FACULTY OF SCIENCE

Development of Novel Electrode Materials for Li-ion Batteries and Na-ion Batteries

This thesis is presented in fulfilment of the requirements for the degree of

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By Dawei Su B. Eng., M. Eng.

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it 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.

Dawei Su

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ABSTRACT

Li-ion batteries have dominated the global market for electronic devices, and are considered to be the most promising power system for electric vehicles (EVs), and hybrid electric vehicles (HEVs). However current Li-ion battery systems are still far from reaching the demands of the high energy density on EVs and HEVs due to limitations on the capacity of the electrodes. Moreover, they cannot match the high charge/discharge current requirements of the next generation of batteries. This doctoral work aims to address these problems by designing nanotechnology and nanomaterials with high power performance. Herein, a series of nanostructured materials with designed morphology: polyhedral nanoparticals, nanowires, 2-dimention nanoplate and mesoporous structure have been developed. By using theoretical calculations, X-ray diffraction, and *Ex-situ* SEM, TEM observation techniques, the relationship between the electrode crystal structure and electrochemical performance was established.

In addition, to overcome the controversial debates regarding the size of reserves and higher cost of obtaining Li, the counterpart to Li-ion batteries, Na-ion batteries, have been researched in this work due to the low cost, abundant supply and widespread terrestrial reserves of sodium mineral salts. However, the analogue intercalation compounds for Li-ion batteries are not appliable for Na-ion batteries due to the higher ionization potential and larger ionic diameter of the Na ((1.02 Å *vs*. Li (0.76 Å)). Consequently, suitable electrode materials for Na-ion batteries were also developed and optimised in this study. Appropriate active materials having sufficiently large interstitial space within their crystallographic structure to host Na ions and achieve a satisfactory electrochemical performance were created.

Following are the corresponding brief introductions to each research task:

The crystal structure and electronic structure of Li_2FeSiO_4 and its delithiated products, $LiFeSiO_4$ and $FeSiO_4$, were systematically investigated through the ab initio calculation based on a monoclinic supercell with the $P2_1$ symmetry. The expansion of the unit cell volume during the lithium extraction process, and the two-step voltage profiles of Li_2FeSiO_4 corresponding to the $Fe^{+2/+3}$ and $Fe^{+3/+4}$ redox couples, respectively, have been studied. Furthermore, the diffusion mechanism of Li ions in Li_2FeSiO_4 and its delithiated product $LiFeSiO_4$ was established base on the energy barriers calculation: the lithium will diffuse along the [101] direction and Li ion layer in the ac plane.

Tuneable porous α-Fe_2O_3 materials were prepared using a novel selective etching method. It was found that the pore size and pore volume can be controlled by adjusting the etching time during the synthesis process. When the porous hematite was applied for lithium storage in lithium ion cells, it demonstrated a reversible lithium storage capacity of 1269 mA h g^{-1}.

Atomistic simulation and calculations on surface attachment energy predicted the polyhedral structure of magnetite nanocrystals with multiple facets. Through a low temperature hydrothermal method, polyhedral magnetite nanocrystals with multiple facets were successfully synthesised and identified by the X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and high resolution transmission electron microscopy (HRTEM). When applied as an anode material in lithium ion cells, magnetite nanocrystals demonstrated outstanding electrochemical performance with a high lithium storage capacity, satisfactory cyclability, and excellent high rate capacity.

One-dimensional single crystal magnetite nanowires were synthesized by the low temperature hydrothermal method. XRD and transmission electron microscopy (TEM) confirmed the cubic structure of Fe_3O_4 nanowires with a space group of $Fd\bar{3}m$. Electrochemical measurement showed as-prepared Fe_3O_4 nanowires exhibited an excellent reversible lithium storage capacity and a satisfactory cycling performance.

Mesoporous nickel oxide nanowires were synthesized by a hydrothermal reaction with subsequent annealing at 400 ºC. When applied as the anode material in Li-ion batteries, nickel oxide nanowires demonstrated an outstanding electrochemical performance with a high lithium storage capacity, adequate cyclability, and outstanding rate capacity. In addition, it also exhibited a high specific capacitance of 348 F g^{-1} as electrodes in supercapacitors.

Mesoporous NiO crystals with dominantly exposed {110} reactive facets was prepared by thermal conversion of hexagonal $Ni(OH)_2$ nanoplatelets. When applied as anode materials in Li-ion batteries, mesoporous NiO crystals exhibited a high reversible lithium storage capacity of 700 mA h g^{-1} at 1 C rate in 100 cycles and excellent cyclability. In particular, the dominantly exposed {110} reactive facets and mesoporous nanostructure of NiO crystals lead to ultrafast lithium storage, which mimics the high power delivery of supercapacitors.

Two types of MnO_2 polymorphs, α-MnO_2, β-MnO_2 nanorods, have been synthesized as cathode materials for Na-ion batteries. Although both can achieve high initial sodium ion storage capacities (278 mA h g^{-1} and 298 mA h g^{-1}, respectively), β-MnO_2 nanorods exhibited a better rate capability and cyclability than that of α-MnO_2 nanorods attributable to its more compact tunnel structure and the one-dimensional architecture of nanorods which could facilitate sodium ion diffusion in the charge and discharge process.

Through an *In-situ* synthesis approach, SnO_2@Graphene nanocomposite was synthesized. FESEM and TEM revealed the homogeneous distribution of octahedral SnO_2 nanoparticles (60 nm in size) on a graphene matrix. When used as an anode for Na-ion batteries the SnO_2@Graphene nanocomposite exhibited a high reversible sodium storage capacity of above 700 mA h g^{-1} and an excellent cyclability. After 100 cycles, the capacity still maintained at 628 mA h g^{-1} at 20 mA g^{-1}due to the 3D architecture of the SnO_2@Graphene nanocomposite.