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Development of advanced electrode materials for use in rechargeable lithium batteries

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Development of Advanced Electrode Materials for use in Rechargeable Lithium Batteries

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by

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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.

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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 semiconductivity 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 $SrTi_xCo_{1-x}O_3$ (x = 0, 0.1, 0.2, 0.5), which has possible magnetic applications, were synthesized in a matter of minutes with either microsized or nanosized 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. $SrTi_xCo_{1-x}O_3$ 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 Co_3O_4–C composite powders were produced by spray pyrolysis of a sugar-metal ion solution. The capacity in cells was > 800 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.

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