Journal of Power Sources 373 (2018) 103–109

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Incorporation of Co into MoS_2/graphene nanocomposites: One effective way to enhance the cycling stability of Li/Na storage

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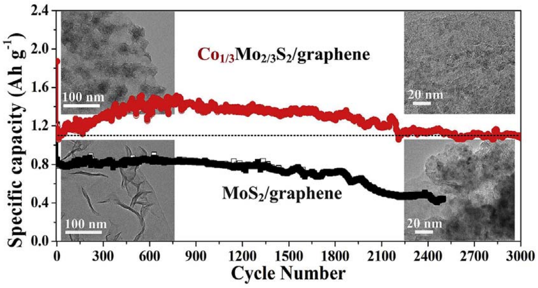
HIGHLIGHTS

- $Co_{1/3}Mo_{2/3}S_2$/graphene hierarchy structure is synthesized by a solvothermal method.
- Co can enhance the conductivity and suppress the aggragation of active materials.
- The cooperation of Co can greatly improve electrochemical reversibility of MoS_2.
- A capacity of 940 mAh g^{-1} can be maintained after 3200 cycle at 2 A g^{-1} in LIBs.
- The obtained samples also show a high capacity and cycle stability in SIBs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
MoS_2
Lithium ion batteries
Sodium ion batteries
Electrochemical reversibility
Long-term stability

ABSTRACT

Layered transition metal dichalcogenides are promising as lithium and/or sodium storage materials for lithium and sodium (Li/Na) ion batteries. However they always exhibit limited rate capability and long-term cycling stability, due to the fact that their 2D structures are easily restacking and agglomeration during cycling process and further result poor electrochemical reversibility. Herein, hierarchical $Co_{1/3}Mo_{2/3}S_2$/graphene nanocomposites without CoS_x and MoS_2 impurities have been synthesized *via* one-pot solvothermal process. The incorporation of Co into MoS_2 at atomic level can not only give rise to thinner and smaller nanosheets in the nanocomposites than MoS_2/graphene nanocomposites, but also significantly decrease the size of *in-situ* formed MoS_2/CoS_x nanoparticles during electrochemical conversion process, which can greatly promoting the ion diffusion and suppressing the aggregation of active materials. Furthermore, the conductivity of $Co_{1/3}Mo_{2/3}S_2$/graphene nanocomposites can be enhanced from 0.46 S m^{-1} (MoS_2/graphene) to 1.39 S m^{-1} *via* changing the semiconducting MoS_2 to metallic $Co_{1/3}Mo_{2/3}S_2$. The simultaneously optimized electron conductivity and ions diffusion dynamics of $Co_{1/3}Mo_{2/3}S_2$/graphene nanocomposites can effectively improve the reversibility of electrochemical conversion reactions. A capacity of 940 mAh g^{-1} and 529 mAh g^{-1} can be maintained at 3200th cycle (2 A g^{-1}) in lithium-ion batteries and 200th cycle (1 A g^{-1}) in sodium-ion batteries, respectively.

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http://dx.doi.org/10.1016/j.jpowsour.2017.10.094
Received 21 June 2017; Received in revised form 30 October 2017; Accepted 31 October 2017

1. Introduction

With increasing global energy consumption, LIBs and SIBs possessing high capacity, long cycle life and eco-friendliness have been regarded as promising and highly efficient energy storage devices in portable electronics and hybrid vehicles [1–3]. Massive efforts have been focused on seeking for novel anode materials with high performances. Recently, molybdenum disulfide (MoS_2) has been widely studied as electrode material in lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), because of its higher capacity and better cycling stability than other sulfides, in which the larger interlayer space with weak van der Waals interaction is favorable for the initial ion intercalation/de-intercalation, and the followed conversion chemistry without remarkable volume change [4,5]. However, the electron transfer between two adjacent S–Mo–S sheets is limited, leading to poor electrochemical reversibility. Thus, the suppressed regeneration of metal sulfides would lead to the formation of more polysulfides, and the shuttling effects of polysulfides would further result in significant capacity loss and poor rate capability [6].

To circumvent these obstacles, many efforts have been devoted to increase the conductivity of the whole electrode materials. Compositing with carbonaceous materials is the most effective way to enhance the cyclic performances of MoS_2 [5,7–9]. For example, MoS_2/mesoporous carbon composites carbonized from oleic acid-protected single-layer MoS_2 nanosheets with dopamine exhibited high reversible specific capacity of 1183 mAh g^{-1} at 0.2 A g^{-1}, excellent rate capability (943 mAh g^{-1} at 6.4 A g^{-1}), and long cycle life ($>$ 90% retention over 500 cycles) [10]. 3D porous composites prepared with MoS_2 nanoparticles, 1D CNTs and 2D graphene *via* electrostatic spray deposition showed enhanced electrochemical performances because of it multi-dimension effects [11]. Our previous work also revealed that the graphene-supported peony-like MoS_2 nanocomposites (MoS_2/graphene) exhibited long-term cyclic stability due to the enhanced conversion reversibility of lithium storage materials [12]. However, the specific capacity gradually decreased after 2000 cycles (Fig. S1), because of the restacking and agglomeration of MoS_2 nanoparticles during the long-term charging/discharging process (Fig. S2).

In comparison of binary compounds, ternary metal oxides have received considerable attention for their good cyclic stability due to the synergistic effects of multi-metals. For example, porous $MnFe_2O_4$ microrods as lithium storage materials exhibited high reversible capacity and outstanding cycling stability ($\sim$630 mAh g^{-1} at 1 A g^{-1} after 1000 cycles) [13]. $MnFe_2O_4$@C nanofibers as sodium storage materials showed good electrochemical performances with high-rate capability (305 mAh g^{-1} at 10 A g^{-1}) and ultra-long cycling life (90% capacity retention after 4200 cycles) [14]. We also found that the improved cycling performances of $MnFe_2O_4$-graphene nanocomposites were derived from the confined aggregation of Fe_3O_4 or MnO nanoparticles because the *in-situ* formed hybrid of Fe_3O_4-MnO in graphene could suppress the diffusion of Fe and Mn atoms [15]. Although Co-Mo-S tenary compounds have been prepared to tune the catalytic activities (hydrogen evolution, hydrodesulfurization *etc.*) of MoS_2 in past years [16–18], their lithium storage performances are seldomly reported. On the other hand, cobalt sulfides, eapecially CoS_2, exhibit a high theoretical capacity of 872 mAh g^{-1} based on the conversion reaction mechanism, and have attracted many attentions as promising lithium and/or sodium storage materials [19–22]. Thus, the incorporation of Co into MoS_2 is expected to improve their electrochemical properties. Herein, hierarchical $Co_{1/3}Mo_{2/3}S_2$/graphene nanocomposites have been designed and prepared *via* a one-pot solvothermal method. The incorporation of cobalt can effectively suppress the restacking and agglomeration of MoS_2 nanoparticles in long-term charging/discharging process, endowing the cycling life of MoS_2 electrode material from 2000 cycles to 3000 cycles in LIBs. Furthermore, the obtained materials also exhibit the improved performances in SIBs.

2. Experimental

2.1. Synthesis

Graphite oxide (GO) was prepared from natural graphite flakes by a modified Hummers method. In a typical process, 0.25 mmol $CoC_4H_6O_4{\cdot}4H_2O$ and 0.5 mmol $Na_2MoO_4{\cdot}2H_2O$ were dissolved in 40 mL ethylene glycol under vigorous stirred for 30 min, then 68 mg sublimed sulfur and 30 mg GO were added for being stirred with another 30 min to form a homogeneous solution, the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and maintained at 200 °C for 24 h. Then the reaction system was allowed to cool to room temperature naturally, The obtained products were collected by filtered, washed with deionized water and ethanol, and then freeze dried for 3 days.

2.2. Characterization

The obtained samples were characterized on a Shimadzu-6000 X-ray powder diffractometer (XRD) with Cu Kα radiation ($\lambda = 1.5418$ Å). The operation voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology were characterized by JEOL JEM-2100F high-resolution transmission electron microscopy (HRTEM). The high-angle annular dark-field scanning TEM (HAADF-STEM) and STEM-energy-dispersive X-ray spectroscopy (STEM-EDS) elemental mapping images were obtained using a JEOL JEM-ARM200F Cs-corrected scanning transmission electron microscope operating at 200 kV. Raman spectra were measured using a Thermo Scientific DXR Raman Microscope with the 532 nm laser excitation (laser power of 1.5 mW) as the light source. X-ray photoelectron spectroscopy (XPS) was conducted with a VG Scientific ESCLAB 220iXL X-ray photoelectron spectrometer.

2.3. Electrochemical measurements

The obtained products as active material (80 wt %), carbon black (10 wt %, Super-P), and sodium carboxymethyl cellulose (CMC, 10 wt %) were mixed into a homogeneous slurry, and then coated onto a Copper foil and dried in a vacuum oven for 8 h at 70 °C. The weight of active material in each electrode was about 1 mg cm^{-2}. Electrochemical test cells were assembled using CR2016 coin cells for LIBs (CR2032 type coin cells for SIBs) in an argon filled glove box ($O_2 \leq 1$ ppm, $H_2O \leq 1$ ppm) with lithium metal foil (sodium metal, for SIBs) as nagtive electrode, and 1M of $LiPF_6$ in a 1:1 (vol) mixture of ethylene carbonate and dimethyl carbonate as the electrolyte (1M of $NaClO_4$ in 1:1 vol/vol mixture of ethylene carbonate and dimethyl carbonate as the electrolyte for SIBs), 10 wt% fluoroethylene cabonate (FEC) was added into electrolytes for LIBs and SIBs. Polypropylene membrane (UBE Industries Ltd.) and glass microfiber filters (Whatman) were used as separator for LIBs and SIBs, respectively. Charge-discharge cycles of cells were measured between 0.001 and 3.0 V on a battery test instrument (LAND-CT2001A model, Wuhan Jinnuo Electronics, China) at room temperature. Cyclic voltammetry (CV) was conducted on the workstation (Zahner Zennium CIMPS-1, Germany) at a scan rate of 0.1 mV/s in a potential range of 1 mV–3.0 V. Electrochemical impedance spectroscopy (EIS) was carried out in a frequency range from 0.01 Hz to 100 kHz at open circuit potential with 5 mV amplitude.

3. Results and discussion

Hierarchical $Co_{1/3}Mo_{2/3}S_2$/graphene nanocomposites were synthesized with cobalt acetate and sodium molybdate as precursors in presence of graphene oxide, in which high boiling point ethylene glycol was used as solvent and complexing/structure-directing agent. For comparison, MoS_2/graphene nanocomposites (Fig. S3) and CoS_x/graphene nanocomposites (Fig. S4) were also prepared in similar system. The chemical composition and phase of the obtained samples were