

**NANOSTRUCTURED MATERIALS
FOR LITHIUM ION BATTERIES**

**A thesis submitted in fulfilment of
requirements for the award of**

Doctor of Philosophy

Mohd Faiz Bin Hassan, B.Sc., M.Sc.



University of Wollongong

Institute for Superconducting and Electronic Materials

Faculty of Engineering

2010

CANDIDATE'S CERTIFICATION

I, Mohd Faiz Bin Hassan, declare that this thesis, submitted in partial fulfilment of the requirements of the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials (ISEM) and the Faculty of Engineering at the University of Wollongong, New South Wales, Australia, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for a qualification at any other academic institution.

Mohd Faiz Bin Hassan

Wollongong, NSW, Australia

2010

ACKNOWLEDGEMENTS

First of all, I would like to express my gratitude to my supervisors, Prof. Dr. Hua Kun Liu and Dr. Zaiping Guo, who gave me lots of ideas, as well as advice, encouragement, guidance, and confidence to complete this thesis.

I would like to thank the Ministry of Higher Education of the Government of Malaysia and the University of Malaysia Terengganu for scholarship support. I also would like to thank the Institute for Superconducting and Electronic Materials (ISEM) and the School of Mechanical, Materials, and Mechatronic Engineering, Faculty of Engineering, University of Wollongong for supporting this project through their facilities. Financial support from the Australian Research Council (ARC) through project LP0775456 and the ARC Centre of Excellence for Electromaterials Science (CE0561616) is also greatly appreciated.

I would also like to express my real appreciation and thanks to the following people for their help with research and technical problems, especially to: Dr. Germanas, Dr. Chen, Dr. Alexey M. Glushenkov and to my colleagues: Guodong Du, Peng Zhang, MD Mokhlesur Rahman, Cheung Kiak Poh, Nurulhayati Idris, Mohammad Ismail, and Lukman Noreochim. Thanks are also due to Dr. Tania Silver for providing great help in editing this thesis.

Finally, I would like to thank my beloved wife (Masnizan) and son (Haziq Naim) for their love, moral support, and encouragement to successfully complete this thesis.

MOHD FAIZ BIN HASSAN

September 2010

ABSTRACT

Lithium ion batteries have become an essential part of everyday life. They are the power source for millions of consumer, business, medical, military, and industrial appliances worldwide. To maintain lithium ion batteries as the most outstanding portable energy resources, their electrochemical performance must continue to be improved in terms of capacity, rate capability, and cycle life. This thesis is written to deal with this challenge through some experimental work, with the aim of exploring and investigating a variety of new types of materials, with a particular focus on the microstructures, morphology, and their electrochemical properties.

The concept of active/inactive or less active materials has been implemented in the study of tin oxide and transition metal oxide (TMO; NiO, Co_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, and $\alpha\text{-MoO}_3$) based nanocomposites. In this work, tin oxide is considered as an active compound and has been incorporated with several TMO compounds, for example Co_3O_4 and NiO, while a number of TMOs ($\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-MoO}_3$, and $\text{SnO}_2\text{-NiO}$) have been integrated with layered amorphous carbon. Another compound, vanadium nitride (VN), was also selected for study. VN is one of the transition metal nitride (TMN) compounds, which have several advantages namely, a high melting point, a great theoretical capacity, and high conductivity, characteristics which make it a promising compound for the lithium ion battery. Furthermore, the effects of the preparation route, which can lead to small particle size, high porosity, and excellent morphology, can automatically fulfil the requirements on the anode materials in this field.

The synthesis process employed here is very simple, convenient, informative, low-cost, and requires only a low treatment temperature. The morphology, microstructure, and electrochemical testing were carried out systematically.

In the study of $\text{SnO}_2\text{-Co}_3\text{O}_4$ nanocomposites, the composites were prepared using a simple molten salts route. The morphology of the samples was changed after the introduction of high Co_3O_4 content. The as-prepared powder electrodes demonstrated satisfactory capacity retention and boosted the lithium ion reaction compared to the sample that contained only a small amount of Co_3O_4 . A reversible capacity of 514 mAh/g for a composite anode sample rich in Co_3O_4 was achieved. The excellent electrochemical performance should be attributed to the good interface between the two types of metal oxide particles, which resulted from the preparation method for the nanocomposite. This is the first report on the synthesis and electrochemical performance of a combination of two metal oxides, based on $\text{SnO}_2\text{-Co}_3\text{O}_4$ as negative electrode using the molten salt method.

MoO_3 is well known as a very stable one dimensional (1D) layered structure which is capable to acting as an impermanent support for intercalated species (protons, solvated lithium, and sodium ions). However its electrochemical performance in the lithium ion battery is not promising due to poor ionic and electronic conductivity. On introducing amorphous carbon through a carbon layering process, the composite displayed a magnificent electrochemical performance. The irreversible capacity dropped to 192 mAh/g, which is much smaller than that of the bare reference sample (492 mAh/g). The C- MoO_3 composite electrode showed stable capacity retention,

with a lithium storage capacity of 1064 mAh/g after 50 cycles. This is the first report on C-MoO₃ composite nanobelts.

The investigation to find out a good compound as a negative material is further carried out on α -Fe₂O₃/C. The synthesis of α -Fe₂O₃/C uses a simple molten salts followed by a carbon coating process which is a quite different method compared to the others reported in the literature. It was found that the particles of α -Fe₂O₃ are surrounded by fine amorphous carbon. Electrochemical results confirmed that the electrode properties of the α -Fe₂O₃/C composite were much better than those of the bare α -Fe₂O₃ nanoparticles. A stable reversible capacity of 903 mAh/g for the α -Fe₂O₃/C composite anode was achieved after 100 cycles.

The analysis on SnO₂-NiO-C nanocomposite as a negative compound revealed that the product has a dual phase and is covered by amorphous carbon. From the viewpoint of electrochemical performance, SnO₂-NiO-C nanocomposite demonstrated high capacity, enhanced rate capability, and excellent cycling stability, better than for the uncoated sample. This outstanding performance can be attributed to the joint effects of the nanosize compound particles, good interface behaviour between the carbon matrix and the SnO₂-NiO structure, and the highly porous nature of the carbon matrix.

Nanosize α -Fe₂O₃ anode material was synthesised via a super basic molten salt. It has a small particle size, in the range of 20 to 40 nm. Electrochemical results revealed that it exhibits two different trends during prolonged cycling, which is seldom reported in previous work and is a useful feature for power tool applications.

VN with a nanoporous structure was prepared through a temperature-programmed NH_3 reduction of V_2O_5 . It has a unique porous framework structure with pore sizes of 15-110 nm. The VN anode exhibited similar phenomena to $\alpha\text{-Fe}_2\text{O}_3$, with stable reversible capacity storage of 1806 mAh/g at the 600th cycle.

The outcomes described above demonstrate that the selected inorganic nanocomposite compounds in the current study possess very good structural morphology and distinctive electrochemical features, and they could be promoted as promising materials for advanced lithium ion rechargeable batteries.