

Development of Functional Nanomaterials for Next Generation Rechargeable Batteries

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By

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CERTIFICATE OF ORIGINAL AUTHORSHIP

This research is supported by an Australian Government Research Training Program Scholarship.

I 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.

February, 2019

DEDICATION

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

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ABSTRACT

This PhD project was focused on the development of functional nanomaterials for the next-generation batteries, particularly for lithium-oxygen batteries and sodium-ion batteries. Electrode materials, comprising the composition, morphology and structure, are crucial to the electrochemical performance of batteries. A rational design of electrode materials based on the understanding of their electrochemistry is highly desirable for high performance cells. In this doctoral work, several different electrode materials were designed and synthesized and their electrochemical properties for the certain kind of batteries were investigated.

A ruthenium-decorated hierarchically ordered macro-mesoporous carbon (MmC@Ru) via a mixed hard and soft template method. The as-prepared MmC@Ru exhibits an ordered macroporous carbon skeleton with well-distributed mesopores, which are uniformly decorated by Ru nanoparticles. Cathodes made of MmC@Ru can provide enough room to accommodate the discharge products, facilitate the oxygen and electrolyte diffusion and then reduce the charge and discharge overpotential. The advantages of the hierarchical porous structure were demonstrated by the enhanced performance compared with the Ru decorated macroporous carbon (MC@Ru) electrode.

Considering the high cost of noble metal catalyst (Ru), an atomic-thin porous NiCo₂O₄ nanosheets material with high catalytic activities toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) was prepared as cathode catalyst for Li-O₂ batteries. With the help of the selected ether-based electrolytes and unique porous 2D architecture and high catalytic activities of the cathode catalysts, the NiCo₂O₄ cathodes deliver a high discharge capacity of 16,400 mAh g⁻¹ at 200 mA g⁻¹ and an excellent cycling performance

up to 150 cycles with a restricted capacity of 1000 mAh g⁻¹. The performance overwhelmed the one in the DMSO-based electrolyte.

Although lithium-oxygen battery has the highest theoretical capacity among the rechargeable batteries, it still stays in its infancy and far away from the practical application. In addition, the increasing concerns of the rising cost of lithium shift researcher's attention to sodium batteries, which are more promising for the commercialization. Here, we developed a facile solution-phase method to fabricate the Sb₂O₃/MXene(Ti₃C₂T_x) hybrid materials for sodium storage with enhanced electrochemical performances. The as-prepared Sb₂O₃/Ti₃C₂T_x composite has a hierarchical structure with Sb₂O₃ nanoparticles (sub-50 nm) uniformly incorporated in the MXene Ti₃C₂T_x 3D networks. The Sb₂O₃ nanoparticles serve as a sufficient sodium ion reservoir; meanwhile, the MXene Ti₃C₂T_x network provides highly efficient pathways for transport of electrons and Na-ions. The volume expansion of Sb₂O₃ during sodiation/desodiation can be buffered and confined between the 2D Ti₃C₂T_x sheets. As a result, the Sb₂O₃/ Ti₃C₂T_x hybrid anodes present good structural stability and superior electrochemical performance based on the conversion and alloying reaction.

Another insertion-type material, MXene Ti₃C₂T_x encapsulated titanium oxide spheres (TiO₂@Ti₃C₂T_x), were fabricated for the first time by a self-assemble strategy for sodium-ion batteries. The MXene layers significantly improve the electronic conductivity of the whole electrode and protect the structural integrity of the TiO₂ spheres from electrochemical pulverization, which hence contributes to the formation of a stable solid-electrolyte interface. Meanwhile, the pseudocapacitance of the as-fabricated TiO₂@Ti₃C₂T_x composites enables high-rate capability and long cycle life in sodium-ion batteries. As a result, the hybrid electrode delivers a high reversible capacity of 116 mAh

g^{-1} at 960 mA g^{-1} up to 5000 cycles. By coupling with a NaCrO_2 cathode, a prototype Na-ion full cell achieved a capacity of 103.4 mAh g^{-1} at 960 mA g^{-1} and an excellent cycling performance with 73.5% capacity retention after 1,000 cycles.