

学 位 論 文 の 要 旨

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学位論文題目	Development of transition metal sulfide composites as the anode materials for sodium-ion batteries（ナトリウムイオン電池用遷移金属複合硫化物アノード材料の創製）		
<p>学位論文要旨</p> <p>Sodium-ion batteries (SIBs) have similar energy storage mechanisms as lithium-ion batteries (LIBs), and possess the advantages of high abundance, wide distribution, and low cost of sodium resources, it has become the most promising alternative to LIBs. However, given the larger ionic radius of Na-ion (Na^+, 1.02 Å) compared to that of Li-ion (Li^+, 0.76 Å). The electrode materials of SIBs face larger volume expansion and more sluggish reaction kinetics than those of LIBs in the charge/discharge operation, thereby hindering the stability of SIBs. Transition metal sulfides (TMSs) possess considerable theoretical capacities as the material of anode in SIBs, but their application is limited by their large volume expansion, sluggish charge transfer kinetics, and poor cycling performance. Although, many strategies have been put forward to solve those issues, including carbon modification, nanostructure design, construction of heterostructures and electrolyte optimization, etc., it is still full of challenges to design TMSs-based anodes with superior reversibility capacity and excellent cycling stability for SIBs. In this dissertation, TMSs with carbon framework and/or heterostructure are designed as the anode materials for SIBs, which exhibit excellent electrochemical performances.</p> <p>Firstly, different from the traditional co-precipitation method to prepare the Prussian blue analog (PBA), the PBA with a tremella-like micro-flower structure is firstly synthesized by the hydrothermal method under the synergistic effect of trisodium citrate dihydrate (TSC, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) and $\text{K}_3[\text{Co}(\text{CN})_6]$, and two kinds of cobalt sulfide nanoparticles embedded in N/S co-doped carbon frameworks (namely, $\text{Co}_3\text{S}_4@\text{C-N/S}$ and $\text{Co}_9\text{S}_8@\text{C-N/S}$) are successfully synthesized by a subsequent solid sulfidation process. Herein, N/S co-doped carbon frameworks improve the electronic conductivity and provide more active sites for sodium storage. As the material for the anode in SIBs, the $\text{Co}_3\text{S}_4@\text{C-N/S}$-based anode exhibits excellent initial charge/discharge specific capacities of 685.3/745.2 mA h g^{-1} with a high initial Coulombic efficiency of 91.97% at 0.1 A g^{-1} and a superior cycling performance (599.1 mA h g^{-1} in the 600th cycle at 1 A g^{-1} with a capacity retention of 89.4%). While the $\text{Co}_9\text{S}_8@\text{C-N/S}$-based anode also delivers considerable initial Coulombic efficiency (86.1% at 0.1 A g^{-1}) with high cycling stability (391.9 mA h g^{-1} even in the 1200th cycle at 2 A g^{-1} with a capacity retention of 78.1%). It provides a material synthesis route for high-performance anode materials used in SIBs and other alkali metal ion batteries.</p> <p>Secondly, micro-flower-like MoS_2-modified Co_9S_8 ($\text{Co}_9\text{S}_8/\text{MoS}_2$) with a three-dimensional (3D)</p>			

heterostructure is first obtained via a simple solvothermal synthesis followed by a solid sulfidation treatment process. As a material for the anode of SIBs, the $\text{Co}_9\text{S}_8/\text{MoS}_2$ -based electrode with an initial Co/Mo molar ratio of 1/1 (denoted as CM55-S) exhibits the best sodium storage performance with a boosted capacity, superior reversibility (424.5 mAh g^{-1} @2 A g^{-1} at the 1600th cycle, 401.1 mAh g^{-1} @5 A g^{-1} at the 800th cycle), and an excellent rate capacity (210.1 mAh g^{-1} @20 A g^{-1}). Density functional theory (DFT) calculations confirm that the $\text{Co}_9\text{S}_8/\text{MoS}_2$ heterostructure has a lower energy barrier (0.30 eV) than the pure Co_9S_8 (0.53 eV). It is expected that such a heterostructured material could be an attractive candidate as the material of the anode for SIBs.

Finally, cobalt sulfide/molybdenum disulfide with heterostructure is fabricated as the anode for SIBs, which can be constructed by combining a one-pot hydrothermal route with a solid-state sulfidation step. Compared with the anodes based on pure cobalt sulfide and pure molybdenum disulfide materials, the cobalt sulfide/molybdenum disulfide-based one displays superior cycling stability (e.g., 510.9 mAh g^{-1} @1 A g^{-1} at the 1000th cycle), and an extraordinary rate performance (341 mAh g^{-1} @10 A g^{-1}). The material characterizations show that the obtained cobalt sulfide/molybdenum disulfide material with abundance of mesopores. The kinetics analysis further confirms the decreasing of charge transfer resistance and the increasing of Na^+ diffusion coefficient with cycling for this material. As a result, the reasonable design of cobalt sulfide/molybdenum disulfide heterostructure can provide abundant active sites for the storage of Na^+ ions and facilitate surface capacity-controlled behavior. It offers useful insights into the utilization of those heterostructured materials for SIBs.