Electrode Materials for Lithium-ion Batteries and Supercapacitors

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Anjon Kumar Mondal certify that the work presented in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Anjon Kumar Mondal

Sydney, Australia

May, 2015

DEDICATION

This thesis is dedicated to my family. Thank you for all of your love and support.

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RESEARCH PUBLICATIONS

1 **A. K. Mondal,** D. Su, S. Chen, A. Ung, H. S. Kim, G. X. Wang, Mesoporous $MnCo_2O_4$ with a flake-like structure as advanced electrode materials for lithium ion batteries and supercapacitors, ***Chemistry–A European Journal***, 2015, 21, 1526-1532. **IF: 5.696**

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3 **A. K. Mondal,** D. Su, S. Chen, X. Xie, G. X. Wang, Highly porous $NiCo_2O_4$ nanoflakes and nanobelts as anode materials for lithium ion batteries with excellent rate capability, ***ACS Applied Materials & Interfaces,*** 2014, 6, 14827-14835. **IF: 5.9**

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9 **A. K. Mondal,** D. Su, Y. Wang, S. Chen, G. X. Wang, Hydrothermal synthesis of nickel oxide nanosheets for lithium-ion batteries and supercapacitors with excellent performance, ***Chemistry - An Asian Journal,*** 2013, 8, 2828-2832. **IF: 3.935**

10 **A. K. Mondal,** B. Wang, D. Su, Y. Wang, X. Zhang, G. X. Wang, Preparation and enhanced electrochemical performance of MnO_2 nanosheets for supercapacitors, ***Journal of the Chinese Chemical Society,*** 2012, 59, 1275-1279. **IF: 0.856**

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

With the increasing demand for energy and growing concern about environmental pollution caused by the enormous consumption of fossil fuels, it is an urgent need of renewable energy and clean energy sources. Development of suitable mobile electronics or energy storage technologies that can be used in electric vehicles would help to address problem. As energy storage devices, lithium-ion batteries have attracted attention due to their high energy density and storage capacity. Supercapacitors have attracted enormous attention due to high power density and long cycle life. The exploration of new electrode materials for lithium-ion batteries and supercapacitors is the focus of research to satisfy the ever-rising demands for better performance including longer cycle life and improved safety. Nanostructured materials exhibit excellent electrochemical performances, and they are regarded as promising materials for high-performance lithium-ion batteries and supercapacitors. In this doctoral study, various nanostructured materials such as, nanosheets, nanospheres, nanobelts, nanoflakes, hybrid nanostructures and mesoporous structures have been successfully synthesized and characterised, using different methods. Their electrochemical properties have also been evaluated by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectra.

Nickel oxide (NiO) nanosheets have been synthesized, using a simple ethylene glycol mediated hydrothermal method. When evaluated as anode materials for lithium ion batteries, NiO nanosheets exhibited high reversible capacities of 1193 mA h g^{-1} at the current density of 500 mA g^{-1} with enhanced rate capability and good cycling stability. While as electrode materials for supercapacitors, NiO nanosheets also demonstrated a

superior specific capacitance of 999 F g^{-1} at the current density of 20 A g^{-1} with excellent cycling performance.

The spherical β-$Ni(OH)_2$ superstructures was successfully synthesised in a single-step microwave-assisted process, without using any templates. Due to its unique morphology, the prepared β-$Ni(OH)_2$ electrode displayed a high and specific capacitance of 2147 F g^{-1} at a discharge current of 1 A g^{-1} with excellent cycling stability (99.5 % capacitance retained after 2000 cycles).

A straight forward microwave reaction was employed to successfully prepare α-Fe_2O_3 nanoparticles with two different sizes. When used as anode materials for lithium ion batteries of both the materials showed good electrochemical performances. Remarkably, the electrode made of larger particles (200-300 nm) exhibited higher reversible capacity of 1012 mA h g^{-1} with better rate capability and excellent cycling stability (88 % retention after 80 cycles) than those of the smaller particles (20-30 nm) (49 % retention after 80 cycles). The better lithium storage properties of the large particles can be attributed to their structural integrity during cycling, which offers adequate spaces to accommodate volume expansion during Li^+ insertion/extraction and shortens the diffusion paths of lithium ions.

Highly porous $NiCo_2O_4$ nanoflakes and nanobelts were prepared in two steps; the $NiCo_2O_4$ intermediates were first formed by a hydrothermal method and the intermediates were simply thermal treated to the final product. Owing to their unique porous structural features, the $NiCo_2O_4$ nanoflakes and nanobelts exhibited high specific capacities of 1033 mA h g^{-1} and 1056 mA h g^{-1}, respectively, good cycling stability and rate capability. These exceptional electrochemical performances could be attributed to the unique structure of high surface area and void spaces within the surface of

nanoflakes and nanobelts, which provides large contact areas between electrolyte and active materials for electrolyte diffusion and cushions the volume change during charge-discharge cycling.

Graphene/MnO_2 hybrid nanosheets were prepared by the incorporating graphene and MnO_2 nanosheets in ethylene glycol. As electrode materials for supercapacitors, graphene/MnO_2 hybrid nanosheets of different ratios were investigated. The graphene/MnO_2 hybrid nanosheets with a weight ratio of 1:4 (graphene: MnO_2) delivered the highest specific capacitance of 320 F g^{-1}, and exhibited good capacitance retention on 2000 cycles.

Mesoporous $NiCo_2O_4$ nanosheets were synthesized by microwave method and applied as electrode materials for lithium ion batteries and supercapacitors. Due to its porous nanosheet structure, the $NiCo_2O_4$ electrodes exhibited a high reversible capacity of 891 mA h g^{-1} at the current density of 100 mA g^{-1} with good rate capability and stable cycling performance. When used as electrode materials for supercapacitors, $NiCo_2O_4$ nanosheets demonstrated a specific capacitance of 400 F g^{-1} at the current density of 20 A g^{-1} and superior cycling stability over 5000 cycles. The excellent electrochemical performance could be ascribed to the thin porous nanosheet structure, which provided high specific surface area to increase electrode-electrolyte contact area and facilitate rapid ion transport.

Mesoporous flake-like Manganese-cobalt composite oxide ($MnCo_2O_4$) was successfully synthesized, using the hydrothermal method. The flake-like $MnCo_2O_4$ was evaluated as anode materials for lithium ion batteries. It exhibited superior rate capability and good cycling stability with a high reversible capacity of 1066 mA h g^{-1}. As electrode materials for supercapacitors, $MnCo_2O_4$ also demonstrated a high super capacitance of

1487 F g^{-1} at the current density of 1 A g^{-1} and superior cycling stability over 2000 charge-discharge cycles.