 50, pp. 11-19, 2013.
- [12] M. Reynaud, G. Rousse, J.-N. Chotard, J. Rodríguez-Carvajal, and J.-M. Tarascon, "Marinite $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M = Co, Fe, Mn) and $\text{LiFe}(\text{SO}_4)_2$: Model Compounds for Super-Super-Exchange Magnetic Interactions," *Inorganic Chemistry*, vol. 52, pp. 10456-10466, 2013/09/16 2013.
- [13] M. Anji Reddy, V. Pralong, V. Caignaert, U. Varadaraju, and B. Raveau, "Monoclinic iron hydroxy sulphate: A new route to electrode materials," *Electrochemistry Communications*, vol. 11, pp. 1807-1810, 2009.
- [14] A. Manthiram and J. Goodenough, "Lithium insertion into $\text{Fe}_2(\text{SO}_4)_3$ frameworks," *Journal of Power Sources*, vol. 26, pp. 403-408, 1989.

- [15] L. Lander, M. Reynaud, J. Carrasco, N. A. Katcho, C. Bellin, A. Polian, *et al.*, "Unveiling the electrochemical mechanisms of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ polymorphs by neutron diffraction and density functional theory calculations," *Physical Chemistry Chemical Physics*, vol. 18, pp. 14509-14519, 2016.
- [16] L. Lander, M. Reynaud, G. Rousse, M. T. Sougrati, C. Laberty-Robert, R. J. Messinger, *et al.*, "Synthesis and Electrochemical Performance of the Orthorhombic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ Polymorph for Li-Ion Batteries," *Chemistry of Materials*, vol. 26, pp. 4178-4189, 2014/07/22 2014.
- [17] C. V. Subban, M. Ati, G. I. Rousse, A. M. Abakumov, G. Van Tendeloo, R. I. Janot, *et al.*, "Preparation, Structure, and Electrochemistry of Layered Polyanionic Hydroxysulfates: LiMSO_4OH (M= Fe, Co, Mn) Electrodes for Li-Ion Batteries," *Journal of the American Chemical Society*, vol. 135, pp. 3653-3661, 2013.
- [18] J. M. Clark, C. Eames, M. Reynaud, G. Rousse, J. N. Chotard, J. M. Tarascon, *et al.*, "High voltage sulphate cathodes $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M = Fe, Mn, Co): atomic-scale studies of lithium diffusion, surfaces and voltage trends," *Journal of Materials Chemistry A*, vol. 2, pp. 7446-7453, 2014.
- [19] S. M. Oh, 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*, vol. 20, pp. 3260-3265, 2010.
- [20] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, and P. Granger, "NMR nomenclature: nuclear spin properties and conventions for chemical shifts. IUPAC Recommendations 2001. International Union of Pure and Applied Chemistry. Physical Chemistry Division. Commission on Molecular Structure and Spectroscopy," *Magnetic Resonance in Chemistry*, vol. 40, pp. 489-505, 2002.
- [21] T. F. Kemp, G. Balakrishnan, K. J. Pike, M. E. Smith, and R. Dupree, "Thermometers for low temperature Magic Angle Spinning NMR," *Journal of Magnetic Resonance*, vol. 204, pp. 169-172, 2010/05/01/ 2010.
- [22] M. F. Hansen and S. Mørup, "Estimation of blocking temperatures from ZFC/FC curves," *Journal of Magnetism and Magnetic Materials*, vol. 203, pp. 214-216, 1999.
- [23] R. Shannon, "Revised Effective Ionic Radii And Systematic Studies Of Interatomic Distances In Halides And Chalcogenides," *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, vol. 32, pp. 751-767, 1976.

- [24] P. C. Burns and F. C. Hawthorne, "Rietveld refinement of the crystal structure of α -CoSO₄," *Powder Diffraction*, vol. 8, pp. 54-56, 1993.
- [25] M. Wildner, "Crystal structure refinements of CoSO₄ and NiSO₄: very short interpolyhedral O—O contacts," *Zeitschrift für Kristallographie-Crystalline Materials*, vol. 191, pp. 223-230, 1990.
- [26] C. W. Pistorius, "Polymorphism in the anhydrous sulphates of Mn, Fe, Co, Ni, Cu and Zn to 140,000 bars and 750° C," *Zeitschrift für Kristallographie-Crystalline Materials*, vol. 116, pp. 220-250, 1961.
- [27] T. Forland, J. Krogh-Moe, M. Moutschen-Dahmen, B. Noer, and L. Reio, "The structure of the high temperature modification of lithium sulfate," *Acta. Chem. Scand*, vol. 11, p. 565, 1957.
- [28] K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *Journal of Applied Crystallography*, vol. 44, pp. 1272-1276, 2011.
- [29] J. Isasi, C. Train, S. Jaulmes, A. Elfakir, and M. Quarton, "Crystal Structure and Magnetic Properties of Li₂Mn₂(SO₄)₃," *Journal of Solid State Chemistry*, vol. 158, pp. 148-153, 2001.
- [30] A. Nord, "Crystal structure of β -Li₂SO₄," *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, vol. 32, pp. 982-983, 1976.
- [31] S. Sinha, N. Deshpande, and D. Deshpande, "Dehydration of crystalline CoSO₄·7H₂O," *Thermochimica acta*, vol. 156, pp. 1-10, 1989.
- [32] S. G. Sinha, N. D. Deshpande, and D. A. Deshpande, "Dehydration of crystalline MnSO₄·4H₂O," *Thermochimica Acta*, vol. 113, pp. 95-104, 3/15/ 1987.
- [33] F. G. Cottrell, "On the Solubility of Manganous Sulphate," *The Journal of Physical Chemistry*, vol. 4, pp. 637-656, 1899/01/01 1899.
- [34] M. Nambu, K. Tanida, and T. Kitamura, "Jôkokuite, MnSO₄·5H₂O, a new mineral from the Jôkoku Mine, Hokkaido, Japan," *Mineralogical Journal*, vol. 9, pp. 28-38, 1978.
- [35] M. Maneva, D. Rizova, L. Genov, and G. Liptay, "On the thermal decomposition of NiSO₄·nH₂O (n= 7, 6, 4, 1) and of their deuterated analogs," *Journal of thermal analysis*, vol. 36, pp. 915-922, 1990.
- [36] M. Jain and A. Gupta, "1054 Diamagnetic susceptibility of Li₂O₄S," in *Diamagnetic Susceptibility and Anisotropy of Inorganic and Organometallic Compounds*, R. R. Gupta, Ed., ed Berlin, Heidelberg: Springer Berlin Heidelberg, 2007, pp. 1104-1104.

- [37] M. McElfresh, "Fundamentals of Magnetism and Magnetic Measurements," Quantum Design, San Diego 1994.
- [38] D. Jiles, *Introduction to magnetism and magnetic materials*: CRC press, 2015.
- [39] C. M. Julien, A. Ait-Salah, A. Mauger, and F. Gendron, "Magnetic properties of lithium intercalation compounds," *Ionics*, vol. 12, pp. 21-32, 2006/05/01 2006.
- [40] B. D. Cullity and C. D. Graham, *Introduction to magnetic materials*: John Wiley & Sons, 2011.
- [41] M. Reynaud, J. Rodríguez-Carvajal, J.-N. Chotard, J.-M. Tarascon, and G. Rousse, "Magnetic structure and properties of orthorhombic $\text{Li}_2\text{Ni}(\text{SO}_4)_2$: A possible magnetoelectric material," *Physical Review B*, vol. 89, p. 104419, 2014.

Chapter 6

Unveiling the Electrochemical Activity of High Voltage Sulphates

Sulphates and fluorosulphates have traditionally demonstrated electrochemical activity only in Fe based compounds except for a Co based hydroxysulphate. This has been consistently observed even for the case of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ ($\text{M}=\text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) class of compounds where system with Fe has thus far been the only electrochemically active compound. Here, for the first time, reversible redox reactions have been reported for Mn and Co analogues of this series of sulphates. Mn and Co were found to operate at an average redox potential of 4.85 V and 5.02 V (vs. Li) respectively. This has been the highest reported voltage for purely Mn or Co based systems and therefore confirms the theory that the inductive effect of sulphate groups raises the potential of operation of cathodes based on them. This chapter also seeks to detail the mechanism of the redox reactions in the cathode through ex-situ XANES and XPS analyses of the Mn based system. The work is seminal in viewing sulphates as potential substitutes for the traditional phosphate based cathode materials because of their higher operational voltages and therefore higher energy density while maintaining safety.

6.1 Introduction

Sulphates and fluorosulphates have traditionally demonstrated electrochemical activity only in Fe based compounds.[1-4] Among the sulphate-based positive-electrode materials the sulphates synthesised through solid-state reactions have shown highest redox potentials for Fe at 3.83 V (*vs.* Li) [2], second only to the ionothermally synthesised fluorosulphate version which shows 3.90 V (*vs.* Li) [1]. The high voltages achieved with Fe were attributed to the inductive effect of the highly electronegative sulphate group [5] and subsequently Co, Mn and Ni which traditionally provided for operation at higher voltages were investigated[6, 7]. However, despite , atomistic modelling/Density Functional Theory (DFT) techniques predicting the redox potential versus Li to be 5.2 V for Co and 4.54 V for Mn systems[8], none of these elements showed electrochemical activity in the conventional voltage window between 3 and 4.8 V (*vs.* Li). The absence of activity was largely attributed to possibility of Jahn-Teller distortion[9] in the case of Mn and absence of stable electrolytes operational at high voltage as in the case of Co.

With the objective of exploring the redox activity at higher voltages, this work sought to improve electrolyte stability. The most feasible candidate for exploring a high voltage range with minimal modification to commercially used electrolyte components was found to be a co-solvent called sebaconitrile. Sebaconitrile has previously[10] been shown to exhibit good electrochemical stability beyond 6 V *vs.* Li in an EC:DMC (ethylene carbonate: dimethyl carbonate) based electrolyte with a glassy carbon electrode and demonstrated its use with polyanionic cathode $\text{Li}_2\text{NiPO}_4\text{F}$. Sebaconitrile was later used to assess performance of another Co based polyanionic cathode, LiCoPO_4 and it was found to lead to higher insertion potential of lithium owing to slower kinetics due to the sebaconitrile co-solvent [11]. The viability of its use with polyanionic systems therefore made sebaconitrile a suitable candidate to trial with sulphate based cathodes as well. Subsequently, $\text{Li}_2\text{M}(\text{SO}_4)_2$ ($\text{M}=\text{Co}, \text{Mn}$) was electrochemically analyzed with this electrolyte.

6.2 Experimental Methods

6.2.1 Three electrode Setup

A 3-electrode setup consisting of Platinum (Pt) as reference electrode, Glassy Carbon as working electrode and Li as Counter Electrode was assembled inside an MBraun Ar filled glovebox with H₂O and O₂ levels less than 0.1 ppm. The electrodes were arranged in a specially made glass vessel which held the electrolyte. 500 μ L of the electrolyte was used for every test performed and tests were repeated twice each to ensure consistency of the result. The electrodes were connected through a port in the glovebox to a portable Biologic SP-200 Potentiostat placed outside the glovebox. The tests were carried out at 25 mV.s⁻¹ between 6 V and 0 V vs. Li.

6.2.2 Electrolyte Preparation

The electrolyte for this work was tested up to 5.6 V to explore the window of operation of Co outlined as 5.2 V in computational studies[8]. The electrolytes synthesised were of three concentrations of increasing sebaconitrile. The composition used was a 1M solution of LiPF₆ in EC:DMC:sebaconitrile of varying volume percentages; 25:25:50, 15:15:70 and 5:5:90. In addition LiBF₄ salt was evaluated, but did not show any electrochemical activity and the reasons for this are still being studied.

6.2.3 Electrode Preparation, Assembly and Testing

The electrochemical tests were carried out in a half-cell configuration using Swagelok[®] cell architecture. The high voltage cathode Li₂Mn(SO₄)₂ was taken with Super P Carbon in a weight ratio of 4:1 and ball milled in a high-energy ball mill (*SPEX 8000M*) for 20 hrs with a cooling period of 10 mins every hour. The carbon coated Li₂Mn(SO₄)₂ powder was then directly placed in a Swagelok[®] cell as positive working electrode and lithium foil as the counter electrode. The loading of the active material was 4 mg.cm⁻². Two pieces of porous glass microfibre (Whatman Cat. No. 1825–047, UK) were used as the separator and soaked in electrolyte solution. This assembled cell was then subjected to cyclic

voltammetry tests using a *Solartron Analytical*. The tests were carried out at a scan rate of 0.05 mV.s^{-1} between a range of 4.2 V and 5.2 V for $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ while a range of 4.2 V and 5.6 V was used for $\text{Li}_2\text{Co}(\text{SO}_4)_2$.

6.2.4 XAS and XPS Analysis

The samples for XAS measurements were prepared by charging (or discharging) the electrode in a Swagelok[®] cell to certain charge (or discharge) states followed by disassembly in the glove box. The electrode was then scraped off in powder form, sealed and then transferred to XPS chamber or XAS sample holder. XPS experiments were carried out using a PHI5802 Multitechnique spectrometer and each spectrum was collected after 1 min Ar⁺ sputtering.

The electrodes along with the representative manganese sulphate and manganese oxide reference standards were measured at the XAFCA beamline [12] of the Singapore Synchrotron Light Source. All XAS measurements were conducted at a ring energy 0.7 GeV and ring current of ca 200 mA. A Si (111) crystal monochromator was used and data were collected on XAFCA in Quick EXAFS transmission mode at ambient temperature under vacuum. Mn K-edge data was collected in the range of 6419 and 7339 eV in a typical scan time of 180 seconds. Repetitions were made to improve the signal/noise. Reference spectra were collected using a Mn metal foil for the measurement of reference materials *ca.* 5 mg of the powder reference sample was mixed with *ca.* 80 mg of Boron Nitride and pressed into a 10-mm diameter pellet and mounted onto the sample holder for measurements in transmission mode. The Mn-K edge XANES and EXAFS data were analysed using *Athena* and *Artemis* software from the *Demeter* suite for XAS analysis [13].

6.3 Results and Discussion

6.3.1 Electrochemical Analysis

6.3.1.1 Screening of Electrolytes for High Voltage Sulphates

$\text{Li}_2\text{Fe}(\text{SO}_4)_2$, the only electrochemically active sulphate in the $\text{Li}_2\text{M}(\text{SO}_4)_2$ class reported thus far has been primarily tested with the electrolyte 1M LiClO_4 in propylene carbonate (PC). Thus, this was used as the baseline and sebaconitrile was added to PC in the ratio 50:50 by vol%. The cyclic voltammetry study on these 2 electrolytes showed that PC was extremely susceptible to degradation at a voltage as low as 4.4 V (Figure 6-1). Upon addition of sebaconitrile, the stability was extended by around 0.3 V, with degradation of the electrolyte setting in 4.7 V. Thus, the degradation much below 5 V was ample proof that PC was an unsuitable solvent for realising high voltage operation.

Figure 6-1: Three electrode CV evaluation of Propylene Carbonate (PC) and Sebaconitrile in the presence of a Pt reference electrode, Glassy Carbon working electrode and Lithium counter electrode

To improve the stability, the conventional EC:DMC electrolyte was evaluated. The salt concentration was maintained as 1M LiClO_4 and a set of electrolytes were prepared with varying concentration of sebaconitrile. Upon testing these

electrolytes in the three-electrode setup, it was found that with increasing concentration of sebaconitrile (Figure 6-2), the stability of the electrolyte was enhanced, all the way up to 6 V.

Figure 6-2: Three electrode CV evaluation of Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) and Sebaconitrile in the presence of a Pt reference electrode, Glassy Carbon working electrode and Lithium counter electrode

The degradation which set in at around 4.6 V for electrolyte based on pure EC:DMC was suppressed immediately by the addition sebaconitrile. This was followed by a decrease in the decomposition current from nearly 55 mA.cm^{-2} for the pure electrolyte to less than 5 mA.cm^{-2} for an addition of 50% sebaconitrile. This 11 fold decrease is remarkable corroborates earlier studies on the same composition [10]. Considering this steep increase in stability, this composition of the electrolyte was used as the baseline for electrochemical analysis of the Mn and Co based electrodes.

6.3.1.2 Electrochemical activity of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$

Figure 6-3, Figure 6-4 and Figure 6-5 show the electrochemical activity of Mn in a sulphate based system ($\text{Li}_2\text{Mn}(\text{SO}_4)_2$) for the first time through a reversible oxidation and reduction cycle consistent over 3 cycles in the voltage window of 4.2 and 5.2 V vs. Li counter electrode. Figure 6-3 shows the presence of an oxidation peak at 5.12 V and a reduction peak at 4.61 V for the first cycle thereby giving an average redox operating potential of approximately 4.85 V. The oxidation and reduction peaks progressively move toward 5.17 V and 4.60 V respectively at the end of the 3rd cycle indicating increasing polarisation. Also of note is the significantly high current in the 1st cycle compared to the subsequent cycles indicating formation of a cathode electrolyte interface. This is uniformly found across different concentrations of sebaconitrile in electrolyte. Another point of interest is at 4.73 V and 4.83 V, where small peaks indicate the presence of an alternate redox species. From earlier studies on monoclinic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ [2, 14, 15] where similar artefacts were observed in CV measurements of the cathode material and were attributed to an orthorhombic polymorph, it is possible that these peaks are due to the formation of a similar polymorph of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ during synthesis however this is still under investigation. A final observation was made on the intensity of current for the oxidation and reduction which is low in comparison to similar studies on $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ (Figure 4-10). The low current is indicative of a only a small percent of participating redox species undergoing reaction while the rest remain inert during the process. Even though the redox species concentration is small, the reversibility is indicated by a consistent current intensity of the reduction peak at 4.6 V vs. Li.

As with the 50% sebaconitrile system, similar trends are observed across 3 cycles for varying concentration of sebaconitrile – 70% and 90% as seen in Figure 6-3 and Figure 6-4.

Figure 6-3: CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (25:25:50) vol%

Figure 6-4: CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (15:15:70) vol%

Figure 6-5: CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (5:5:90) vol%

A comparison of the 3 concentrations of electrolytes over each cycle as shown in Figure 6-6 however brings out several interesting conclusions. Firstly, in the 1st cycle the system with 70% sebaconitrile has a higher oxidation peak as compared to 50% and 90% systems. This indicates a higher decomposition of electrolyte in the 70% system contrary to the expected higher decomposition in the 50% system which has a higher EC:DMC concentration which is prone to decomposition at high voltages.

Secondly, a progressive shift in the voltage at which oxidation and reduction occurs is observed with the oxidation peak moving toward higher voltages while reduction peak moving toward lower voltages. This is a strong sign of polarisation and it is observed that across all 3 cycles, the polarisation in each cycle is highest for the 90% sebaconitrile system.

Finally, comparison of the reduction peak current for the 3 different concentrations indicates that the 90% system shows the highest reduction. This corroborates the finding reported earlier [11] that increased sebaconitrile content improves insertion/de-insertion efficiency due to the slowing down of kinetics by sebaconitrile.

Figure 6-6: Comparison of the CV of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ for varying concentration of sebaconitrile from 50, 70 and 90 vol%

6.3.1.3 Electrochemical activity of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ and Co in Sulphates

Figure 6-7 shows the electrochemical activity of Co in a sulphate based system ($\text{Li}_2\text{Co}(\text{SO}_4)_2$) for the first time through a reversible oxidation and reduction cycle over 3 cycles in the voltage window of 4.2 and 5.6 V vs. Li counter electrode. In comparison to the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ system in Figure 6-3, the most important observation is the voltage at which the oxidation and reduction occurs at 5.30 V and 4.74 V vs. Li respectively, thereby giving an average redox potential of 5.02 V. This is the highest reported potential for a Co only cathode system. The

requirement of extending the voltage window can also be understood as the high polarisation in the system means that the oxidation takes place at 5.3 V and beyond.

Figure 6-7: CV of $\text{Li}_2\text{Co}(\text{SO}_4)_2$ carried out with an electrolyte of 1M LiPF_6 in EC:DMC:Sebaconitrile (25:25:50) vol%

Figure 6-7 also reveals the extensive decomposition of the electrolyte in the first cycle through the huge current intensity, going beyond $150 \mu\text{A} \cdot \text{cm}^{-2}$. In comparison, Figure 6-3 shows that $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ displayed current intensity of much lower value at around $120 \mu\text{A} \cdot \text{cm}^{-2}$. This is due to the extended voltage window going up to 5.6 V vs. Li. Also in comparison, the intensity of the reduction current is much lower close to $10 \mu\text{A} \cdot \text{cm}^{-2}$. This reduction peak further is completely absent in the 3rd cycle indicating an irreversibility within the first 3 cycles. This indicates a need for further studies to modify the structure to fully realise the benefits of such a high voltage system. Nevertheless, the reversibility shown in the first 2 cycles, albeit with high inefficiency, is promising for utilising such polyanionic sulphate based cathodes as high voltage cathode materials.

6.3.2 Understanding the Mechanism of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$

In order to understand if the mechanism of redox reactions is consistent with the Fe based system reported in Chapter 4, the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ cathode was subjected to similar ex-situ XAS analysis as in the first chapter. Further confirmation was also sought through an ex-situ XPS analysis of the material before and after cycling.

6.3.2.1 XAS Analysis

XANES analysis of the Mn – K edge compared the pristine electrode with the completely charged and discharged electrodes. The references used to analyse the oxidation states of the electrode were MnSO_4 in the +2-oxidation state and Mn_2O_3 in the +3-oxidation state. As seen in Figure 6-8, the absorption edge of the reference standards was noted to increase with oxidation state, from 6548 eV for Mn^{+2} and 6553 eV for Mn^{+3} . This indicates a 5 eV for an increase of +1 in the oxidation state.

The absorption edge of the pristine uncharged electrode was observed to overlap with the Mn^{+2} reference plot. This indicates that despite the intensive 20 hrs of high energy ball milling of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ with carbon, the oxidation state of the system remain unchanged in the +2 state.

When the absorption edge of the pristine uncharged, fully charged and fully discharged electrodes were compared to the reference standards, it was observed in Figure 6-8 that all the three states of charge overlapped with the Mn^{+2} reference plot. This is indicative that the variation in oxidation state of Mn is not clearly observed using a XANES plot. Earlier the CV plot (Figure 6-3) of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrode showed that the intensity of the current for the oxidation and reduction processes was low and thereby indicated that only a low concentration of the redox species was active and taking part in the reaction. It is possible therefore that if the Mn species was the active species, it would be low in concentration

Figure 6-8: Top: Mn K-edge XANES spectra showing the Fe absorption edge of the uncharged, fully charged and fully discharged states compared to Mn references, Bottom: Computed first derivative plots of the XANES data indicating the Mn absorption edge position of the 2 different oxidation states of the references are at 6548 eV for Mn^{2+} and 6553 eV for Mn^{3+} .

and therefore, any changes in oxidation state would average out over the entire set of species in the bulk, both the active and inactive. This in turn would not reflect on a transmission based XAS measurement and hence does not provide conclusive evidence that the Mn ion is not an active redox species in the electrochemistry of this system.

To ascertain the role of Mn, XPS measurements were carried which probe surface oxidation states and are more sensitive to low concentrations of Mn than XAS.

6.3.2.2 XPS Analysis

Ex-situ XPS analysis of the system was carried out similar to the XAS measurements on three electrodes of different states of charge; (i) pristine uncharged, (ii) fully charged and (iii) fully discharged. The measurements were carried out for 5 elements; (i) Mn-2p, (ii) Li-1s, (iii) S-2p, (iv) O-1s and (v) C-1s where the C served for baseline correction.

6.3.2.2.1 Mn 2p Spectra

In the case of Mn-2p spectra analysis, the main peaks considered were the Mn(2p_{1/2}) and Mn(2p_{3/2}) peaks between the binding energies of 640 eV and 660 eV. The individual binding energies are listed in Table 6-1. The main trend observed is an increase of binding energy across all peaks as one moves from the uncharged to discharged state, indicating a higher oxidation state[16]. Subsequently, decrease in binding energy upon return to a fully discharged state indicates a lower oxidation state. Also of note is that the values of binding energy for all the peaks in the fully discharged state are of higher value (i.e.) higher oxidation state) compared to binding energy for all the peaks in the pristine state. This indicates some percentage of Li involved in the oxidation reaction has not participated in the reduction reaction thereby leading to some irreversible capacity loss [16]. This is also reflected in Figure 6-9 where there is no complete overlap of the pristine and fully discharged states.

Table 6-1: Binding energies of main peaks of Mn-2p XPS spectra for 3 different electrodes

Electrode	State of charge	Binding Energy of Mn(eV)			
		2p _{1/2}	2p _{1/2}	2p _{3/2}	2p _{3/2}
		satellite	main	satellite	main
Pristine	Uncharged at 3.5 V	654.8	653.3	643.7	641.7
Charge	Fully charged to 5.4 V	658.8	654.8	646.6	642.87
Discharge	Fully discharged to 4.2 V	656.1	654.4	644.1	642.1

Figure 6-9: Manganese Mn-2p *ex-situ* XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes

One of the main features in Figure 6-9 is the growth of a satellite peak as the battery progresses from an uncharged to fully charged state. This peak at 646.6 V then overlaps with the main peak again after full discharge. An earlier report on MnO oxidation[17] shows the formation of a similar satellite peak upon increased exposure of MnO to O_2 at 673 K. This was attributed to the layered

growth of Mn_2O_3 and therefore the XPS spectra was distinguished as a characteristic of Mn in its 3+ oxidation state. Similarly, the mechanism here can be attributed to a Mn +2/+3 redox couple similar to that of Fe illustrated in the 1st chapter.

6.3.2.2.2 S 2p Spectra

Figure 6-10: Sulphur S-2p *ex-situ* XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes

S-2p spectra is critical to evaluate as it is likely that the polyanionic part of the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ compound could participate in the electrochemistry of the battery and thereby cause changes in capacity or voltage. Here analysis of the spectra as in Figure 6-10 shows that the binding energies of all the three states of charge are almost similar to each other. The only discrepancy is the marginal shift of the spectra of the fully charged electrode towards higher Binding Energy (i.e. higher oxidation state). However, S in sulphate is known to have a +6 oxidation state with the possible higher oxidation state being +7. This is a rather rare state for the system to adopt and requires further investigation. Nevertheless, after

complete discharge the spectra of the fully discharged electrode overlaps with that of the pristine electrode, indicating that this reaction is reversible.

6.3.2.2.3 O and Li 1s Spectra

Figure 6-11: Oxygen O-1s *ex-situ* XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes

Analysis of the O-1s spectra in Figure 6-11 shows the presence of a dual peak in the pristine state which shifts significantly towards higher energy upon complete charging. However this peak maintains its position upon complete discharge. Since the voltage of this system pushes the electrolyte to beyond 5.4 eV, decomposition of the electrolyte is expected and also corroborated by the high currents in the CV tests of the material seen in Figure 6-3. Taking this into consideration, it is possible that the shift in the peak is due to the formation of an cathode electrolyte interface (CEI) layer involving a different bonding of the O atom.

Analysis of the Li-1s spectra in Figure 6-12 shows the presence of 1 major peak at 49 eV and 1 satellite peak at 56 eV in the in the pristine state. The satellite

peak grows during charging and subsides during discharge showing the activity of Li in the redox reactions of the system.

Figure 6-12: Lithium Li-1s *ex-situ* XPS spectra of pristine, charged and discharged state of $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ electrodes

6.4 Conclusion

The work in this chapter demonstrated electrochemical activity of Mn and Co in $\text{Li}_2\text{M}(\text{SO}_4)_2$ based lithium battery cathodes for the first time. The reversibility of the redox couple was evaluated through cyclic voltammetry (CV) tests which showed that although in the case of Mn, the reversibility was consistent over 4 cycles while the Co based system lost reversibility in the 3rd cycle. The Mn system operated at an average redox potential of 4.85 V *vs.* Li while Co system operated at 5.02 V *vs.* Li. These are the highest voltages reported for compounds consisting purely of a single transition element and heralds the viability of a new of sulphate based polyanionic compounds that can operate at high redox

potentials. The high voltage operation was enabled by a suitable high voltage electrolyte which used a conventional electrolyte mixed with sebaconitrile as a co-solvent. The high voltage capability of electrolytes of different concentrations of sebaconitrile were analysed and evaluated to choose the most suitable candidate for testing cell performance. Finally, the mechanism of operation of the Mn based system was investigated in detail using a combination of X-Ray Absorption Spectroscopy (XAS) and X-Ray Photoelectron Spectroscopy (XPS) to conclude that the Mn +2/+3 redox couple was active. The Co system requires further improvement before it is subjected to similar analysis in the future.

6.5 References

- [1] P. Barpanda, M. Ati, B. C. Melot, G. Rousse, J. N. Chotard, M. L. Doublet, *et al.*, "A 3.90 V Iron-Based Fluorosulphate Material For Lithium-Ion Batteries Crystallizing In The Triplite Structure," *Nature Materials*, vol. 10, pp. 772-779, 2011.
- [2] M. Reynaud, M. Ati, B. C. Melot, M. T. Sougrati, G. Rousse, J.-N. Chotard, *et al.*, "Li₂Fe(SO₄)₂ as a 3.83 V positive electrode material," *Electrochemistry Communications*, vol. 21, pp. 77-80, 2012.
- [3] C. Masquelier and L. Croguennec, "Polyanionic (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries," *Chemical Reviews*, vol. 113, pp. 6552-6591, 2013.
- [4] P. Barpanda, G. Oyama, S.-i. Nishimura, S.-C. Chung, and A. Yamada, "A 3.8-V earth-abundant sodium battery electrode," *Nature communications*, vol. 5, 2014.
- [5] A. Gutierrez, N. A. Benedek, and A. Manthiram, "Crystal-Chemical Guide for Understanding Redox Energy Variations of M^{2+/3+} Couples in Polyanion Cathodes for Lithium-Ion Batteries," *Chemistry of Materials*, vol. 25, pp. 4010-4016, 2013.
- [6] M. Reynaud, M. Ati, S. Boulineau, M. T. Sougrati, B. C. Melot, G. Rousse, *et al.*, "Bimetallic Sulfates A₂M(SO₄)₂ · nH₂O (A= Li, Na and M= Transition Metal): as New Attractive Electrode Materials for Li-and Na-Ion Batteries," *ECS Transactions*, vol. 50, pp. 11-19, 2013.
- [7] M. Reynaud, G. Rousse, J.-N. Chotard, J. Rodríguez-Carvajal, and J.-M. Tarascon, "Marinite Li₂M(SO₄)₂ (M = Co, Fe, Mn) and LiFe(SO₄)₂:

- Model Compounds for Super-Super-Exchange Magnetic Interactions," *Inorganic Chemistry*, vol. 52, pp. 10456-10466, 2013/09/16 2013.
- [8] J. M. Clark, C. Eames, M. Reynaud, G. Rousse, J. N. Chotard, J. M. Tarascon, *et al.*, "High voltage sulphate cathodes $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M = Fe, Mn, Co): atomic-scale studies of lithium diffusion, surfaces and voltage trends," *Journal of Materials Chemistry A*, vol. 2, pp. 7446-7453, 2014.
- [9] G. Rousse and J.-M. Tarascon, "Sulfate-Based Polyanionic Compounds for Li-Ion Batteries: Synthesis, Crystal Chemistry, and Electrochemistry Aspects," *Chemistry of Materials*, vol. 26, pp. 394-406, 2013.
- [10] M. Nagahama, N. Hasegawa, and S. Okada, "High voltage performances of $\text{Li}_2\text{NiPO}_4\text{F}$ cathode with dinitrile-based electrolytes," *Journal of The Electrochemical Society*, vol. 157, pp. A748-A752, 2010.
- [11] E. Nanini-Maury, J. Światowska, A. Chagnes, S. Zanna, P. Tran-Van, P. Marcus, *et al.*, "Electrochemical behavior of sebaconitrile as a cosolvent in the formulation of electrolytes at high potentials for lithium-ion batteries," *Electrochimica Acta*, vol. 115, pp. 223-233, 2014.
- [12] Y. Du, Y. Zhu, S. Xi, P. Yang, H. O. Moser, M. B. Breese, *et al.*, "XAFCA: A New XAFS Beamline for Catalysis Research," *Journal of Synchrotron Radiation*, vol. 22, pp. 839-843, 2015.
- [13] B. Ravel and M. Newville, "ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy using Ifeffit," *Journal of Synchrotron Radiation*, vol. 12, pp. 537-541, 2005.
- [14] L. Lander, M. Reynaud, J. Carrasco, N. A. Katcho, C. Bellin, A. Polian, *et al.*, "Unveiling the electrochemical mechanisms of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ polymorphs by neutron diffraction and density functional theory calculations," *Physical Chemistry Chemical Physics*, vol. 18, pp. 14509-14519, 2016.
- [15] L. Lander, M. Reynaud, G. Rousse, M. T. Sougrati, C. Laberty-Robert, R. J. Messinger, *et al.*, "Synthesis and Electrochemical Performance of the Orthorhombic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ Polymorph for Li-Ion Batteries," *Chemistry of Materials*, vol. 26, pp. 4178-4189, 2014/07/22 2014.
- [16] R. Zhang, X. Yu, K.-W. Nam, C. Ling, T. S. Arthur, W. Song, *et al.*, " α - MnO_2 as a cathode material for rechargeable Mg batteries," *Electrochemistry Communications*, vol. 23, pp. 110-113, 2012.
- [17] V. Di Castro and G. Polzonetti, "XPS study of MnO oxidation," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 48, pp. 117-123, 1989.

Chapter 7

All Iron Full-Cell – Electrochemical Performance and Economic Comparison

This chapter focuses on assembling a full-cell with a sulphate based cathode and demonstrating its performance. The Fe based high voltage $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode was coupled with high capacity and inexpensive Fe_2O_3 anode for a novel full-cell combination consisting of Fe based redox couple at both electrodes. This all Iron full-cell assembly was then tested for its electrochemical performance and subsequently its cycling performance. After the successful demonstration of the functioning of the cell, a cost estimation exercise to determine the potential cost of the cathode material was carried out. The cost estimation so obtained was then used to make a techno-economic comparison between the novel full-cell and other full-cells comprising commercially used cathodes and anodes.

7.1 Introduction

The current worldwide rechargeable battery market is mainly dominated by lead acid (PbA) batteries with the competing technology of Lithium ion batteries (LIB) a distant second (Figure 7-1).

Figure 7-1: Battery market in 2015 by technology[1]

With the LIB market expected to triple in terms of energy by 2025 [1], the volume of waste batteries generated would assume significant scale surpassing 500,000 tonnes by 2020 [2]. The waste or spent LIBs are made up of 5–20% cobalt, 15% organic chemicals, 5–10% nickel, 5–7% lithium, and 7% plastics [2–4] with another report estimating 5–33% cobalt, 5–7% lithium, 15–20% manganese and 0.02–0.3% nickel [5]. The major component is that of Co, which apart from being expensive at 33.6 USD.kg⁻¹ [6] in 2015 is also low in availability with only an estimated 13 million tons available globally[2]. Apart from the toxicity of cobalt, using recycled Co would still yield only less than 50% savings in fossil fuels [7].

All these factors make the case for adopting alternate battery chemistries that do not leave an adverse impact on the environment. The factors that determine the impact of an LIB on the environment have been succinctly encompassed in an equation [8];

$$\begin{aligned} \text{Total impact of the cell} = \\ \sum_{\text{Components}} \text{Chemical Composition} + \sum_{\text{Components}} \text{Synthesis process} + \\ \sum_{\text{Components}} \text{Recycling} + \sum_{\text{Components}} \text{Implementation in the system} \end{aligned}$$

Fe based cathode materials such as LiFePO_4 are an example of the viability of benign materials that satisfy the requirements of having a low impact on the environment. Amongst the Fe based cathodes, $\text{Li}_2\text{Fe}(\text{SO}_4)_2$, synthesised earlier in this work in Chapter 4, is another option benign battery chemistries and is of relevance here.

In terms of anodes as well impact needs to be minimised. In 2014, graphite consumption in the US automobile industry alone was estimated at 16,000 tons [9, 10] and over 90% of worldwide anode markets was graphite based [11]. The graphite is as much as 11 times the weight of Lithium but the low price of graphite at 1.36 USD.kg⁻¹ (in 2013) does not make economic sense in terms of recycling [12]. Here again alternate chemistries would provide a valuable way of meeting the demand while minimising environmental impact.

In this regard Fe_2O_3 anode material with a theoretical specific capacity of 1007 mAh.g⁻¹ [13] ensures an anode capable of high specific capacity while being of low cost, non-toxic and of high natural abundance [14]. In addition, the iron content from both the anode and cathode would make iron extraction from the spent LIBs feasible despite the low value of Iron at 1.54 USD.kg⁻¹ in the case of recycled LiFePO_4 [15].

Thus, a novel full-cell consisting of Fe based redox couple at the positive and negative electrodes would be a valuable step toward realising environmentally benign energy storage devices. This work seeks to utilise the high voltage cathodes among Fe based materials, $\text{Li}_2\text{Fe}(\text{SO}_4)_2$, and couple it with Fe_2O_3 anode and determine its electrochemical compatibility. In addition, a techno-economic

comparison of this LIB with other full-cells to determine the pros and cons of such a full-cell.

7.2 Experimental Methods

7.2.1 Material Synthesis

7.2.1.1 $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode material

Solid state synthesis was used to synthesise the $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode material using anhydrous FeSO_4 and Li_2SO_4 . First, the anhydrous FeSO_4 was obtained by heating green coloured $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma Aldrich) in a tube furnace under argon flow for 2 hours at 350 °C at a heating rate of 2.5 °C min⁻¹. Anhydrous Li_2SO_4 was obtained by heating white coloured $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Sigma Aldrich) in a tube furnace under argon flow for 1 hour at 200 °C at a heating rate of 2.5 °C min⁻¹. The anhydrous precursors were then mixed with a few drops of ethanol and placed in ball mill vials sealed in argon. They were then ball milled in a *SPEX 8000M* high energy ball mill for two periods of 18 minutes each separated by 10 mins to prevent oxidation of Fe^{2+} to Fe^{3+} . The powder was then pressed into a pellet at a force of 8 kN after which it was heated to 350 °C for 12 hours with a 2.5 °C.min⁻¹ ramp rate in a tube furnace under argon flow.

7.2.1.2 Fe_2O_3 anode material

Hydrothermal synthesis was used to synthesised the Fe_2O_3 anode material. 0.3 mol NaOH pellets (Aldrich, 99.5%) were dissolved in 50 ml DI water to form a 6 M NaOH solution. 8 ml of 6 M NaOH solution were added drop wise into 16 ml of 1 M solution with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, Riedel-de Haën) under constant stirring. The solution was then transferred to a 43 ml autoclave with teflon-lined stainless steel for hydrothermal treatment at 180 °C for 16 hrs. The product was naturally cooled down to room temperature after reaction, and collected by centrifugation with deionized water and ethanol. The sample was dried overnight at 60 °C, and a product with red color was obtained.

7.2.2 Electrode Preparation

7.2.2.1 $\text{Li}_2\text{Fe}(\text{SO}_4)_2$

The $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode was prepared by high energy ball milling of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ with Super P Carbon in an inert atmosphere in a ratio of 80:20 wt% for three periods of 12 minutes, each separated by 10 mins. This carbon coated cathode material was then dried in a vacuum oven (Buchi) for 4 hrs at 230 °C before assembly.

7.2.2.2 Fe_2O_3

The electrodes were prepared by dissolving 60% active material, 20% of conductive additives (Super P Li carbon, Timcal) and 20% of PVDF binder (Kynar 2801) in n-methyl 2-pyrrolidone (NMP) (Sigma-Aldrich, 99.5%) solvent to form the slurry. The slurry was mixed under magnetic stirring overnight to form a homogenous mixture. The as-prepared slurry was then coated on a copper foil by the doctor blade technique, with a gap width of 200 μm . The coated sample was then dried in a convection oven at 60°C overnight, roll-pressed and cut into circular pieces with diameter of 12 mm. The circular electrodes were then dried in a vacuum oven before being cell assembled in a glovebox. The Fe_2O_3 electrodes were then used to make a half cell for pre-lithiation. They were assembled into a 2016-coin cell with Li foil as the counter electrode and polypropylene (Celgard) soaked in 1M LiPF_6 in ethylene carbonate (EC) and diethyl carbonate (DEC) (50:50 vol%) as separator. The cell was subjected to pre lithiation by cycling between 0.05 V to 1.5 V vs. Li for 10 cycles at a current rate of C/15. The coin cell was then disassembled in the Ar filled glovebox and washed with DEC solvent to prepare it for full-cell assembly.

7.2.3 Cell Assembly

The cell assembly was done in a Swagelok[®] type cell in an argon filled glove box (MBRAUN). First, the finely mixed $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ powder was directly placed in a Swagelok[®] cell as positive working electrode where the loading of the active

material was 8 mg.cm^{-2} . Secondly, two pieces of porous glass microfibre (Whatman Cat. No. 1825–047, UK) were used as the separator and placed over the powder. Next 250 μL of electrolyte consisting of 1M LiPF_6 in ethylene carbonate (EC) and diethyl carbonate (DEC) (50:50 vol%) was injected onto the separator to soak it completely. Thirdly, the Fe_2O_3 coated Cu foil was placed over the separator as the negative electrode. Finally, the Swagelok[®] cell components were assembled tightly and taken out of the glovebox and subjected to galvanostatic charge-discharge (GCD) cycling tests at different current rates from 0.4 V to 3.5 V.

7.3 Results and Discussion

7.3.1 Electrochemical Characterisation

The GCD tests carried out in the voltage window from 0.4 V to 3.5 V showed a discharge capacity of 58 mAh.g^{-1} in the first cycle as seen in Figure 7-2. The full-cell showed consistent cycling with similar charge discharge profiles across all cycles in the first 25 cycles at a charge rate of C/15. The deintercalation of Li ion from the $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode during charging occurs at 2.92 V illustrated by a plateau at this voltage in Figure 7-2. During discharge, the intercalation of Li ion back into the cathode begins at 2.22 V but is spread out over a large voltage range up until 0.4 V. This behaviour is seen across all cycles but with a progressive decrease in the discharge capacity to 48 mAh.g^{-1} in the 25th cycle.

The efficiency of charge and discharge of the cell shown in Figure 7-3 drops initially till the 5th cycle as the lithiation of the Fe_2O_3 and solid-electrode interface layer (SEI) stabilises. Subsequently the efficiency of the cell remains stable even up to 25 cycles. Correspondingly, the specific capacity initially increases from 58 mAh.g^{-1} to over 60 mAh.g^{-1} in the first three cycles but from then on drops consistently to 48 mAh.g^{-1} . Thus, at low current rates the cycling performance of

the full-cell is consistent with optimisation of pre-lithiation of the anode required to provide better efficiencies.

Figure 7-2: GCD test of a $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ full-cell showing a specific capacity of 58 mAh.g^{-1} in an operational window of 0.4 V to 3.5 V

Figure 7-3: Cycling Performance of $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ full-cell over 25 cycles at C/15

Subsequently, the rate performance tests were conducted at 4 different C-rates and this is shown in Figure 7-4. It was observed that upon doubling the charge rate from the C/15, used for analysing the cycling performance, the discharge capacities dropped by nearly 40% to 30 mAh.g⁻¹. Upon doubling the C-rate further, it dropped to 10 mAh.g⁻¹ and further to 2 mAh.g⁻¹.

Figure 7-4: Rate Performance of Li₂Fe(SO₄)₂/Fe₂O₃ full-cell over 55 cycles

This indicates that the full-cell performs extremely poorly at high charge-discharge rates which could be attributed to factors of poor electronic or ionic conductivity thereby requiring surface modifications or coatings to enable higher discharge capacities. However, upon lowering the C-rate to C/15 again, the discharge capacity was again seen to show a comparatively high value of 40 mAh.g⁻¹. It must be noted that although the capacity is high, the efficiency drops sharply upon cycling after switching back to the low current rate. This shows that the electrochemical reactions at high currents might affect the structure of the Li₂Fe(SO₄)₂ cathode adversely as the poor efficiency indicates a discrepancy between the charge and discharge capacities.

7.3.2 Cost Estimation and Comparison of All Iron Full-cell

The first step in estimating the cost of a full-cell is to estimate the price of the electrodes themselves.

7.3.2.1 Raw material cost estimation and comparison

$\text{Li}_2\text{Fe}(\text{SO}_4)_2$ (LFS) is made by a straightforward solid state reaction between FeSO_4 and Li_2SO_4 at 350 °C. The cost of the constituents has been shown to be around 124 USD.ton⁻¹ [16]. To estimate the price of Li_2SO_4 the process of manufacture of Li_2CO_3 needs to be understood. Li_2CO_3 is made by mining a mineral, β -spodumene which is roasted with concentrated sulfuric acid at 250 °C. This generates Li_2SO_4 and an insoluble ore residue. After further treatment with limestone, soda ash and multiple-effect evaporation, the lithium carbonate (Li_2CO_3) is precipitated, washed, and dried [17]. Thus, Li_2SO_4 is an intermediary in the synthesis of Li_2CO_3 . Since, Li_2CO_3 is priced at 6.4 USD.kg⁻¹ [18], the price of Li_2SO_4 is estimated at 6 USD.kg⁻¹.

LiFePO_4 (LFP) costs 24 USD.kg⁻¹ [18] with the raw materials cost of FePO_4 and Li_2CO_3 constituting 16.4% of the total price for production as seen in Figure 7-5. Since, LFP and LFS are based on similar solid state synthesis techniques albeit with a lower energy requirement, it is assumed that the production cost breakdown of LFS will mirror LFP. Thus, with a raw material cost of 6.124 USD.kg⁻¹, the total production cost of LFS is estimated to be 37.3 USD.kg⁻¹.

Figure 7-5: Production cost of LFP

To get a perspective of the costs involved, five commercially used cathodes were used as a benchmark for comparison; LiCoO_2 (LCO), $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC), LiMn_2O_4 (LMO), $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) and LFP. When the price of LFS was compared with other commercial cathodes (Figure 7-6) it was seen that LFS had the lowest weight per unit mass. The low price is attributed primarily to the inexpensive FeSO_4 raw material.

Figure 7-6: Cost comparison of popular cathode materials with LFS [18]

With regard to Fe_2O_3 , since the battery grade material is unavailable, the highest price of the highest quality of Fe_2O_3 currently available in the market was taken

for purposes of estimation and listed as 1.85 USD.kg⁻¹ [19]. Similar to LFS, Fe₂O₃ has a big price advantage over other commercially available cathodes such as Graphite and Lithium Titanate Li₄Ti₅O₁₂ (LTO) as seen in Figure 7-7.

Figure 7-7: Cost comparison of popular cathode materials with Fe₂O₃ [20, 21]

7.3.2.2 Energy density comparison

The two major factors that go towards determining the specific energy density of a battery are its operating potential and specific discharge capacity. Table 7-1 at the end of this section lists these two parameters for the various electrodes. Here it needs to be noted that the specific capacities for Graphite, Fe₂O₃ and LFS have been based on their theoretical values of 372 mAh.g⁻¹, 1007 mAh.g⁻¹ and 102 mAh.g⁻¹ respectively. In the case of LFS and Fe₂O₃, a correction factor of 85% has been used as this reflects the difference in real and theoretical capacities for LFP[18] which is also based on an Fe redox couple. These values are then compared graphically with other cathode and anode materials in Figure 7-8 and Figure 7-9. It was noticed that while LFS had the highest operating potential among all the cathodes evaluated, Fe₂O₃ had the highest specific capacity among all the anodes.

Figure 7-8: Comparison of different cathode technologies in terms of their specific capacity and operating potential

Figure 7-9: Comparison of different anode technologies in terms of their specific capacity and operating potential

Using the values for specific capacity, operating potential and cost per unit mass, the energy density and cost per unit of energy stored was calculated and graphically represented in Figure 7-10. It was noted that the highest energy densities were from LCO and NCA, the workhorse cathodes in the LIB industry. The energy density of LFS being the least and thereby proving to be the biggest impediment to its commercialisation. In terms of cost however, it was found that LFP was the most expensive despite the use of relatively inexpensive Fe. Interestingly, LFS was found to have the cheapest per kWh and hence poses an interesting opportunity for use in applications that do not require high energy density. The complementary attributes of LFS and Fe_2O_3 make them an interesting proposition in a full-cell and this is explored in the next section.

Figure 7-10: Comparison of different cathode technologies in terms of specific energy density and cost per unit energy stored

Table 7-1: Comparison of the most popular cathodes with LFS and anodes with Fe_2O_3 [18, 20, 21]

Electrode Material		Real Capacity (mAh.g ⁻¹)	Operating Potential (V vs. Li)	Cathode material price (USD.kg ⁻¹)	Energy Density (Wh.kg ⁻¹)	Cathode material price (USD.kWh ⁻¹)
Anode	LTO	175	1.5	12	-	-
	Graphite	372	0	18.5	-	-
	Fe_2O_3	859	1.50	1.85	-	-
Cathode	LCO	155	3.7	28	574	48.8
	NMC	155	3.6	25	558	44.8
	LMO	110	3.8	19	418	45.5
	NCA	155	3.6	27	558	48.5
	LFP	145	3.3	24	478	50.2
	LFS	87	3.83	14.6	334	43.7

7.3.2.3 Full-cell cost estimation and comparison

A choice of two cathodes was made to compare with LFS while being coupled with the three anodes listed earlier. From the results, earlier, NCA was chosen due to its high energy density and LFP was chosen as the only commercialised polyanionic cathode similarity. Each of these electrodes, along with LFS was coupled with the three anodes, Graphite (Gr), LTO and Fe_2O_3 to theoretically estimate the cost and weight of the resulting full-cells. Thus, there were nine LIBs that were compared and here it needs to be noted that the masses of other components that would normally accompany the cells such as aluminium and copper foil, casing, *etc.* were not considered in the weight contribution. The computation was purely to determine the effectiveness of the high operating potential of LFS despite its poor specific capacity.

First, the masses of the LIBs were compared (Figure 7-11) across the entire range and it was found that the NCA/Gr cell had the least mass. This is especially of value in portable applications and automotive technologies where weight is of concern. All LTO based cells had high mass loadings making them unsuitable

for applications sensitive to weight of the LIBs. The low specific capacity of the LFS cathode clearly shows here as with every set of anodes, it has a higher mass loading compared to LFP and NCA. The trend here for a particular class of anode is that $\text{LFS} > \text{LFP} > \text{NCA}$ in terms of kg.kWh^{-1} .

Figure 7-11: Comparison of full-cells in terms of the electrode mass per unit energy stored

With respect to Fe_2O_3 , the impact of its high operating potential is felt as even when coupled NCA it has higher mass loading than the LFP/Gr cell and is on par only with the LFS/Gr full-cell. So, in terms of mass loading, the negatives of LFS in poor specific capacity and Fe_2O_3 in high operating voltage are a clear disadvantage. The next step was to evaluate the strengths of both these materials in terms of their cost competitiveness.

Figure 7-12 details the comparison of the 9 LIBs in terms of the cost per unit power stored. Here the results are not as straightforward as in the case of mass

loading. The most inexpensive full-cell was that of LFS/Gr while most expensive was LFP/LTO. The trend here across any particular class of anode in terms of cost per unit energy stored is $\text{NCA} \sim \text{LFP} > \text{LFS}$. Both NCA and LFP based systems marginally shade each other except in the case of a full-cell using LTO, where the price of LFP/LTO is higher by nearly 30 USD.kWh⁻¹.

It was seen that the LFS/Fe₂O₃ full-cell which is the subject of this chapter compares favourably with the market standard NCA/Gr in terms of cost per kWh. However, its usage is limited primarily due to its high mass loading. It is also noted that despite the huge cost advantage of LFS seen in Figure 7-6, the proportion of LFS cost in totality across different anodes compares with NCA indicating that the cost advantage is minimised as higher quantities are required to achieve the same energy densities.

Figure 7-12: Comparison of full-cells in terms of the electrode cost per unit energy stored. In terms of Fe₂O₃ it was noted that the proportion of anode cost across the different cathodes was minimal. Thus, the inexpensive nature of the anode trumps

its high working potential and has uniformly proven to be a much stronger substitute to LTO.

The LFS/ Fe_2O_3 full-cell does not have any advantage in terms of mass of the battery per unit energy stored ruling out its use in weight sensitive applications such as portable electronics or automobiles. However, the cost is comparable to full-cells of LFP or NCA with Graphite and therefore allows for their use in applications where weight is not a concern such as energy storage systems.

7.4 Conclusion

The $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ full-cell was assembled and successfully demonstrated in an electrochemical cell. Pre-lithiation of Fe_2O_3 was required on account of the high intake of Li ions in the first few cycles of operation. The cycling performance was found to be consistent at low C-rate but at high C-rates the cell showed negligible capacity. This indicates the system is not suitable for high power applications. The efficiency loss in rate performance tests also indicates the need for further optimisation of the system and its mass loading. Subsequently a techno-economic comparison of the full-cell was carried out with a combination of NCA/LFP cathode and LTO/Graphite anodes to yield a spectrum of full-cells capable of different energy densities at different price points. It was found that the $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ system had no major cost advantage compared to traditional cathodes despite the relatively inexpensive electrode materials. It was also noted that the system suffered from low energy density and hence was more suited to non-portable applications.

7.5 References

- [1] C. Pillot, "The Rechargeable Battery Market and Main Trends 2015-2025," 2016.
- [2] X. Zeng, J. Li, and N. Singh, "Recycling of Spent Lithium-ion Battery: A Critical Review," *Critical Reviews in Environmental Science and Technology*, vol. 44, pp. 1129-1165, 2014.
- [3] J. Ordoñez, E. J. Gago, and A. Girard, "Processes and technologies for the recycling and recovery of spent lithium-ion batteries," *Renewable and Sustainable Energy Reviews*, vol. 60, pp. 195-205, 2016/07/01/ 2016.
- [4] X. Guo, X. Cao, G. Huang, Q. Tian, and H. Sun, "Recovery of lithium from the effluent obtained in the process of spent lithium-ion batteries recycling," *Journal of Environmental Management*, vol. 198, pp. 84-89, 2017/08/01/ 2017.
- [5] P. K. Choubey, K.-S. Chung, M.-s. Kim, J.-c. Lee, and R. R. Srivastava, "Advance review on the exploitation of the prominent energy-storage element Lithium. Part II: From sea water and spent lithium ion batteries (LIBs)," *Minerals Engineering*, vol. 110, pp. 104-121, 2017.
- [6] A. Vezzini, "23 - Manufacturers, Materials and Recycling Technologies A2 - Pistoia, Gianfranco," in *Lithium-Ion Batteries*, ed Amsterdam: Elsevier, 2014, pp. 529-551.
- [7] J. Dewulf, G. Van der Vorst, K. Denturck, H. Van Langenhove, W. Ghyoot, J. Tytgat, *et al.*, "Recycling rechargeable lithium ion batteries: critical analysis of natural resource savings," *Resources, Conservation and Recycling*, vol. 54, pp. 229-234, 2010.
- [8] D. Larcher and J. M. Tarascon, "Towards greener and more sustainable batteries for electrical energy storage," *Nat Chem*, vol. 7, pp. 19-29, 01/print 2015.
- [9] J. B. Dunn, L. Gaines, M. Barnes, M. Wang, and J. Sullivan, "Material and energy flows in the materials production, assembly, and end-of-life stages of the automotive lithium-ion battery life cycle," Argonne National Laboratory (ANL)2012.
- [10] L. Gaines and P. Nelson, "Lithium-ion batteries: possible materials issues," in *13th international battery materials recycling seminar and exhibit*, Broward County Convention Center, Fort Lauderdale, Florida, 2009, p. 16.

- [11] L. Natalia, D. P. Franco, and B. Lois, "Lithium ion battery value chain and related opportunities for Europe," Publications Office of the European Union 2016.
- [12] B. Moradi and G. G. Botte, "Recycling of graphite anodes for the next generation of lithium ion batteries," *Journal of Applied Electrochemistry*, vol. 46, pp. 123-148, February 01 2016.
- [13] N. K. Chaudhari, M.-S. Kim, T.-S. Bae, and J.-S. Yu, "Hematite (α -Fe₂O₃) nanoparticles on vulcan carbon as an ultrahigh capacity anode material in lithium ion battery," *Electrochimica Acta*, vol. 114, pp. 60-67, 2013.
- [14] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. Proietti Zaccaria, and C. Capiglia, "Review on recent progress of nanostructured anode materials for Li-ion batteries," *Journal of Power Sources*, vol. 257, pp. 421-443, 2014/07/01/ 2014.
- [15] L. Gaines, "The future of automotive lithium-ion battery recycling: Charting a sustainable course," *Sustainable Materials and Technologies*, vol. 1, pp. 2-7, 2014.
- [16] F. a. Sullivan. (2010). *Supply Analysis for the European Ferrous Sulphate Market*. Available: <https://www.frost.com/prod/servlet/cpo/221887167>
- [17] L. T. Peiró, G. V. Méndez, and R. U. Ayres, "Lithium: sources, production, uses, and recovery outlook," *Jom*, vol. 65, pp. 986-996, 2013.
- [18] F. Renard, "2020 cathode materials cost competition for large scale applications and promising LFP best-in-class performer in term of price per kWh," in *First International Conference on Olivines for Rechargeable Batteries OREBA 1.0*, Montreal, Canada, 2014.
- [19] (26 July 2017). Available: https://www.alibaba.com/product-detail/Ultra-high-purity-iron-oxide-for_60194919376.html?spm=a2700.7724857.0.0.bi0EpW
- [20] K. G. Gallagher and P. A. Nelson, "6 - Manufacturing Costs of Batteries for Electric Vehicles A2 - Pistoia, Gianfranco," in *Lithium-Ion Batteries*, ed Amsterdam: Elsevier, 2014, pp. 97-126.
- [21] G. Patry, A. Romagny, S. Martinet, and D. Froelich, "Cost modeling of lithium - ion battery cells for automotive applications," *Energy Science & Engineering*, vol. 3, pp. 71-82, 2015.

Chapter 8

Conclusion and Future Work

This chapter provides a summary of the results obtained during this research study and puts them in the perspective of the current state of lithium battery research. The results obtained are compared with the objectives initially laid out for this work and are evaluated in terms of the novel contributions. The limitations of the work are also highlighted target to aid in streamlining the research of future investigators in this field.

The chapter subsequently outlines those studies that are currently underway such as the opportunity to use sulphate based cathodes to offset the intrinsically lower voltage that Sodium ion batteries have in comparison to Lithium. It also discusses the ways forward in utilising these results as a diving board to investigate the electrochemical activity of other fluorosulphate and hydroxysulphate compounds that had faced similar challenges earlier.

8.1 Perspective

The aim of this study was to understand the fundamental and electrochemical properties of the $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M = transition element – Fe, Co, Mn and Ni) class of sulphates and utilise this insight to test the electrochemical activity of the high voltage Mn, Co and Ni analogues. The literature survey, in this regard, was focused on the understanding the need for high voltage cathode materials and subsequently the current landscape of research in this field. Polyanionic cathodes were of focus because of their thermal stability and in particular, sulphate based cathodes as they offer the prospect of high operational voltages and therefore high energy density.

This research work limits the studies to $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of sulphates on account of their ease of synthesis and simplicity of translation to commercial applications. In this class of sulphates only Fe has been shown to be electrochemically active with only a few studies detailing its structure and electrochemical mechanism [1-5]. The Co and Mn analogues have been theoretically shown to be electrochemically active as in Figure 8-1 but have not been experimentally proven.

Figure 8-1: A perspective of operational $\text{Li}_2\text{M}(\text{SO}_4)_2$ class of sulphates in comparison to other popular high voltage cathode materials [6, 7]. The red stars indicate the focus of this work

In addition, the fundamental properties of $\text{Li}_2\text{M}(\text{SO}_4)_2$ and its solid solution series of bimetallic sulphates $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2 = \text{Mn}, \text{Co}$ and Ni) has been rarely explored [3, 4, 8, 9] prompting the need for a deeper understanding that can be applied to other sulphate based species as well.

8.2 Summary of Results

8.2.1 Lithium Iron Sulphate – Electrochemical mechanism and effect of additives

1. Monoclinic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ was successfully synthesised and a detailed study of its electrochemical mechanism was carried out to establish a baseline for comparison of other materials in this study. The operational voltage of this system was at 3.83 V vs. Li and yielded a discharge capacity of 55-60 mAh.g⁻¹ at low currents.
2. *Ex-situ* x-ray absorption spectroscopy was employed for the first time to determine the electrochemical mechanism operating in this class of sulphates.
3. The effect of fluorinated and non-fluorinated binders during the charge-discharge process was elucidated through the *ex-situ* x-ray absorption spectroscopy analysis and electrochemical tests. It was found that both types of binders had a negative effect on performance at high charge-discharge rates compared to a system without binders.
4. The effect of 4 types of carbon additives; a) Super P Carbon, b) multi walled carbon nanotubes (MWCNT), c) single walled carbon nanotubes (SWCNT) and d) Graphene on electrochemical performance was studied. This was the first occasion extended cycling performance (50 cycles) of such sulphate based electrodes was studied. Cycling and rate performance studies showed that the SWCNT additive showed poor cycling performance while MWCNTs showed the highest consistency.

8.2.2 Synthesis of a novel solid solution series of bi-metallic sulphates and their fundamental properties

1. A novel solid solution series of $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($x = 0$ to 1 , $\text{M}^1, \text{M}^2 = \text{Mn, Co and Ni}$) was successfully synthesised and the structural characteristics were confirmed using powder X-ray diffraction. The lattice parameters were found to vary linearly with substitution and demonstrated the transition between monoclinic phases of Co and Mn and the orthorhombic phase of Ni.
2. Parent sulphates of the series, $\text{Li}_2\text{M}(\text{SO}_4)_2$ (where $\text{M} = \text{Co, Mn, Ni}$) were subjected to thermal stability tests. It was found that this class of sulphates was found to be stable upto 550°C after which the materials decompose into their constituent components with three different degradation mechanisms for each of the three. One of the major impediments to handling sulphates throughout the course of this study was their sensitivity to humidity. The moisture sensitivity analysis yielded a pronounced impact of atmospheric moisture on the chemical stability of the material. Approximately, 90% of the original phase degraded over 40 days with hydrated sulphates identified as the major crystalline decomposition products. Since this phenomenon has also been observed with fluorosulphates [10] the moisture sensitivity of these materials needs to be taken into consideration to realise the practical applications of such sulphate based battery electrode materials.
3. The NMR and magnetic studies of the materials were successfully carried out to probe and understand the local environment within the $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ samples.

8.2.3 Unveiling the electrochemical activity of Mn and Co based sulphates

1. Sebaconitrile was used as a co solvent with conventional electrolytes to define new compositions of electrolyte that can operate in larger voltage windows. The high voltage capability of this set of electrolytes with novel

compositions were electrochemically analysed and evaluated to choose the most suitable candidate for $\text{Li}_2\text{M}(\text{SO}_4)_2$ cell performance.

2. Electrochemical activity of Mn and Co in $\text{Li}_2\text{M}(\text{SO}_4)_2$ based lithium battery cathodes was demonstrated for the first time through a combination of cathode material modification by high energy ball milling and the use of sebaconitrile based electrolytes in an extended voltage window of 4.2 to 5.6 V *vs* Li. The reversibility of the redox couple was evaluated through cyclic voltammetry tests. The highest operating potential of a pure Mn based system was observed through reversible redox reactions at 4.85 V *vs*. Li. The Co based system operated at 5.02 V *vs*. Li but lost reversibility in the 3rd cycle. Ni was not found to be electrochemically active in the voltage window tested. These are the highest voltages reported for compounds consisting purely of a single transition element.
3. The mechanism of operation of the Mn based system was investigated in detail using a combination of *ex-situ* X-Ray Absorption Spectroscopy (XAS) and X-Ray Photoelectron Spectroscopy (XPS) to conclude that the Mn +2/+3 redox couple was active. The Co system requires further improvement before it is subjected to similar analysis in the future.

8.2.4 All Iron full-cell based on a sulphate cathode

1. A novel $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ full-cell was assembled with Fe based redox couples on both the positive and negative electrode. The system was successfully demonstrated in an electrochemical cell with a pre-lithiated Fe_2O_3 anode.
2. The full-cell operated in a window from 0.5 to 3.5 V with the redox couple above 2 V. This is the highest voltage for an Fe based redox couple operating with a non-carbonaceous anode. The cycling performance was found to be consistent at low C-rate with a discharge capacity of 50-60 mAh.g⁻¹ but at high C-rates the cell showed negligible capacity.

3. A techno-economic comparison of the full-cell was carried out with a combination of NCA/LFP cathode and LTO/Graphite anodes. It was found that the $\text{Li}_2\text{Fe}(\text{SO}_4)_2/\text{Fe}_2\text{O}_3$ system had no major cost advantage compared to traditional cathodes despite the relatively inexpensive electrode materials. It was also noted that the system suffered from low energy density and hence was more suited to non-portable applications.

8.3 Novel Contributions

8.3.1 Scientific Contribution

1. Understanding the electrochemical mechanism of a sulphate based material, $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ through X-ray Absorption Spectroscopy.
2. Synthesis of a novel solid solution series of bi-metallic sulphates $\text{Li}_2\text{M}^1_x\text{M}^2_{1-x}(\text{SO}_4)_2$ ($\text{M}^1, \text{M}^2 = \text{Co}, \text{Mn}$ and Ni) and understanding their structural, thermal and magnetic properties. These studies in addition to the moisture sensitivity analysis aid in building awareness of the challenges to commercial application of these materials.

8.3.2 Technological significance

1. Unveiling the reversible electrochemical activity in $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}(\text{SO}_4)_2$ (Figure 8-2). This was done through a combination of mechanical processing of the material by milling and incorporation of a novel composition of electrolyte that allows for electrochemical testing in an extended voltage window. The *ex-situ* X-ray Absorption Spectroscopy and X-ray Photoelectron Spectroscopy studies to determine the mechanism of operation were also novel in its application to these materials.
2. Assembly and testing of a novel all iron full-cell consisting of a $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ cathode and Fe_2O_3 anode was successfully demonstrated. The techno-economic comparison of such a cell with commonly used LIB

cathodes and anodes was carried out to evaluate the pros and cons of the full-cell.

Figure 8-2: Contribution of this work compared to other high voltage olivines

8.4 Future Work

8.4.1 Electrochemical analysis of bi-metallic sulphates

It is hoped that with the impetus from this work, there would be a deeper analysis of the Co based system and the effects of substitution by Ni and Mn. Alternate electrolytes which might prove suitable for reversible cycling of the Co based sulphate as well as enhance the stability window further to test Ni electrochemical activity would also stretch the potentials at which lithium ion batteries can operate. Coatings and additives which enhance the conductivity as well as

hydrophilic nature of these compounds would be valuable in their path to commercialisation.

8.4.2 Analysis of magnetic properties of solid solution series

The presence of three transition elements Co, Mn and Ni all exhibit hugely different exchange interactions as seen in the Bethe-Slater curve [11]. This makes for a very interesting study of the variation in their magnetic properties on substitution. The SQUID and NMR studies in this work focussed only on the end and central members which resulted in a good start but not in a complete understanding of the behaviour of the solid solution series. NMR may also be used to study the effect of doping on the local structure [12]. This can be used to better understand how the electronic properties are affected by material modification mentioned in the next section.

8.4.3 Material modification

The polyanionic sulphate based cathode materials provide a lot of scope for optimisation and altering the stoichiometry of the three major components – the Li ion, polyanion and Transition Metal (TM) ion - will be studied. These optimisation methods are briefly outlined below.

8.4.3.1 Extraction of multiple lithium ions

Apart from operating potential[13], the energy density of a LIB is dependent on the number of Lithium ions that can be extracted from the system. Utilising multiple transition metals of variable oxidation states allows for the enriching of the Li ions in the cathode material and enables greater extraction.

8.4.3.2 Modification of the Polyanionic group

Sulphates in its other forms such as sulfite (SO_3^{2-}), dithionite ($\text{S}_2\text{O}_4^{2-}$), persulfate (SO_5^{2-}), disulfate ($\text{S}_2\text{O}_7^{2-}$) and trisulfate ($\text{S}_3\text{O}_{10}^{2-}$) each exhibit different electronegative character. Their synthesis and study provides the prospect of realising a whole new family of high voltage compounds much like what was achieved with pyrophosphates [14] for the phosphate family.

8.4.3.3 Variation in Oxygen stoichiometry

Oxygen deficient stoichiometry has shown to improve electrochemical performance in olivines [15] and with sulphate based compounds having high oxygen concentration, incorporating such deficiencies would allow better understanding of how the crystal structure affects battery performance.

8.4.3.4 Doping with alternative TM ions

Keeping the polyanion constant and substituting the cations results in a combination of three effects which play a role in determining the shift of the redox potential [16];

1. Inductive effect – The electropositive character of the dopant alters the M-O covalency and therefore the redox voltage. Higher the electropositive character, lower the redox potential.
2. Changes in M-O bond length – Smaller the TM ion, shorter the M-O bond, resulting in a highly covalent bond and therefore lower redox potential.
3. Interactions of M-O-M ions – In the presence of a low voltage redox couple (M_L), a high voltage couple (M_H) gets destabilised because of super exchange interactions of M_L^{3+} -O- M_H^{2+} [17].

8.4.3.5 Doping with non-TM ions

When a non-TM ion such as Mg^{2+} , Al^{3+} without any redox behavior substituted for a TM ion has been predicted to stabilise the redox couple through super-exchange interactions and improve electronic conductivity. [13, 18]

8.4.4 Sulphates for sodium ion batteries (NIBs)

Sulphates have been of immense interest in NIBs on account of their ability to offset the lower redox potential of Na in comparison to Li. A spate of recent publications featuring allaudite [19-21] based sulphates have proven to be extremely interesting to the battery community and hold immense opportunities.

8.5 Concluding Remarks

The thesis titled “Unveiling the Fundamental Properties of Sulphate based Cathodes for Next Generation Lithium Ion Batteries”, has successfully demonstrated reversible electrochemical activity in the $\text{Li}_2\text{Mn}(\text{SO}_4)_2$ and $\text{Li}_2\text{Co}(\text{SO}_4)_2$ compounds which had so far proven to be elusive. The study carried out extensive electrochemical, structural and spectroscopy studies to understand the mechanism of operation of these redox chemistries. Novel bi-metallic sulphates were also synthesised and characterised to understand the effects of substitution. The maturity of the technology was evaluated by construction of a full-cell and demonstration of its electrochemical stability. Finally, a techno-economic comparison of this full-cell put this class of sulphate based cathodes in perspective with respect to the conventional cathode and anode chemistries.

8.6 References

- [1] L. Lander, M. Reynaud, J. Carrasco, N. A. Katcho, C. Bellin, A. Polian, *et al.*, "Unveiling the electrochemical mechanisms of $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ polymorphs by neutron diffraction and density functional theory calculations," *Physical Chemistry Chemical Physics*, vol. 18, pp. 14509-14519, 2016.
- [2] L. Lander, M. Reynaud, G. Rousse, M. T. Sougrati, C. Laberty-Robert, R. J. Messinger, *et al.*, "Synthesis and Electrochemical Performance of the Orthorhombic $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ Polymorph for Li-Ion Batteries," *Chemistry of Materials*, vol. 26, pp. 4178-4189, 2014/07/22 2014.
- [3] M. Reynaud, "Design of new sulfate-based positive electrode materials for Li- and Na-ion batteries," Ph.D., Materials Science, Université de Picardie Jules Verne, 2013.
- [4] M. Reynaud, M. Ati, S. Boulineau, M. T. Sougrati, B. C. Melot, G. Rousse, *et al.*, "Bimetallic Sulfates $\text{A}_2\text{M}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ (A= Li, Na and M= Transition Metal): as New Attractive Electrode Materials for Li-and Na-Ion Batteries," *ECS Transactions*, vol. 50, pp. 11-19, 2013.
- [5] M. Reynaud, M. Ati, B. C. Melot, M. T. Sougrati, G. Rousse, J.-N. Chotard, *et al.*, " $\text{Li}_2\text{Fe}(\text{SO}_4)_2$ as a 3.83 V positive electrode material," *Electrochemistry Communications*, vol. 21, pp. 77-80, 2012.

- [6] C. Julien and A. Mauger, "Review of 5-V electrodes for Li-ion batteries: status and trends," *Ionics*, vol. 19, pp. 951-988, 2013.
- [7] J. M. Clark, C. Eames, M. Reynaud, G. Rousse, J.-N. Chotard, J.-M. Tarascon, *et al.*, "High voltage sulphate cathodes $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M= Fe, Mn, Co): atomic-scale studies of lithium diffusion, surfaces and voltage trends," *Journal of Materials Chemistry A*, vol. 2, pp. 7446-7453, 2014.
- [8] L. Lander, M. Reynaud, J. Rodríguez-Carvajal, J.-M. Tarascon, and G. Rousse, "Magnetic Structures of Orthorhombic $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M= Co, Fe) and $\text{Li}_x\text{Fe}(\text{SO}_4)_2$ (x= 1, 1.5) Phases," *Inorganic chemistry*, vol. 55, pp. 11760-11769, 2016.
- [9] M. Reynaud, G. Rousse, J.-N. Chotard, J. Rodríguez-Carvajal, and J.-M. Tarascon, "Marinite $\text{Li}_2\text{M}(\text{SO}_4)_2$ (M = Co, Fe, Mn) and $\text{LiFe}(\text{SO}_4)_2$: Model Compounds for Super-Super-Exchange Magnetic Interactions," *Inorganic Chemistry*, vol. 52, pp. 10456-10466, 2013/09/16 2013.
- [10] L. Zhang, J.-M. Tarascon, M. T. Sougrati, G. Rousse, and G. Chen, "Influence of relative humidity on the structure and electrochemical performance of sustainable LiFeSO_4F electrodes for Li-ion batteries," *Journal of Materials Chemistry A*, vol. 3, pp. 16988-16997, 2015.
- [11] B. D. Cullity and C. D. Graham, *Introduction to magnetic materials*: John Wiley & Sons, 2011.
- [12] C. P. Grey and N. Dupré, "NMR Studies of Cathode Materials for Lithium-Ion Rechargeable Batteries," *Chemical Reviews*, vol. 104, pp. 4493-4512, 2004/10/01 2004.
- [13] A. Kraytsberg and Y. Ein-Eli, "Higher, Stronger, Better ... A Review of 5 Volt Cathode Materials for Advanced Lithium-Ion Batteries," *Advanced Energy Materials*, vol. 2, pp. 922-939, 2012.
- [14] P. Barpanda, S. i. Nishimura, and A. Yamada, "High - Voltage Pyrophosphate Cathodes," *Advanced Energy Materials*, vol. 2, pp. 841-859, 2012.
- [15] B. Kang and G. Ceder, "Electrochemical performance of LiMnPO_4 synthesized with off-stoichiometry," *Journal of The Electrochemical Society*, vol. 157, pp. A808-A811, 2010.
- [16] T. Muraliganth and A. Manthiram, "Understanding the Shifts in the Redox Potentials of Olivine $\text{LiM}_{1-y}\text{M}_y\text{PO}_4$ (M= Fe, Mn, Co, and Mg) Solid Solution Cathodes," *The Journal of Physical Chemistry C*, vol. 114, pp. 15530-15540, 2010.

- [17] A. Gutierrez, N. A. Benedek, and A. Manthiram, "Crystal-Chemical Guide for Understanding Redox Energy Variations of $M^{2+}/3+$ Couples in Polyanion Cathodes for Lithium-Ion Batteries," *Chemistry of Materials*, vol. 25, pp. 4010-4016, 2013.
- [18] S. M. Rommel, N. Schall, C. Brünig, and R. Wehrich, "Challenges in the synthesis of high voltage electrode materials for lithium-ion batteries: a review on $LiNiPO_4$," *Monatshefte für Chemie-Chemical Monthly*, vol. 145, pp. 385-404, 2014.
- [19] P. Barpanda, G. Oyama, S.-i. Nishimura, S.-C. Chung, and A. Yamada, "A 3.8-V earth-abundant sodium battery electrode," *Nature communications*, vol. 5, 2014.
- [20] P. Barpanda, "Pursuit of sustainable iron-based sodium battery cathodes: two case studies," *Chemistry of Materials*, vol. 28, pp. 1006-1011, 2016.
- [21] H. Kim, H. Kim, Z. Ding, M. H. Lee, K. Lim, G. Yoon, *et al.*, "Recent Progress in Electrode Materials for Sodium-Ion Batteries," *Advanced Energy Materials*, vol. 6, pp. 1600943-n/a, 2016.