

Synthesis of hierarchical MoS₂ microspheres composed of nanosheets assembled via facile hydrothermal method as anode material for lithium-ion batteries

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Received: 15 September 2015 / Accepted: 10 February 2016 / Published online: 24 February 2016
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Abstract A hierarchical MoS₂ architecture composed of nanosheet-assembled microspheres with an expanded interplanar spacing of the (002) planes was successfully prepared via a simple hydrothermal reaction. Electron microscopy studies revealed formation of the MoS₂ microspheres with an average diameter of 230 nm. It was shown that the hierarchical structure of MoS₂ microspheres possesses both the merits of nanometer-sized building blocks and micrometer-sized assemblies, which offer high surface area for fast kinetics and buffers the volume expansion during lithium insertion/deinsertion, respectively. The micrometer-sized assemblies were found to contribute to the enhanced electrochemical stabilities of the electrode materials. The mentioned

advantages of the MoS₂ electrode prepared in this work allowed enhanced cyclability and high rate capability of the material. Along with this, the material delivered a high initial discharge capacity of 1206 mAh g⁻¹ and a reversible discharge capacity of 653 mAh g⁻¹ after 100 cycles at a current density of 100 mA g⁻¹. Furthermore, the material delivered a high reversible capacity of 480 mAh g⁻¹ at a high current density of 1000 mA g⁻¹.

Keywords Lithium-ion battery · Nanocomposite materials · Energy storage · MoS₂ anode · Hierarchical MoS₂ microspheres · Hydrothermal synthesis

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Introduction

Rapid development of portable electronics and a wide implementation of electricity-powered transport along with expansion of the renewable energy sources use and integration into the electric grids, demand for high-performance and reliable power storage and conversion systems. Lithium-ion batteries (LIBs) lead the path for such devices, and many efforts have been devoted to develop the next generation of anode materials for LIBs with both high specific capacity and high energy density. Theoretical capacity of a common commercial anode, graphite, is 372 mAh g⁻¹, which is relatively low especially considering the recent development of high capacity cathodes for

example sulfur (Zhao et al. 2012; Zhang et al. 2011; Birrozzi et al. 2014). Therefore, development of advanced anode materials attracts great attention of the researchers worldwide. Among them, metal sulfides are promising material due to their high capacities (Zhong et al. 2012; Vaughn et al. 2012; Lai et al. 2012; Liu et al. 2012a; Gu et al. 2013; Fei et al. 2013). Molybdenum disulfide (MoS_2) is an “inorganic analogue of graphene”, which has drawn particular research interest: it has a very high capacity about 670 mAh g^{-1} upon insertion of 4 mol of Li^+ (Wang et al. 2013). This material can accommodate lithium cations at lower potential through conversion reaction, and thus it can be used as anode material paired with high voltage ($>4 \text{ V}$) lithiated cathodes (Sen and Mitra 2013). Despite these advantages, poor electrical/ionic conductivity of MoS_2 prevents achieving its full capacity, and the large volume changes upon reversible lithiation/delithiation leads to the material degradation and rapid capacity fading. Therefore tremendous efforts have been devoted towards the electrochemical performance enhancement of MoS_2 anode for LIBs (Wang et al. 2013; Sen and Mitra 2013; Zhao et al. 2014; Zhang et al. 2012). For example, nanostructured MoS_2 materials have been extensively explored. Due to its nanostructure, this system provides a facile strain relaxation during structure/volume change and shortens diffusion paths for Li^+ insertion/deinsertion due to a large contact area with the electrolyte (Zhao et al. 2014; Zhang et al. 2012; Qiu et al. 2010). However, the agglomeration of nanostructured MoS_2 during electrochemical cycling can lead to a rapid loss of the composite conductivity and subsequent capacity decay, which restricts consideration of MoS_2 anode for practical use and commercialization. In our previous works (Zhang et al. 2014a), the advantages of hierarchical architecture towards improving electrochemical response of galvanic cell have been discussed. This promising strategy could be applicable in case of MoS_2 anode, benefiting from the advantages of using single component and providing novel properties due to the synergistic interactions between nanometer-sized building blocks (Hu et al. 2014a). Ding et al. reported that the hierarchical MoS_2 spheres composed of ultrathin nanosheets exhibit a high specific discharged capacity of $\sim 600 \text{ mAh g}^{-1}$ at 100 mA g^{-1} after 70 circles (Ding et al. 2012). Li et al. prepared 3D (three-dimensional) flowerlike MoS_2 which exhibits a

capacity of $\sim 565 \text{ mAh g}^{-1}$ at a current density of 100 mA g^{-1} after 100 circles (Li et al. 2009). However, the hierarchical structured MoS_2 reported in these studies own micrometer dimensions with inhomogeneous distribution of components and particle sizes. These parameters of the system cannot allow for accumulation of the large volume expansion and agglomeration of MoS_2 during charge/discharge cycling, and it shows poor rate performance and low cycling stability.

To overcome this issue, in this study we optimized the size and structure of hierarchical MoS_2 , and hierarchically structured MoS_2 microspheres with small (233 nm) and homogeneous particle size were successfully synthesized using a simple hydrothermal process. The nanostructural properties of the obtained MoS_2 microspheres and their electrochemical performance as an anode for a lithium-ion cell were investigated.

Experiment

The synthetic procedures for hierarchical structure of MoS_2 were adopted from the literature (Ma et al. 2013) with some modification. 2.2 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Tianjin Chengyang, $\geq 98\%$) and 2.0 g H_2NCSNH_2 (Tianjin Chengyang, $\geq 99\%$) were dissolved in 70 mL deionized water. The aqueous solution was stirred for 10 min, followed by a dropwise addition of 12 M HCl (Tianjin Fuchen, 36–38%) to adjust the solution pH below 1. The solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at $200 \text{ }^\circ\text{C}$ for 24 h. After the autoclave cooled down to room temperature, the resulting MoS_2 precipitate was collected by filtration, and washed using deionized water and ethanol. The resulting black powder was dried for 24 h at $60 \text{ }^\circ\text{C}$.

The morphologies and structure of the MoS_2 sample were characterized using scanning electron microscopy (SEM, S-4800, Hitachi Limited), selected area electron diffraction (SAED, JEM-2100F, JEOL), and high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL) at an accelerating voltage of 160 kV. The crystalline phases of the sample were determined by Powder X-ray diffraction (XRD, smart lab, Rigaku Corporation) equipped with $\text{Cu K}\alpha$ radiation. The Brunauer–Emmett–Teller (BET) specific surface area of the sample was detected

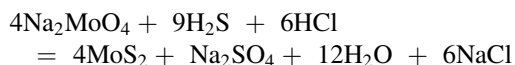
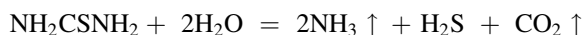
at 77 K using Micromeritics Tristar 3000 analyzer. The pore size distribution was calculated based on Barrett–Joyner–Halanda (BJH) model.

The electrochemical performance of the MoS₂ sample was investigated using coin cells (CR2025), with metallic Li as counter and reference electrodes, microporous polypropylene as a separator, and 1 M LiPF₆ in a mixture of ethylene carbonate/dimethyl carbonate/ethylenemethyl carbonate with a volume ratio of 1:1:1 as an electrolyte. The working electrode was prepared by mixing MoS₂, carbon black, and polyvinylidene fluoride (PVDF) (Kynar, HSV900) in 1-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, ≥99.5 % purity) in a weight ratio of 8:1:1. The resultant slurry was uniformly spread onto nickel foam using a doctor blade and dried in a vacuum oven at 50 °C for 12 h, and was cut into circular electrodes with 1 cm in diameter. The active material loading in each electrode was 2 mg cm⁻². The cells were assembled in an Ar (99.9995 %)-filled glove box (MBraun). Galvanostatic cycling of the cells were carried out on a multichannel battery tester (BTS-5V5 mA, Neware) within a cut-off potential window of 0.001–3.0 V versus Li⁺/Li. Cyclic voltammetry (CV) measurements were conducted at 0.5 mV s⁻¹ with a potentiostat (VMP3, Biologic) between 0 and

3.0 V versus Li⁺/Li. All electrochemical measurements were performed at room temperature.

Results and discussion

Hierarchical MoS₂ microspheres were synthesized by hydrothermal synthesis method. The reaction mechanism can be expressed as follows (Ma et al. 2013):



The schematic of formation of hierarchical MoS₂ microspheres is illustrated in Fig. 1a. The MoS₂ cores are formed via a reaction of Na₂MoO₄ and H₂S. Strong ionic/covalent force leads to the growth of the two-dimensional MoS₂ nanosheets. Ultimately, the growing MoS₂ nanosheets overlap and assemble hierarchical microsphere structure of MoS₂ due to the Van der Waals interactions (Liang et al. 2013). Figure 1b shows the XRD patterns of the MoS₂ product. The diffraction peaks at 11.8°, 32.6°, 43.6°, 57.8° can be indexed as crystalline planes of (002), (100), (103), (110) for hexagonal MoS₂ (JPDFS No. 37-1492). All of

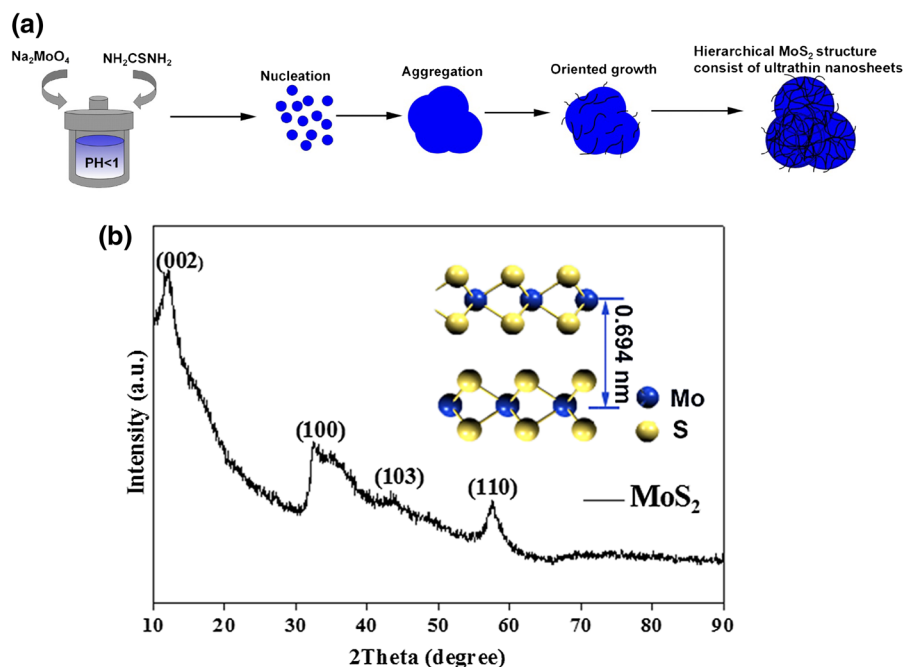


Fig. 1 **a** Schematics of preparation of the hierarchical MoS₂ microspheres; **b** XRD pattern of the hierarchical MoS₂ microspheres; *inset* atomic structure model of MoS₂

the diffraction peaks are weak, indicating a lower crystallinity of the MoS₂ material due to the fact that the material was not annealed; this feature does not affect the electrochemical performance of as-prepared MoS₂ (Qian et al. 2015). The diffraction peak at 11.8°, corresponding to the MoS₂ crystalline plane (002), is lower than that of the hexagonal MoS₂ ($2\theta = 14.4^\circ$, $d = 0.615$ nm). Moreover, the atomic structure model of as-prepared MoS₂ (inset of Fig. 1b) can be described as a sandwich-like structure of S–Mo–S (Haesuk et al. 2011). The average interlayer distance of the prepared MoS₂ nanosheets, calculated according to Bragg's equation, is 0.694 nm. This is larger than that of the crystalline plane 002 (0.615 nm), which was caused by the formation of a new lamellar structure of MoS₂ during the hydrothermal process, demonstrating that the space between the neighboring planes is extended (Xie et al. 2013; Hu et al. 2014b). The enlarged interplanar spacing shortens the path length and provides enhanced channeling for Li-ions diffusion (Liu et al. 2012b).

The porous structure of the hierarchical MoS₂ microspheres was confirmed by nitrogen adsorption/desorption isotherms (Fig. 2a) and pore size distribution analysis (Fig. 2b). It can be seen from these figures the isotherms present a typical type IV adsorption with a hysteresis loop at a relative pressure of 0.45, corresponding to the mesoporous structured material. Furthermore, the pore size distribution (Fig. 2b), calculated based on BJH model, presents a significant ratio of pore size distributed around 3.2 nm, which confirms our suggestion on mesoporous features of the prepared material. This structure of the hierarchical MoS₂ microspheres has resulted in a high BET specific area of 92 m² g⁻¹ compared with

other MoS₂ materials (Hu et al. 2014b; Xia et al. 2016; Li et al. 2015). It was found that the pore volume for this sample is 0.271 cm³ g⁻¹ with the average pore size of 6.1 nm, which could also be attributed to the hierarchical structure and highly developed interlaces of the ultrathin nanosheets. These structure and morphology specifics can strongly affect the electrochemical performance of the materials providing rapid electrolyte transport, carrier-ion diffusion, and accommodating the volume changes upon electrochemical cycling.

Figure 3a presents the SEM images of as-prepared MoS₂. It can be seen that the hierarchically structured MoS₂ was successfully synthesized, featuring homogeneous MoS₂ microsphere morphology. These hierarchical MoS₂ microspheres are made up by ultrathin nanosheets with a thickness less than 16 nm as it was shown by the high magnification SEM image (inset of Fig. 3a). Figure 3b presents the particle size distribution for the prepared material. It can be seen that the MoS₂ microspheres present homogeneous particle size distribution with the dominant sizes in a range of 200–260 nm, and average size of 233 nm. These particular structural properties offer enlarged surface area for fast lithium diffusion and enable buffering the volume changes during lithium insertion/deinsertion (Hu et al. 2014b).

The magnified TEM image (Fig. 3c) shows the stacks and clusters of MoS₂ nanosheets. The SAED patterns (inset of Fig. 3c) exhibit three distinct diffraction rings which can be indexed as the different lattice planes of the hexagonal MoS₂. The lattices of MoS₂ microspheres can be identified by the HRTEM image presented in Fig. 3d. The lattice d-spacing is calculated to be 0.694 nm, and can be indexed as the

Fig. 2 **a** Nitrogen adsorption/desorption isotherms; **b** pore size distribution of the hierarchical MoS₂ microspheres. *Inset* magnification of pore size distribution between 2 and 10.0 nm

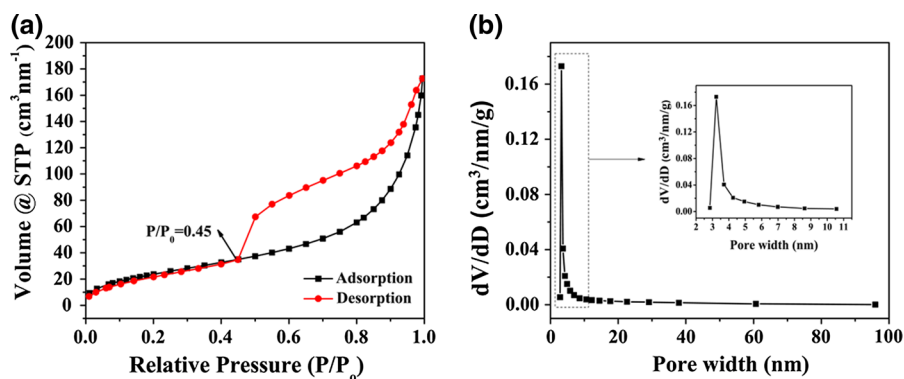
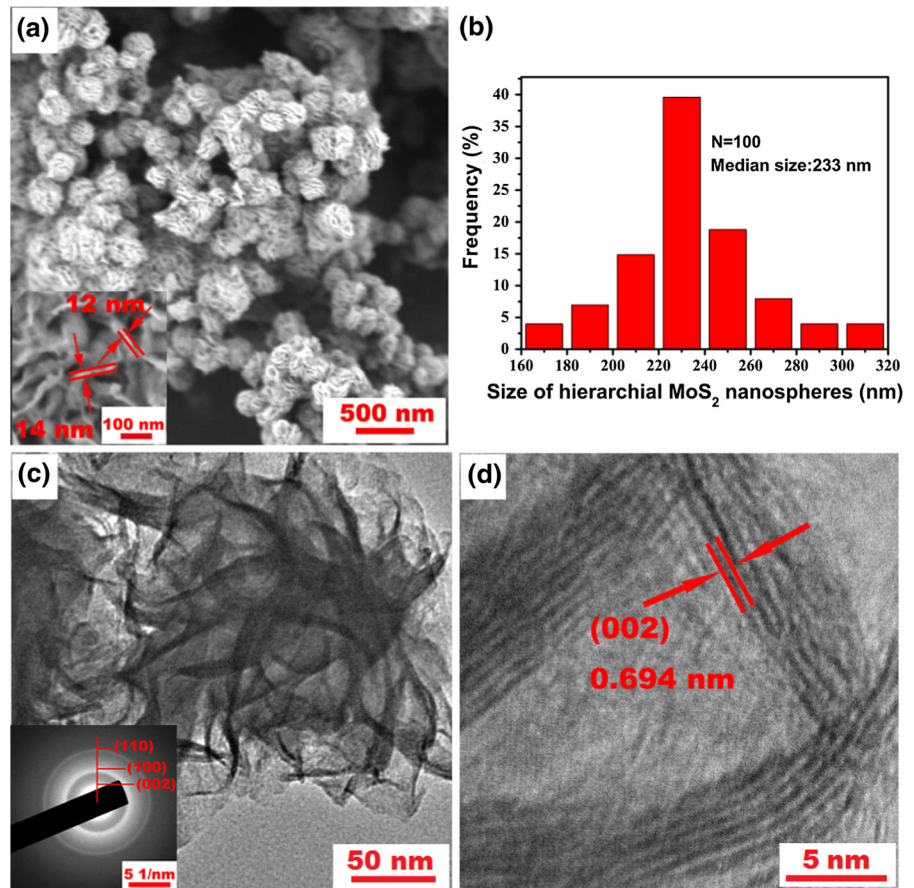


Fig. 3 **a** Low magnification SEM of the hierarchical MoS₂ microspheres; *inset* high magnification SEM of the hierarchical MoS₂ microspheres; **b** particle size distribution of the hierarchical MoS₂ microspheres; **c** TEM of the hierarchical MoS₂ microspheres, *inset* SAED pattern of the hierarchical MoS₂ microspheres; **d** HRTEM of the hierarchical MoS₂ microspheres



(002) plane of MoS₂. The interplanar spacing of 0.694 nm is enlarged compared with the hexagonal MoS₂ (0.615 nm), and corresponds with the XDR result.

The electrochemical performance of the hierarchical MoS₂ microspheres as anode material for LIBs was investigated in lithium half cells. Figure 4 shows the initial cyclic voltammogram (CV) of the hierarchical MoS₂ microspheres at a scan rate of 0.5 mV s⁻¹. During the initial discharge cycle, two oxidation peaks were observed at ~0.33 and ~0.95 V vs. Li⁺/Li, respectively. A peak at ~0.95 V could be related to a process of formation of Li_xMoS₂ upon Li-ions intercalation into MoS₂, whereas a peak at ~0.33 V could be associated with the MoS₂ conversion process via Li_xMoS₂ → Li₂S + Mo/Li_y and formation of solid electrolyte interphase (SEI) due to the electrolyte decomposition (Sen and Mitra 2013; Hu et al. 2014b; Liu et al. 2012b). During the first anodic sweep, a low intensity peak at ~1.64 V could be a reflection of the

Mo → MoS₂ conversion process, and an obvious peak at ~2.35 V corresponds to the oxidation process of sulfur Li₂S → S (Xiao et al. 2011). In the following

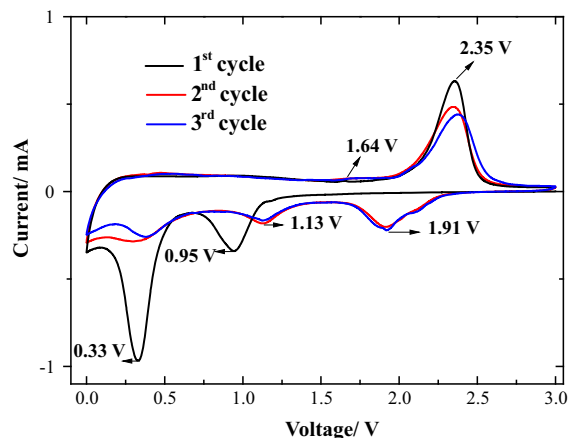


Fig. 4 CV profiles of the hierarchical MoS₂ microsphere anode

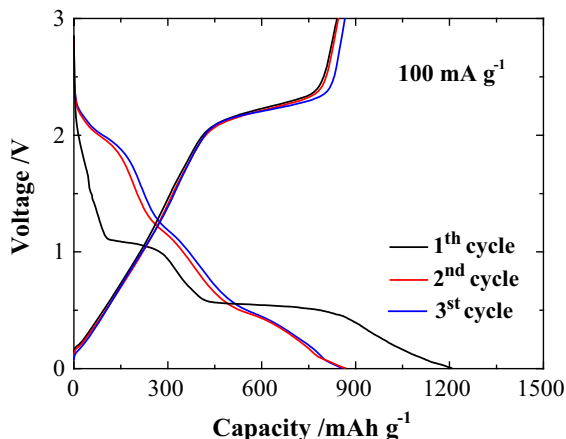


Fig. 5 Charge–discharge profiles of the hierarchical MoS₂ microsphere anode at 100 mA g⁻¹

cycles, a peak at ~ 0.33 V diminishes, indicating irreversible character of the SEI formation. New peaks appear at ~ 1.91 and ~ 1.13 V, which might result from conversion of S to LiS₂ and association of Li with Mo, respectively. Figure 5 shows the charge–discharge curves of the hierarchical MoS₂ microspheres at a current density of 100 mA g⁻¹, and consists of two potential plateaus at ~ 0.55 and ~ 1.08 V, indicating the two-step lithiation reaction of MoS₂. It should be noted that the initial discharge curve has a prolonged feature which could be due to the formation of SEI and related irreversible energy loss. In the following discharge curves, the plateaus observed in the first discharge shift towards the higher potentials of ~ 1.15 and ~ 1.94 V, respectively, which could be due to the completion of the SEI formation and electrochemical activation of the system (Wang et al. 2013). The hierarchical MoS₂ microsphere system shows a highly reversible electrochemical property, which is indicated by nearly overlapping potential profiles starting from the 2nd cycle (see Fig. 5). The results of charge–discharge curves of the hierarchical MoS₂ microspheres correspond well with the CV results discussed above.

Figure 6 presents both the cyclic performance and the coulombic efficiency data for the hierarchical MoS₂ microsphere electrode. It can be seen that this material exhibits a stable cycling ability at a current density of 100 mA g⁻¹, and after 100 cycles it retains a capacity of 653 mAh g⁻¹, which is about 75 % of the second discharge capacity. Along with this excellent cycling performance, the hierarchical MoS₂ microsphere

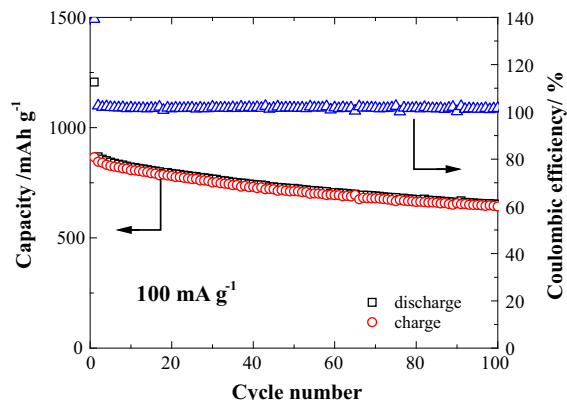


Fig. 6 Cyclability of the hierarchical MoS₂ microsphere anode at 100 mA g⁻¹

electrode exhibits a high coulombic efficiency of about 100 %. This performance enhancement of the material could be attributed to large specific area and increased interplanar spacing of the (002) crystal plane of the MoS₂ microspheres, which increases the area of the interface between electrode and electrolyte, and thus provides more active sites for the Li-ion insertion/desertion (Zhang et al. 2014b; Qian et al. 2015). Secondly, the hierarchical nanosheet structure of MoS₂ buffers the volume expansion and destruction of the electrode during the lithiation–delithiation processes (Zhang et al. 2014c).

The ability of an electrode material to operate within a wide range of current densities or charge–discharge rates is another important property-determining perspectives of its practical application. Therefore, the rate capability of the hierarchical MoS₂ microspheres was studied at different current densities. Figure 7 presents the rate capability data. It can be seen that the hierarchical MoS₂ microspheres possess a high capacity of 836 mAh g⁻¹ at a current density of 100 mA g⁻¹ after the first ten cycles. With an increase in current density to 200 and 500 mA g⁻¹, the discharge capacity of the electrode gradually decreases to 770 and 681 mAh g⁻¹, respectively. The cell could still maintain a high capacity of 480 mAh g⁻¹ even at a high current density of 1000 mA g⁻¹. Upon reducing the current density back to 100 mA g⁻¹, the cell regains its capacity and exhibits a stable cycling at a value of 814 mAh g⁻¹ up to 60 cycles. The improved rate and cycling performance of the material can be resulted from the shortened lithium-ion diffusion distance and an enhanced

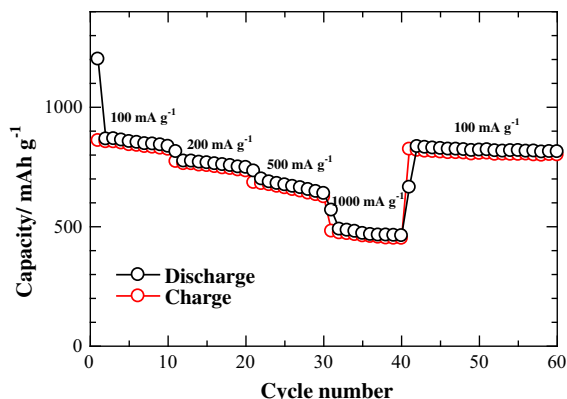


Fig. 7 Rate capability of the hierarchical MoS₂ microsphere anode

structural stability of the hierarchical MoS₂ microspheres. Furthermore, the electrochemical performance of our hierarchical MoS₂ microsphere electrode was compared with that of the MoS₂-based anodes reported in the literature (Table 1). It can be seen that a remarkably enhanced performance was achieved for the hierarchical MoS₂ anode in the present study.

The results of the studies on the hierarchical MoS₂ microspheres in the present work provide insights into the design of desirable structures of the material and preparing its hybrids and composites with other materials, such as carbon nanotubes, graphene, and other carbonaceous framework systems. Graphene-based MoS₂ composite exhibits enhanced reversible capacity and smaller capacity degradation due to graphene's desirable chemical stability and high

conductivity (Chang et al. 2013; Xiang et al. 2016). Therefore, the present work could be considered as a step towards in an advanced research on a new approach to prepare hierarchically structured MoS₂-based composites with excellent electrochemical performance for lithium-ion batteries.

Conclusions

In this work, nanosized (~ 233 nm) and homogeneously distributed hierarchical MoS₂ microspheres were fabricated via a simple cost-effective hydrothermal synthesis method. The crystalline phases and morphology of the material were characterized by XRD, SEM, TEM, and HRTEM methods. It was shown that the prepared hierarchical MoS₂ microspheres are composed of ultrathin nanosheets with an extended interlayer spacing. Hierarchical MoS₂ microspheres with such unique structural characteristics possess enlarged specific surface area and are able to accommodate the significant volume changes upon lithium insertion/deinsertion. Electrochemical performance tests showed that the hierarchical MoS₂ microspheres could deliver a high specific capacity of 653 mAh g⁻¹ at 100 mA g⁻¹ after 100 cycles. Furthermore, it can reach a very high capacity of 480 mAh g⁻¹ even at an elevated current density of 1000 mA g⁻¹. These excellent lithium storage properties of the hierarchical MoS₂ microspheres are believed to be contributed by its small and homogeneous size as well as the enlarged layer distance of

Table 1 Comparison of the electrochemical data for MoS₂-based anode for Li-ion batteries in present work and published in the literature

Material	Reversible capacity (mAh g ⁻¹)	Cycle number	Current density (mA g ⁻¹)	Refs.
MoS ₂ -RGO composites	305	50th	100	Fei et al. (2013)
Hierarchical MoS ₂ microspheres	~ 600	70th	100	Ding et al. (2012)
Flowerlike MoS ₂	~ 565	100th	100	Li et al. (2009)
MoS ₂ nanosheets on Carbon nanotubes	539.9–504.6	100th	50	Haesuk et al. (2011)
MoS ₂ nanotubes	770	40th	40	Feng et al. (2009)
Mesoporous MoS ₂	630	20th	35	Fang et al. (2009)
Hierarchical MoS ₂ microspheres	745	50th	100	Our work
	653	100th	100	

(002) crystal plane, and make this material a promising candidate anode for lithium-ion batteries.

Acknowledgments The authors acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 21406052), the Program for the Outstanding Young Talents of Hebei Province (Grant No. BJ2014010), Natural Science Foundation of Hebei Province of China (Project No. E2015202037), and Science and Technology Correspondent Project of Tianjin (Project No. 14JCTPJC00496). ZB acknowledges the research grant 4649/GF from the Ministry of Education and Science of Kazakhstan.

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