

# Contents

	page
Abstract	I
Acknowledgements	iii
Contents	v
List of Figures	viii
List of Tables	x
List of Symbols	xi
List of Abbreviations	xii
<b>Chapter 1: Introduction</b>	
1.1 Introduction	1
1.2 Classification of Batteries	3
1.3 Working Principle of Li-ion Battery	3
1.4 Characteristic Parameters of Battery	4
1.4.1 Nominal Voltage	4
1.4.2 Capacity	4
1.4.3 Colombic Efficiency	4
1.4.4 Energy Density	5
1.4.5 Power Density	5
1.4.6 Rate Performance	4
1.4.7 State of Charge and Depth of Discharge	4
1.4.8 Cyclability	4
1.4.9 Internal Impedance	5
1.4.10 Temperature Dependence	5
1.4.11 Cost Factor	5
1.5 Why is the Li-ion Battery?	5
1.6 Electrode Materials for Li-ion Battery	6
1.7 Closing Remarks	6
<b>Chapter 2: Literature Survey and Scope of Thesis Work</b>	
2.1 Introduction	7
2.2 Synthesis Methods	7
2.2.1 Solid State Reaction Method	7
2.2.2 Sol-Gel Method	8
2.2.2.1. Chelate Compound Based Method	8
2.2.2.2 Emulsion Drying Method	8
2.2.2.3 Hydrothermal Method	9
2.2.2.4. Molten Salt Method	9
2.2.2.5. Organic Solvent Method	9
2.2.2.6. Pechini Process	9
2.2.2.7. Self-combustion Method	9
2.3 Challenges of LiMn <sub>2</sub> O <sub>4</sub> Cathode Material	10
2.4 Reviews of Spinel Framework Cathode Materials	10
2.4.1 Transition Metal Dual and Ternary Doping	11
2.4.2 Alkaline Earth Metal Doping	11
2.4.3 Rare-Earth Metal Doping	12
2.4.4 Rare-Earth and Transition Metal Dual Doping	15
2.5 Scope of Thesis Work	17
2.6 Closing Remarks	17
<b>Chapter 3: Synthesis and Characterization of Cathode Materials</b>	
3.1 Introduction	19
3.2 Cathode Material Synthesis	19
3.2.1 Analytical Grade Chemicals	19
3.2.2 Organic Sol-gel Synthesis Method	20
3.3 Physical Characterization Techniques	21
3.3.1 X-ray Diffraction Technique	21
3.3.2 Scanning Electron Microscopy and Elemental Detection Technique	22

3.3.3	Tunneling Electron Microscopy Technique	22
3.3.4	Raman Spectrum Technique	22
3.3.5	Thermo-gravimetric Technique	22
3.3.6	Specific Surface Area Measurement Technique	22
3.4	Electrochemical Characterizations of Synthesized Material	23
3.4.1	Cathode Fabrication and Swagelok Cell Assembly	23
3.4.1.1	Slurry Preparation	23
3.4.1.2	Slurry Spread and Drying	23
3.4.1.3	Cutting the Cathode	23
3.4.1.4	Swagelok Cell Assembly	24
3.4.2	Cyclic Voltammetry Technique	24
3.3.3	Galvanostatic Charge Discharge Performance	24
3.3.4	Rate Performance and Cyclability Analysis	25
3.3.5	Electrochemical Impedance Spectroscopy	25
3.5	Closing Remarks	25

#### **Chapter 4: Rare-Earth (RE : Gd, Dy, Tb , Yb) doped LiMn<sub>1.95</sub>RE<sub>0.05</sub>O<sub>4</sub> Cathodes**

4.1	Introduction	27
4.2	Physical Characterization of Rare-Earth Doped LiMn <sub>1.95</sub> RE <sub>0.05</sub> O <sub>4</sub> Cathodes	28
4.2.1	X-ray Diffraction and Structural Analysis	28
4.2.2	Surface Morphology and Elemental Analysis	30
4.2.3	Thermal Gravimetric Analysis (TGA)	32
4.3	Electrochemical Characterization of Rare-Earth Doped LiMn <sub>1.95</sub> RE <sub>0.05</sub> O <sub>4</sub> Cathodes	33
4.3.1	Cyclic Voltammetry and Its Analysis	33
4.3.2	Galvanostatic Charge - Discharge Performance	35
4.3.3	Rate Performance and Cyclability Analysis	39
4.3.4	Electrochemical Impedance Spectroscopy	42
4.4	Closing Remarks	43

#### **Chapter 5: Gadolinium Doped LiMn<sub>2-x</sub>Gd<sub>x</sub>O<sub>4</sub> (x=0, 0.01, 0.04, 0.05) Cathodes**

5.1	Introduction	45
5.2	Physical Characterization of Gadolinium Doped LiMn <sub>2-x</sub> Gd <sub>x</sub> O <sub>4</sub> Cathodes	46
5.2.1	X-ray Diffraction and Structural Analysis	46
5.2.2	Surface Morphology and its Analysis	47
5.2.3	Energy Dispersive X-ray Spectra (EDX) and Its Analysis	49
5.2.4	Thermogravimetry and its Analysis(TGA)	49
5.2.5	Raman Spectra and Its Analysis	50
5.3	Electrochemical Characterization of Gadolinium Doped LiMn <sub>2-x</sub> Gd <sub>x</sub> O <sub>4</sub> Cathodes	51
5.3.1	Cyclic Voltammetry and Its Analysis	51
5.3.2	Galvanostatic Charge Discharge Performance	52
5.3.3	Rate Performance and Cyclability Analysis	56
5.3.4	Electrochemical Impedance Spectroscopy	58
5.4	Closing Remarks	58

#### **Chapter 6: Dysprosium Doped LiMn<sub>2-x</sub>Dy<sub>x</sub>O<sub>4</sub> (x=0, 0.01, 0.02, 0.03, 0.04, 0.05) Cathodes**

6.1	Introduction	59
6.2	Physical Characterization of Dysprosium Doped LiMn <sub>2</sub> O <sub>4</sub> Cathodes	59
6.2.1	X-ray Diffraction and Structural Analysis	60
6.2.2	Surface Morphology and Its Analysis	62
6.2.3	Energy Dispersive X-ray Diffraction and Its Analysis	63
6.2.4	Porosity and Specific Surface Area Analysis	63
6.3	Electrochemical Characterization of Dysprosium Doped LiMn <sub>2</sub> O <sub>4</sub> Cathodes	64
6.3.1	Cyclic Voltammetry and Its Analysis	65
6.3.2	Galvanostatic Charge Discharge Performance and Its Analysis	66
6.3.3	Rate Performance and Its Analysis	68
6.3.4	Electrochemical Impedance Spectroscopy	70
6.4	Closing Remarks	71

<b>Chapter 7: Rare -Earth (Gd, Nd and Dy) doped LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> Cathodes</b>		
7.1	Introduction	73
7.2	Physical Characterization of Rare-Earth Doped LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub> Cathodes	74
	7.2.1 X-ray Diffraction and Structural Analysis	74
	7.2.2 Surface Morphology and Elemental Analysis	75
	7.2.3 Raman Spectrum and Its Analysis	78
	7.2.4 Porosity and Specific Surface Area Study	79
7.3	Electrochemical Characterization of Rare-Earth Doped LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub> Cathodes	80
	7.3.1 Cyclic Voltammetry and Its Analysis	81
	7.3.2 Galvanostatic Charge Discharge Performance and Its Analysis	82
	7.3.3 Rate Performance and Cyclability Analysis	84
	7.3.4 Electrochemical Impedance Spectroscopy	85
	7.3.5 Comparison of Current Work with Previous Work	87
7.4	Closing Remarks	88
<b>Chapter 8: Summary and Conclusion</b>		
8.1	Summary	89
8.2	Concluding Remarks	90
8.3	Closing Comments	90
<b>Annexure A</b>		
A.1	List of Published Papers	91
	References	93