

ADVANCED MATERIALS FOR
LITHIUM RECHARGEABLE BATTERY

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Advanced Materials For Lithium Rechargeable Battery

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Declaration

I, Nurul Hayati Idris, declare that the work presented in this thesis is original and was carried out at the Institute for Superconducting and Electronic Materials, Faculty of Engineering, University of Wollongong, New South Wales, Australia. This thesis is wholly my own work and contains no work previously published or written by another person, unless otherwise acknowledged and referenced. This work is original and has not been submitted to qualify for any other degree elsewhere.



Nurul Hayati Idris

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Abstract

Due to the rapid increase in the use of portable computers, mobile phones, and electric vehicles, there is an increasing demand for larger capacity, smaller size, lighter weight and lower priced rechargeable batteries. Lithium ion battery technology offers the highest energy densities by weight of all the commercial rechargeable battery technologies, with high voltage, long cycle life, and a wide environmental operation range. Commercial lithium ion battery electrodes today contain expensive and hazardous cathode (lithium cobalt oxide) and low specific capacity anode (carbonaceous materials). It is desirable to replace these materials with potentially cheaper, less toxic materials that have high specific capacity. In this doctoral work, several nanostructured materials and nanocomposites were examined and characterized as potential electrode material in lithium storage applications. In an attempt to improve the performance of nickel oxide (NiO), NiO-polypyrrole (PPy) and NiO-graphene nanocomposite were prepared and investigated as possible anode materials. Meanwhile, several cathode materials were studied: LiV_3O_8 /carbon nanocomposite and nickel sulfide (NiS). The superior performance of poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMA) gel polymer electrolyte in lithium-polymer batteries was also demonstrated.

NiO-PPy nanocomposites for lithium-ion batteries were prepared by a chemical polymerization method, with sodium *p*-toluenesulfonate as the dopant, Triton X-100 as the surfactant, and FeCl_3 as the oxidant. The new composite material was characterized by Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron

microscopy (SEM), and field-emission scanning electron microscopy (FESEM). Nanosize conducting PPy particles with a cauliflower-like morphology were uniformly coated onto the surface of the NiO powder. The electrochemical results were improved for the NiO-PPy composite compared with the pristine NiO. After 30 cycles, the capacities of the NiO and the NiO-PPy composite were about 119 and 436 mAh g⁻¹, respectively, indicating that the electrochemical performance of the composite was significantly improved.

Graphene-metal-oxide composites as anode materials for Li-ion batteries have been investigated extensively, but these attempts have been mostly limited to moderate rate charge-discharge applications. Here, NiO-graphene nanostructures have been synthesized using a controlled hydrothermal method, which enables in situ formation of NiO with a coralloid nanostructure on graphene. Graphene/NiO (20%), graphene/NiO (50%), and pure NiO show stable discharge capacities of 185 mAh g⁻¹ at 20 C (1 C = 300 mA g⁻¹), 450 mAh g⁻¹ at 1 C, and 400 mAh g⁻¹ at 1 C, respectively. High rate capability and good stability in prolonged charge-discharge cycling permit the application of this material in fast charging batteries for upcoming electric vehicles. To the best of our knowledge, such fast rate performance of graphene/metal oxide composite as anode and such stability for pure NiO as anode have not been reported previously.

To improve the rate capability and cyclability of LiV₃O₈ cathode for Li-ion batteries, LiV₃O₈ was modified by forming LiV₃O₈/carbon nanosheet composite. LiV₃O₈/carbon nanosheet composite was successfully achieved *via* a hydrothermal route followed by a carbon coating process. The morphology and structural properties of the samples were

investigated by X-ray diffraction (XRD), TGA, SEM, and transmission electron microscopy (TEM). TEM observations demonstrated that the LiV_3O_8 /carbon composite has a very flat sheet-like morphology, with each nanosheet having a smooth surface and a typical length of 400-700 nm, width of 200-350 nm, and thickness of 10-50 nm. Each sheet is surrounded by a thick layer of amorphous carbon. Electrochemical tests showed that the LiV_3O_8 /carbon composite cathode features long-term cycling stability (194 mAh g^{-1} at 0.2 C after 100 cycles) and excellent rate capability (110 mAh g^{-1} at 5 C, 104 mAh g^{-1} at 10 C, and 82 mAh g^{-1} at 20 C after 250 cycles). Electrochemical impedance spectra (EIS) indicated that the LiV_3O_8 /carbon composite electrode has very low charge-transfer resistance compared with pristine LiV_3O_8 , indicating the enhanced ionic conductivity of the LiV_3O_8 /carbon composite. The enhanced cycling stability is attributed to the fact that the LiV_3O_8 /carbon composite can prevent the aggregation of active materials, accommodate the large volume variation, and maintain good electronic contact.

To reduce the reaction time, electrical energy consumption, and cost, binary α -NiS- β -NiS has been synthesized by a rapid, one-pot, hydrothermal autoclave microwave method within 15 minutes at temperatures of 160-180 °C. The microstructure and morphology of the α -NiS- β -NiS products were characterized by means of XRD, FESEM, and TEM. At 140 °C, pure hexagonal NiAs-type α -NiS phase was identified from the XRD patterns. With increasing reaction temperature (160-180 °C), the XRD evidence indicates that an increasing fraction of rhombohedral millerite-like β -NiS is formed as a secondary phase. The α -NiS- β -NiS sample synthesized at 160 °C yielded good electrochemical performance in terms of high reversible capacity (320 mAh g^{-1} at 0.1 C up to 100 cycles). Even at high rates, the sample operated at a good fraction of its

capacity. The most likely contributing factor to the superior electrochemical performance of the α -NiS- β -NiS sample could be the improved morphology. TEM imaging confirmed that needle-like protrusions connect the clusters of α -NiS particles, and the individual protrusions indicated a very high surface area including folded sheet morphology, which helps to dissipate the surface accumulation of Li^+ ions and facilitate rapid mobility. These factors help to enhance the amount of lithium intercalated within the material.

Microporous PVDF/PMMA membranes were prepared using the phase-separation method. Then, the membranes were immersed in liquid electrolyte to form polymer electrolytes. The effects of PMMA on the morphology, degree of crystallinity, porosity, and electrolyte uptake of the PVDF membrane were studied. The addition of PMMA increased the pore size, porosity, and electrolyte uptake of the PVDF membrane, which, in turn, increased the ionic conductivity of the polymer electrolyte. The maximum ionic conductivity at room temperature was $1.21 \times 10^{-3} \text{ S cm}^{-1}$ for Sample E70. The polymer electrolyte was investigated, along with lithium iron phosphate (LiFePO_4) as cathode for all solid-state lithium-ion rechargeable batteries. The lithium metal/E70/ LiFePO_4 cell yielded a stable discharge capacity of 133 mAh g^{-1} after up to 50 cycles at a current density of 8.5 mA g^{-1} .