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Development of Advanced Electrode Materials for use in Rechargeable Lithium Batteries

A thesis submitted in fulfillment of the requirements
for the award of

DOCTOR OF PHILOSOPHY

by

SCOTT ANDREW NEEDHAM, BEng (Hons 1), MMgmt

University of Wollongong



Institute for Superconducting and Electronic Materials
and the
Faculty of Engineering

2007

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Declaration

I, Scott Andrew Needham, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, in the Faculty of Engineering, University of Wollongong, is wholly original work unless otherwise referenced or acknowledged. This thesis has not been submitted for qualifications at any other academic institution.



Wollongong, Australia

December 2006

For Anita, Benjamin and Oliver

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Abstract

Batteries are a necessary companion to most portable electronic devices, and the rechargeable lithium battery is the most energy dense and lightest of all the competing battery types. These features make it the most likely battery to be used in future electronic devices, which will be smaller and have increased functionality. Therefore, the performance of the rechargeable lithium battery must continue to be improved in terms of capacity, rate capability, and cycle life. This thesis contributes to this goal by developing new materials and novel synthesis techniques for application in advanced rechargeable lithium batteries.

A significant contribution to the ever-growing collection of works on the doping of LiCoO_2 and LiFePO_4 structures in an attempt to raise their practical storage capacities is presented. The practical capacity of these materials can sometimes be increased by aliovalent doping due to the formation of charge-carrying holes, which impart a higher electrical conductivity. In the case of LiCoO_2 doped with Mg, V and Mo prepared by traditional solid-state methods, the lithium storage capacity was not improved compared to the un-doped LiCoO_2 . This was attributed to the formation of lithium-containing secondary phases, which resulted in a lithium deficient primary phase and a higher concentration of Jahn-Teller Co^{4+} ions. These effects disrupted the intercalation framework and produced a poor electrochemical performance. In contrast, work on the doping of titanium into LiFePO_4 confirmed that a complete solid solution could be formed using a sol-gel method, despite several previous works suggesting that the aliovalent doping of this structure was impossible. Doping 1 mol% titanium into the LiFePO_4 structure improved the capacity to only 5 % less than the theoretical maximum attainable capacity. The mechanism for this improvement was related to increased *p*-type semiconductority in the material.

A novel materials synthesis technique, electric discharge assisted mechanical milling (EDAMM), was applied for the first time to the preparation of functional oxides. LiCoO_2 and LiFePO_4 cathode materials and $\text{SrTi}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0, 0.1, 0.2, 0.5$), which has possible magnetic applications, were synthesized in a matter of minutes with either micro-sized or nano-sized powder morphologies. The electrochemical performance of the cathode materials

was shown to be comparable to those delivered by powders synthesized by traditional solid-state techniques. $\text{SrTi}_x\text{Co}_{1-x}\text{O}_3$ powders could be formed as complete solid solutions with interesting magnetic properties. The EDAMM method shows commercial potential, as it can synthesize a wide range of functional oxide powders in high quantities. Concerning the synthesis of novel materials, this work also reports on the first ever formation of uniform and aligned NiO nanotubes. The nanotubes were up to 60 μm long, had an outer diameter of 200 nm and a wall thickness of 20-30 nm. Compared to nanocrystalline NiO, the nanotubes delivered a 30 % increase in the discharge capacity after repeated cycling. Electrochemical impedance spectroscopy suggests that this improvement was due to kinetic advantages.

Finally, unique carbon-based SnSb and transition metal oxide nanocomposite materials formed by various chemical techniques are shown to offer promise as anode materials due to their high capacity and excellent cycle life. The use of SnSb alloys has previously been hindered by their poor cyclability, which is caused by volume changes during cycling that result in a loss of electrical contact. Physically mixing carbon in a 1:1 weight ratio with the active material does not improve the cyclability of the electrode, but improves the realized capacity by increasing the electrical conductivity. A superior method of utilizing carbon in a composite form is to synthesize a SnSb-CNT powder, in which the SnSb is chemically bonded onto the carbon nanotube (CNT) nano-network. These powders demonstrated a high reversible capacity and stable cyclability. This method is an effective and promising option to address the problem of volume changes in all high capacity alloys. The $\text{Co}_3\text{O}_4\text{-C}$ composite powders were produced by spray pyrolysis of a sugar-metal ion solution. The capacity in cells was $> 800 \text{ mAh g}^{-1}$ for over 50 cycles, which solved the capacity fade problems. The improved electrochemical properties were related to the presence of a carbon sheath formed during processing, which acted to prevent excessive electrolyte reduction and retard the development of a thick solid electrolyte interphase (SEI). A disordered C matrix was also formed throughout the bulk powder during processing, which assisted in cushioning the volume changes associated with the electrochemical reaction.

Table of Contents

1. Introduction	1
2. Literature review	6
2.1 Rechargeable Lithium Batteries	6
2.1.1 A Brief History	6
2.2 Fundamental Considerations	10
2.2.1 Principles of Operation	10
2.2.2 The Cell Voltage	11
2.3 Cathode Materials	13
2.3.1 Lithium Cobalt Oxide	14
2.3.1.1 Structural and Electrochemical Properties	14
2.3.1.2 Doping of LiCoO ₂ Compounds <i>via</i> Solid-State Methods	18
2.3.1.3 Alternative Synthesis Methods	20
2.3.2 Lithium Iron Phosphate	22
2.3.2.1 A Shifting Ideology	22
2.3.2.2 Structural and Electrochemical Properties	23
2.3.2.3 Effect of Dopants	26
2.3.2.4 Alternative Synthesis Methods	27
2.4 Anode Materials	28
2.4.1 Carbon	28
2.4.1.1 Forms of Carbon	29
2.4.1.2 Lithium Intercalation and Failure Mechanisms	32
2.4.1.2.1 Dependence on Carbon Type	32
2.4.1.2.2 Electrolyte Considerations	34
2.4.1.3 Composites using Carbon from Agricultural Sources	36
2.4.2 SnSb Metal Pnictide	37
2.4.2.1 Crystal Structure	39
2.4.2.2 Reactions with Lithium and Synthesis Techniques	41

2.4.3	Transition Metal Oxides	45
2.4.3.1	Reactions of Co_3O_4 with Lithium	47
2.5	Nanostructures	49
2.5.1	Synthesis of Nanotube Materials <i>via</i> the Template Method	52
2.6	Battery Electrolytes	54
2.6.1	Organic Solvents	54
2.6.2	Lithium Salts and Other Active Components	55
3.	Experimental	56
3.1	Overview	56
3.2	Methods of Synthesis	57
3.2.1	Solid-State	57
3.2.2	Sol-Gel	57
3.2.3	Electric Discharge Assisted Mechanical Milling	58
3.2.4	Nanoscale Templating	60
3.2.5	Reductive Precipitation	61
3.2.6	Spray Pyrolysis	62
3.3	Methods of Characterization	63
3.3.1	Structure and Morphology	63
3.3.2	Particle Surface Area Measurements	64
3.3.3	Electrical Conductivity	65
3.3.4	Magnetic Measurements	66
3.3.5	XAFS and XANES	66
3.4	Electrochemical Assessment	69
3.4.1	Electrode Fabrication and Test Cell Assembly	69
3.4.2	Galvanostatic Charge/Discharge Cycling	70
3.4.3	Cyclic Voltammetry	71
3.4.4	Electrochemical Impedance Spectroscopy	71
4.	$\text{LiM}_x\text{Co}_{1-x}\text{O}_2$ Compounds Prepared <i>via</i> a Solid-State Method	73
4.1	Introduction	73

4.2	Experimental	73
4.3	Results and Discussion	74
4.3.1	Structural and Morphological Characterization	74
4.3.2	Electrochemical Properties	83
4.4	Summary	85
5.	The Effect of Titanium Doping on LiFePO₄ Prepared <i>via</i> a Sol-Gel Method	86
5.1	Introduction	86
5.2	Experimental	87
5.3	Results and Discussion	88
5.3.1	Structural and Morphological Characterization	88
5.3.2	Electrochemical Properties	95
5.4	Summary	97
6.	Functional oxides Prepared <i>via</i> a Novel Electric Discharge Assisted Mechanical Milling Method (EDAMM)	98
6.1	Introduction	98
6.2	Experimental	99
6.3	Results and Discussion	100
6.3.1	Synthesis and Characterization of LiCoO ₂	100
6.3.2	Electrochemical Properties of LiCoO ₂	103
6.3.3	Synthesis and Characterization of LiFePO ₄	104
6.3.4	Electrochemical Properties of LiFePO ₄	106
6.3.5	Synthesis and Characterization of SrTi _{1-x} Co _x O ₃	108
6.3.6	Magnetic Properties of SrTi _{0.5} Co _{0.5} O ₃	110
6.4	Scalability and Commercialization of EDAMM	112
6.5	Summary	113
7.	NiO Nanotubes Prepared <i>via</i> a Nanoscale Templating Method	114
7.1	Introduction	114

7.2	Experimental	114
7.3	Results and Discussion	115
7.3.1	Structural and Morphological Characterization	115
7.3.2	Electrochemical Properties	117
7.3.3	Electrochemical Impedance Spectroscopy	121
7.4	Summary	122
8.	SnSb-Carbon Composites Prepared <i>via</i> a Reductive Precipitation Method	123
8.1	Introduction	123
8.2	Experimental	124
8.3	Results and Discussion	125
8.3.1	Structural and Morphological Characterization of SnSb Alloys	125
8.3.2	Electrochemical Properties of SnSb-C	126
8.3.3	Summary on SnSb-C	130
8.3.4	Structural and Morphological Characterization of SnSb-CNT	130
8.3.5	Electrochemical Properties of SnSb-CNT	134
8.3.6	Summary on SnSb-CNT	137
9.	Transition Metal Oxide-Carbon Composites Prepared <i>via</i> the Spray Pyrolysis Method	138
9.1	Introduction	138
9.2	Experimental	138
9.3	Results and Discussion	139
9.3.1	Structural and Morphological Characterization	139
9.3.2	Electrochemical Properties	142
9.3.3	Electrochemical Impedance Spectroscopy	144
9.4	Summary	147

10. Conclusions and Recommendations	148
11. References	150
List of Symbols and Abbreviations	168
List of Materials and Chemicals	172
List of Figures	174
List of Tables	182
List of Author Publications	183