Novel Nanomaterials for Lithium-ion Batteries and Lithium-sulfur Batteries

A thesis presented for the award of the degree of

Doctor of Philosophy

from

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By

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September, 2017

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Jing Xu, 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.

Jing Xu

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DEDICATION

This thesis is dedicated to my parents. Especially thanks for their deep love and selfless dedication.

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ABSTRACT

Advanced energy storage is an intrinsic driving force for modern life. There is a large spectrum of storage technologies with wide variations in terms of energy and power density, service life, efficiency, cost, etc. Batteries have achieved great triumphs in this landscape, as they can be utilized conveniently at low cost. The properties of electrode materials are of great significance for the electrochemical performances of batteries. In this doctoral work, a series of electrode materials were designed and fabricated and their electrochemical properties for lithium-ion batteries and lithium-sulfur batteries were investigated.

Novel porous $NiCo_2O_4$ nanoparticles are synthesized by a solvothermal method using poly (vinylpyrolidone) (PVP) as the structure-directing agent followed by a simple thermal annealing treatment. Through the XRD, FESEM, TEM, and N_2 sorption analyses, it has been found that the as-prepared $NiCo_2O_4$ nanoparticles show hierarchical rose flower-like architecture constituted by 2D hierarchically porous nanosheets. The 2D porous nanosheets provide sufficient void space generated during thermal annealing treatment, benefiting electrolyte penetration and fast electron transfer. The porous structure also can tolerate the volume variation upon prolonged charge/discharge cycling. Therefore, when the as-prepared $NiCo_2O_4$ nanoparticles are used as anode materials for the Li-ion batteries, they exhibit high capacity, remarkable capacity retention at increased current densities, and outstanding cycling stability.

Lithium-sulfur batteries have attracted extensive attentions because of their high theoretical capacity and high energy density compared with lithium-ion batteries. Highly ordered mesoporous nitrogen doped yolk-shell carbon spheres were synthesized via a facile sol-gel method, this sulfur host possesses large pore volume and interconnected mesopore structure, which can effectively prevent polysulfide diffusion and stabilize the dissolved polysulfides. The inner mesoporous “yolk” acts as a sulfur reservoir to entrap polysulfide species; Meanwhile, the outer “shell” serves as a physical barrier to confine the dissolution of polysulfides and also enhances the cycling stability of the cathode. When applied as cathode material for lithium-sulfur (Li-S) batteries, these mesoporous nitrogen doped yolk-shell carbon spheres exhibit a high specific capacity of 1329 mAh g^{-1} at 0.2C and an extended cycle life, demonstrating a promising cathode host material for lithium-sulfur batteries.

3D nitrogen–sulfur co-doped porous graphene matrix was synthesized via chemical activation of polypyrrole (PPy) functionalized graphene sheets using K_2CO_3. The dopant N and S atoms act as electron attracting atoms, leading to the nearby C atoms and causing oxygen functional groups to be polarized and more active for anchoring sulfur and polysulfides. Meanwhile, highly developed defects and edges, as well as porous structure derived from graphene chemical activation, not only achieve a high sulfur loading in a well dispersed amorphous state, but also serve as polysulfide

reservoirs to alleviate the shuttle effect. When applied as cathode hosts for lithium-sulfur batteries, the nitrogen-sulfur co-doped porous graphene architecture exhibited a high specific capacity of 1178 mAh g^{-1} at 0.2C, 1103 mAh g^{-1} at 0.5C, 984 mAh g^{-1} at 1C rate, and excellent cycling stability for 600 cycles with a retained capacity of 780 mAh g^{-1} (0.2C).

Nitrogen-doped hollow Co_3O_4 nanoparticles coated with reduced graphene oxide (rGO) were synthesized by a facile solid-state pyrolysis process that using metal organic framework (ZIF-67) as precursor. The obtained rGO/N-C-Co_3O_4 architecture offer different types of polar interactions to suppress polysulfide shuttle effect. The open metal centre in the obtained rGO/N-C-Co_3O_4 architecture serving as the Lewis acid sites show high affinity to the polysulfide, the doped nitrogen introduces more defects, active sites and can additionally immobilize lithium polysulfide within the cathode. Moreover, the well-defined porous structure and the rGO simultaneously contribute to the electron transfer and remarkably buffer the volume expansion/contraction of active materials upon cycling. Owing to these synergistic interactions between rGO/N-C-Co_3O_4 and sulfur species, the rGO/N-C-Co_3O_4@S composite generated a high reversible capacity (1205 mAh g^{-1} at 0.2C) and excellent stability (865 mAh g^{-1} at 1C after 300 cycles). Ex situ Raman, Ex situ X-ray Photoelectron Spectroscopy, UV-vis absorption spectra and first-principle calculations further confirmed that rGO/N-C-Co_3O_4 nanoparticles can effectively bind polysulfides in the electrode over cycles and exhibit high binding energies.

A binder-free cathode was developed by chemisorption of Co_3O_4 to activated carbon cloth (CC), which was used as a 3D current collector to accommodate a large amount of sulfur, multiwall carbon nanofiber (MWCNF) and carbon black (CB) hybrids within the conductive scaffold, enabling the fabrication of ultrahigh sulfur loaded electrodes. The interconnected carbon fibers established a long-range conductive matrix for an efficient electron transport, the multiple conductive pathways guarantee high sulfur utilization. More importantly, the polar Co_3O_4 could also effectively entrapped the intermediated polysulfides preventing their free diffusion to the lithium anode, guaranteeing good cycling stability. Consequently, the Co_3O_4-CC-S electrodes exhibit excellent electrochemical performance with sulfur loading of 4.3 mg cm^{-2}.