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「課程博士用」

学 位 論 文 の 要 旨

専　　攻	安全システム工学　専攻	ふりがな 氏　　名	がく　しがん 岳　　喜岩
学位論文題目	MoS_2-based anode for sodium ion batteries （ナトリウムイオン電池用の MoS_2 ベースアノード材料の開発）		

学位論文要旨

Sodium ion batteries (SIBs), as a promising candidate for lithium ion batteries (LIBs), have attracted researchers' great attention because of the abundant resources and low cost. Looking for suitable anode materials is very essential for developing SIBs. Layered metal sulfides (MS_2) are considered as one of potential anode materials for SIBs due to their structural stability and high theoretical capacity. However, low conductivity, large volume expansion, and slow electrochemical kinetics cause in poor cycling stability and bad rate performance, which severely limit its application as an anode material for SIBs. Recently, numerous efficient strategies such as nanostructure designing, electrolyte selecting, voltage range cutting off and combination of MS_2 with carbon materials have been applied to enhance the electrochemical performance of such anode materials for SIBs. The purposes are to effectively provide more actives sites for Na^+ storage, shorten Na^+ diffusion path, enhance the conductivity, and buff the volume expansion. Unfortunately, most of strategies are too complex to limit their applications in the preparation of anode materials. Therefore, it is still full of challenges to find facile method to prepare anode materials with excellent electrochemical performance for SIBs. In this dissertation, simpler strategies for enhancing the electrochemical performances of MoS_2-based anode have been developed.

Firstly, to improve the conductivity and cycling stability, coral reef-like MoS_2 microspheres (MoS_2-MS) with 1T/2H phase are synthesized by a simple one-step hydrothermal method. It is found that this material has disordered structure, rich defects and large interlayer spacing. As it is used as the anode material for sodium ion batteries (SIBs), a stable specific capacity of 467 mAh g^{-1} at a current density of 100 mA g^{-1} after 100 cycles is delivered. Moreover, after 500-cycle test at 1 A g^{-1}, a highly stable specific capacity is still maintained at 412 mAh g^{-1}. In addition, even at a high current density of 20 A g^{-1}, the MoS_2-MS electrode delivers a specific capacity of 100 mAh g^{-1}. It is considered that the 1T/2H phase MoS_2-MS with the disordered structure can effectively enhance the electrical conductivity for the rate performance improvement, and furthermore, the rich defects provide more active sites for Na^+ storage and the large interlayer spacing allows the rapid diffusion of the Na^+ ions.

Secondly, in order to further improve the electronic conductivity and sluggish electrochemical kinetics and specific capacity of MoS_2-based anode, vanadium is combined into the framework of MoS_2 to form $VMoS_2$ (VMS_2) through a facile one-step hydrothermal method. Combined the experiment results with the density functional theory calculations, it is found that V mediating not only significantly increases the electronic conductivity due to metallic property but also decreases the energy barrier (0.069 eV) of sodium ion transportation when compared with that of the pure MoS_2 (0.12 eV), resulting in excellent electrochemical performance with rapid electrochemical kinetics. Furthermore, the disordered structure with rich defects in the VMS_2 could provide more active sites for Na^+ storage. As a result, when it is used as the anode material of SIBs, a high specific capacity (548.1 mAh g^{-1} at a current density of 100 mA g^{-1}) with excellent cycling stability (451.6 mAh g^{-1} retaining after 800 cycles at 2 A g^{-1}) and superb rate performance (207.4 mAh g^{-1} retained at 20 A g^{-1}) is achieved.

Finally, even though vanadium mediating can effectively promote the sluggish electrochemical kinetics and electronic conductivity, the specific capacity is still low, which cannot meet the demand of society. In order to achieve higher specific capacity, a novel orderly layered $VMoS_2$ (OL-VMS) anode material is synthesized through a facile hydrothermal self-assembly method followed by a heating treatment process. As it is used as the anode material for the SIBs, the unique structure of OL-VMS not only facilitates the rapid migration of sodium ions between the stacked layers but also provides stable framework for the volume expansion during charging/discharging process. In addition, vanadium mediating in the framework causes more defects to produce more active sites for the sodium ion storage. As such, the OL-VMS based anode exhibits high reversible capacities of 602.9 mAh g^{-1} at 0.2 mA g^{-1} and 534 mAh g^{-1} even after 190 cycles at 2 A g^{-1}. Furthermore, the OL-VMS based anode delivers a high reversible capacity of 626.4 mAh g^{-1} after 100 cycles at 2 A g^{-1} in a voltage range of 0.01-3 V. In particular, even in the absence of conductive carbon, it still shows outstanding reversible capacity of 322.6 mAh g^{-1} at 1 A g^{-1} in a voltage range of 0.3-3 V, which should be benefit for the cost reduction and energy density increase.

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