Development of Electrode Materials for Lithium-ion Batteries and Sodium-ion Batteries

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By

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Xiuqiang Xie, 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.

Xiuqiang Xie

Sydney, Australia

October, 2016

DEDICATION

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

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Xiuqiang Xie

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ABSTRACT

Electrode materials are vital to the performance of lithium-ion batteries and sodium-ion batteries. A rational design of electrode materials depends critically on understanding of their electrochemical processes, which is highly desirable for the development of high performance electroactive materials towards different applications. The composition, morphology, structure and preparation method can affect the electrochemical performance. In this doctoral work, a series of electrode materials were designed and fabricated and their electrochemical properties for lithium-ion batteries and sodium-ion batteries were investigated.

Single crystalline spinel $LiMn_2O_4$ nanorods were prepared as stable cathode materials for lithium-ion batteries. The preparation involves infiltration of LiOH into porous Mn_3O_4 nanorods by a vacuum-assisted impregnation route, which facilitates the homogeneous reaction to prepare $LiMn_2O_4$. The reaction parameters were optimized and Li-rich single crystalline $LiMn_2O_4$ nanorods were prepared, which retained 95.6 % of its initial capacity after 1000 cycles at 3C rate as cathode material for lithium-ion batteries.

Considering the concerns of the increasing cost of lithium salts, the development of low-cost sodium-ion batteries is becoming a hot topic. In this doctoral work, a series of anode materials were explored for sodium-ion storage. The electrochemical performances of SnO_2/nitrogen-doped graphene and SnO_2/graphene were compared to investigate the effects of nitrogen-doping into graphene on enhancing the electrochemical performance for sodium-ion batteries. In contrast to the previous reports which often ascribe the enhanced electro-activity of nitrogen-doped graphene based composites to two nitrogen-doping effects (improving the electron transfer efficiency and increasing electro-active sites within the graphene network)

in one single declaration, it was demonstrated that the improved electron transfer efficiency of SnO_2/nitrogen-doped graphene due to nitrogen-doping plays a more important role than the increased electro-active sites within graphene network in enhancing the electro-activity of SnO_2/nitrogen-doped graphene nanohybrids compared to the SnO_2/graphene counterpart.

MoS_2/reduced graphene oxide (RGO) nanocomposites with intimate two-dimensional heterointerfaces were prepared by a facile one-pot hydrothermal method. The synergistic effect between MoS_2 and graphene contributing to the enhanced reversible capacity of MoS_2/RGO nanocomposites was investigated by experimental and computational studies. It was revealed that Na prefers to be adsorbed on MoS_2 in the MoS_2/RGO heterostructure rather than intercalate into the MoS_2/RGO heterointerface. Interestingly, the MoS_2/RGO heterointerfaces can significantly increase the electronic conductivity of MoS_2, and store more Na ions, while maintaining the high diffusion mobility of Na atoms on MoS_2 surface and high electron transfer efficiency from Na to MoS_2.

SnS_2 nanoplatelet@graphene nanocomposites were prepared by using a morphology-controlled hydrothermal method. The as-prepared materials achieved a high reversible specific sodium-ion storage capacity of 725 $mA\,h\,g^{-1}$, stable cyclability, and an enhanced high-rate capability as anode materials for sodium-ion batteries.

Three dimensional interconnected SnO_2/graphene aerogels with a hierarchically porous structure were constructed by a facile *in situ* process. Such a functional architecture not only facilitates the electrode–electrolyte interaction but also provides an efficient electron pathway within the graphene networks. The as-prepared SnO_2/graphene aerogels exhibited an initial reversible capacity of 451 $mA\,h\,g^{-1}$ with a stable cycling performance at a current

density of 20 mA g^{-1}. Even at a high current density of 1000 mA g^{-1}, the electrode achieved a capacity of 168 mA h g^{-1} after 500 cycles.

A series of freestanding electrodes with distinct architectures and promising electrochemical performance for sodium-ion storage were prepared, including:

1) Three dimensional freestanding electrodes consisting of Sn@CNT nanopillar arrays grown on carbon paper, which achieved a reversible capacity of 887 μA h cm^{-2} in the first cycle and good cyclability extending to 100 cycles.

2) Vertically aligned MoS$_2$ nanosheets/carbon paper electrodes as highly reversible anode materials. Coating with carboxy methyl cellulose sodium salt improved the cycling performance and a high reversible capacity of 286 mA h g^{-1} was achieved after 100 cycles at a current density of 80 mA g^{-1}. The as-prepared electrodes delivered a high initial Coulombic efficiency of 79.5% and promising rate capability. Even at a high current density of 1000 mA g^{-1}, a reversible capacity of 205 mA h g^{-1} was maintained.

3) Heterostructured Ti$_3$C$_2$ MXene/CNTs porous films with high volumetric capacity for sodium-ion storage. The open structure facilitates electrolyte transport and access of ions to the electrode and produces functional MXene-based electrodes for sodium-ion storage. When applied as freestanding electrodes for sodium-ion storage, the built-to-order Ti$_3$C$_2$ MXene/CNTs porous films showed a volumetric capacity of 421 mA h cm^{-3} at 20 mA g^{-1}, good rate performances, and excellent cycling stability.