Studies on intrinsic phase-dependent electrochemical properties of

MnS nanocrystals as anodes for lithium-ion batteries

Yong Hao^a, Chunhui Chen^a, Xinyi Yang^b, Guanjun Xiao^c, Bo Zou^c, Jianwen Yang^{a,d} and

Chunlei Wang^{a,e,f *}

Abstract

Manganese sulfide (MnS), a member of transition metal sulfides, has been considered as a promising anode material for reversible Li storage due to its high theoretical capacity and structural advantages. However, the intrinsic electrochemical performance of MnS with different phases in lithium-ion batteries is yet to be fully investigated. Herein, high purity rock-salt (RS), zinc-blende (ZB) and wurtzite (WZ) MnS nanocrystals with different morphologies were successfully synthesized via a facile solvothermal method. The RS-MnS, ZB-MnS and WZ-MnS electrodes showed the capacities of 232.5 mAh g⁻¹, 287.9 mAh g⁻¹ and 79.8 mAh g⁻¹ at the 600th cycle, respectively. ZB-MnS displayed the best performance in terms of specific capacity and cyclability in comparison to RS-MnS and WZ-MnS nanocrystals. Interestingly, all the three kinds of MnS electrodes exhibited an unusual phenomenon of capacity increase upon cycling along with reduced particle sizes and without change in crystallinity. The main contribution of capacity increase was ascribed to the decreased cell resistance and enhanced interfacial charge storage, which facilitated more effective Li⁺ diffusion into electrode materials.

Keywords: Manganese sulfide nanocrystals; Lithium-ion Batteries; Anode; Electrochemical performance; Capacity increase

1. Introduction

Transition metal sulfides, such as copper sulfides, iron sulfides, cobalt sulfides, nickel sulfides and molybdenum sulfides, have recently received much attention owing to their diverse crystal structures and potential applications in solar cells, sensors, thermoelectric devices, fuel cells, supercapacitors and lithium-ion batteries (LIBs) [1-13]. In general, most transition metal sulfides M_xS_y , analogous to typical transition metal oxides, could be associated with two lithiation reaction mechanisms. One is a lithium insertion reaction to form an intermediate $Li_nM_xS_y$, followed by a conversion reaction to form the metallic nanoparticles M and Li_2S alloy. The overall M_xS_y lithiation/delithiation mechanism can be described as $M_xS_y + 2yLi^+ + 2ye^- \leftrightarrow yLi_2S + xM$ [14-17]. On the one hand, the nanosized metal particles, as reported in the case of other transition metal oxides (such as NiO [18, 19], Fe_3O_4 [20] and ZnO [21]), have a positive effect on the electrochemical reaction activity. On the other hand, typical sulfide electrodes exhibit poor cycle life due to their low electrical conductivity and relatively large volume expansion during lithiation/delithiation process [22-25], which hinders the sulfides in commercial energy storage application.

Among the sulfides, manganese sulfide (MnS) with widely varied nanostructures (e.g., nanorod, nanocube, nanowire, nanosaw and nanosphere) has been regarded as one of the promising anode materials due to its relatively high theoretical capacity of 616 mAh g^{-1} (Graphite: 372 mAh g^{-1}) [26-30]. Generally, MnS has three different phases: RS-MnS or α -MnS with a cubic rock-salt crystal structure ($a=b=c=5.224 \text{ \AA}$), ZB-MnS or β -MnS with a cubic zinc-blende crystal structure ($a=b=c=5.615 \text{ \AA}$) and WZ-MnS or γ -MnS with a hexagonal wurtzite crystal structure ($a=b=3.979 \text{ \AA}$ and $c=6.446 \text{ \AA}$) [17], as shown in insets of Fig. 1. Both metastable tetrahedrally coordinated phases ZB-MnS and WZ-MnS are stable below 100°C and

can transform into octahedrally coordinated phase RS-MnS at 100-400 °C or at high pressure [31]. So far, few works about single phase RS-MnS with polyhedron [32] and hollow microbox [33] structures as well as WZ-MnS with nanosaws [28] structure as anode materials in LIBs have been investigated. For example, Zhang et al. [32] first synthesized and utilized stable RS-MnS submicrocrystals for LIBs and the large particle RS-MnS in size of 2 μm manifested capacity of 339.6 mAh g⁻¹ at the 20th cycle, indicating the particle size and the degree of crystallinity played key roles in the electrochemical performance of RS-MnS submicrocrystals. In another work, it was found that RS-MnS microboxes with high crystallinity and structural integrity exhibited a much better specific capacity of 495 mAh g⁻¹ compared with RS-MnS porous microcubes of 340 mAh g⁻¹ at the 100th cycle, which implies that not only crystallinity, but also contact surface area is a crucial factor [33]. Furthermore, Chen et al. [34] focused on improving electrical conductivity and structural stability by compositing MnS with graphene and at the 30th cycle, MnS composite electrode delivered the specific discharge and charge capacities of 987 mAh g⁻¹ and 976 mAh g⁻¹, respectively.

It is well known that selecting nanoscale active materials and making composite electrodes are generally accepted strategies to improve charge-transfer and interfacial charge storage [35-37]. However, a thorough investigation of MnS phase-dependent electrochemical performance remains missing to date. We believe a detailed understanding of structural transformation and intrinsic performance of the MnS with different crystallinity will be essential to further develop high performance electrode materials. In our recent work, RS-MnS, ZB-MnS and WZ-MnS nanocrystals (NCs) with well-controlled morphology and dimensionality have been successfully synthesized via a facile one-pot solvothermal route [27, 30]. Herein, three single phase MnS samples have been fabricated and evaluated as anode materials in LIBs. It was

found that the capacities of as-assembled RS-MnS, ZB-MnS and WZ-MnS electrodes showed a decreasing trend in the initial ~40 cycles and gradually increased in the following cycles. At the 600th cycle, RS-MnS, ZB-MnS and WZ-MnS electrodes exhibited the capacities of 232.5 mAh g⁻¹, 287.9 mAh g⁻¹ and 79.8 mAh g⁻¹, respectively. Further studies revealed that reduced particle size and decreased charge transfer impedance were beneficial for Li⁺ transport during charge-discharge process, and further beneficial for capacity increase.

2. Experimental

2.1. Material synthesis

For a typical synthesis procedure of RS-MnS NCs, a mixture of 0.063 g (0.5 mmol) anhydrous MnCl₂ powder, 0.038 g (0.5 mmol) Thioacetamide (TAA, 99%), 1.0 ml oleic acid (OA, 90%) and 5.0 ml oleylamine (OLA, 70%) was added to a 50-ml three neck flask. This mixture was heated to 80 °C for 60 min under nitrogen flow. The solution was then slowly heated to 250 °C (5 °C/min) and kept for 30 min, then cooled to room temperature naturally. To synthesize ZB-MnS NCs, 0.063 g of anhydrous MnCl₂ and 4.0 ml of OLA were first added to a 50-ml three necked flask. The mixture was heated to 140 °C under nitrogen flow, and pink MnCl₂ powder was completely dissolved under stirring. After the mixture was cooled down to room temperature, a clear mixture solution of 1.0 ml OLA and 0.038 g TAA prepared in a glovebox was added into the flask. After that, the clear red solution was transferred to a 10-ml Teflon-lined autoclave. The autoclave was kept in a furnace at 200 °C for 30 min. To synthesize WZ-MnS NCs, the autoclave was kept in a furnace at 250 °C for 30 min while other conditions were the same as the parameters used for synthesizing ZB-MnS NCs. All the samples were isolated using methanol

and acetone, followed by centrifuging for 10 min at 10000 rpm. Subsequently, the residual samples were redispersed in toluene for microscopy characterization.

2.2. Characterization

X-ray diffraction (XRD) was used to determine the crystallographic structures of as-synthesized MnS powders and disassembled MnS electrodes after cycling. Data were collected from a Shimadzu XRD-6000 diffractometer and a Siemens D-5000 diffractometer both working with Cu-K α targets. Transmission electron microscopy (TEM) images, High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns of as-synthesized MnS NCs and TEM images as well as HRTEM images of disassembled MnS electrodes were obtained with JEOL JEM-2200FS transmission electron microscope with an emission gun operating at an acceleration voltage of 200 kV.

2.3. Electrochemical measurements

The 2032 coin cells were assembled to examine the electrochemical performance of MnS NCs. As-synthesized MnS samples (70 wt%) were mixed into slurry with conductive carbon black (15 wt%) and polyvinylidene fluoride (PVDF) binder (15 wt%) in N-methyl-2-pyrrolidinone (NMP) solvent. Then, the slurry was cast onto disc shaped copper foils, followed by transferring the electrodes into a vacuum oven and dried at 80 °C for 12 h. The coin cells were assembled in an argon-filled glovebox with MnS samples as working electrodes and lithium foils as counter and reference electrodes. Celgard 2400 polypropylene was used as separators and 1 M lithium bis(perfluoroethylsulfonyl)imide (LiBETI) dissolved in ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) in the volume ratio of 1:1:1 was used as

electrolyte. Cyclic voltammetry (CV) was conducted on the VMP3 multi-channel potentiostat at the scanning rate of 0.2 mV s^{-1} in the voltage range of $0.01 - 3 \text{ V vs. Li/Li}^+$. For each phase type of MnS samples, at least 10 cells have been assembled. Both galvanostatic charge-discharge cyclability test at a current density of 0.1 A g^{-1} and rate capability test at various current densities of $0.1, 0.2, 0.5, 1$ and 2 A g^{-1} were carried out on the NEWARE BTS-610 Battery Test System in the voltage window between 0.01 V and 3 V vs. Li/Li^+ . Electrochemical impedance spectroscopy (EIS) measurement was performed before and after cell cycling on VMP3 at an input AC signal of 10 mV amplitude within the frequency range of 100 kHz to 10 mHz . All the electrochemical characterization procedures were performed at room temperature.

3. Results and Discussion

Fig. 1. XRD patterns and corresponding JCPDS files of (a, b) RS-MnS, (c, d) ZB-MnS and (e, f) WZ-MnS. The insets illustrate the crystalline structures of RS-, ZB- and WZ-MnS, respectively.

Fig. 2. TEM images, HRTEM images and SAED patterns of as-synthesized (a,b,c) RS-MnS, (d,e,f) ZB-MnS and (g,h,i) WZ-MnS, respectively.

The crystallographic structures of as-synthesized MnS powders were examined by XRD. Fig. 1 shows the XRD diffraction patterns of three different phases of MnS. It can be observed that all the diffraction peaks are in good agreement with the JCPDS standard values. Five characteristic peaks can be observed in curve (a) corresponding to the (111), (200), (220), (222) and (400)

planes, which can be indexed to cubic RS-MnS phase with a space group of $Fm-3m(225)$ (JCPDS No.65-2919, curve (b)). Three diffraction peaks in curve (c) can be assigned to the planes of (111), (220) and (311) in cubic ZB-MnS phase with a $F-43m(216)$ space group (JCPDS No.40-1288, curve (d)). The diffraction peaks in the curve (e) can be indexed to hexagonal WZ-MnS phase with planes of (100), (002), (101), (110), (103) and (112), and a $P63mc(186)$ space group (JCPDS No. 40-1289, curve (f)). There are no impurity peaks detected in any of the three patterns, indicating that the synthesized samples are pure RS-MnS, ZB-MnS and WZ-MnS single phase, respectively.

The morphology and crystalline structure of as-prepared RS-MnS, ZB-MnS and WZ-MnS NCs were characterized by TEM and HRTEM, respectively. The phases of these three kinds of MnS samples were also identified by the SAED patterns. As shown in Fig. 2a, RS-MnS is in a nanocube shape with an average particle size of ~25 nm. As in Fig. 2b, the HRTEM image of a typical RS-MnS NC, it can be observed that periodic lattice fringe with an interplanar distance of 2.64 Å comes from (200) plane of cubic RS-MnS. The SAED (Fig. 2c) pattern shows four diffraction rings, which can be indexed as pure RS-MnS, indicating high crystallinity of as-synthesized RS-MnS NCs. Fig. 2d-f show the TEM image, HRTEM image and corresponding SAED pattern of ZB-MnS. It can be clearly seen from Fig. 2d that ZB-MnS NCs are in irregular shapes with particle size distribution from 5 nm to 25 nm and an average size of ~10 nm. From the HRTEM image (Fig. 2e), the measured lattice spacing of 3.23 Å is consistent with the (111) plane of cubic ZB-MnS. The SAED pattern (Fig. 2f) further confirms the existence of single phase ZB-MnS NCs. From Fig. 2g, it can be observed that the WZ-MnS NCs display anisotropic nanorod structure. Some of the nanorods are assembled into 2-branch V-shape and some are in 3-branch Y-shape (Fig. S1e). The lattice fringe from HRTEM image (Fig. 2h) taken on a typical

individual nanocrystal shows the inter-plane spacing of 3.22 Å, which is attributed to the (002) plane of hexagonal WZ-MnS phase. The diffraction concentric rings from the SAED pattern (Fig. 2i) correspond well with the (100), (002), (101), (110), (103) and (112) planes of the hexagonal structured WZ-MnS. The TEM, HRTEM and SAED results indicate that highly crystalline single phase RS-, ZB- and WZ-MnS NCs were successfully fabricated, which are in good agreement with the results obtained from the XRD patterns in Fig. 1.

Fig. 3. (a-c) Cyclic voltammetry at a scanning rate of 0.2 mV s⁻¹ and (d-f) galvanostatic discharge/charge curves at a current density of 0.1 A g⁻¹ of RS-, ZB- and WZ-MnS in the voltage range of 0.01 - 3 V vs. Li/Li⁺, respectively.

The electrochemical properties of RS-, ZB- and WZ-MnS NCs as anode materials for LIBs were investigated. From the CV curves of RS-MnS (Fig. 3a), two peaks can be observed during the cathodic process of the first cycle. One reduction peak is observed at 1.59 V, which could be ascribed to the process of Li⁺ insertion into the MnS lattice to form intermediate

Li_xMnS phase [38]. In the voltage range of 0.01 - 1.0 V, there is a broad shoulder observed on the curve, which could be assigned to the conversion process of Mn^{2+} to Mn [28]. Meanwhile, the other minor reduction peak is observed at around 0.75 V in this range for RS-MnS, representing the non-aqueous electrolyte decomposition and solid electrolyte interphase (SEI) formation process [39]. During the anodic process of first cycle, there are four oxidation peaks centered around 1.04 V, 1.42 V, 1.92 V and 2.37 V, respectively, observed on anodic branch of RS-MnS, indicating the delithiation process of RS-MnS. The oxidation peaks at around 1.04 V and 1.42 V might be attributed to the conversion reaction of Mn to Mn^{2+} , and the following two peaks at around 1.92 V and 2.37 V may be due to Li^+ extraction from the MnS lattice process [28]. From the second cycle and onward, one cathodic peak shifts its position from initial 1.59V to 1.42V for RS-MnS. From Fig. 3b, three reduction peaks at around 1.41V, 0.75 V and 0.50 V can be observed during the first cathodic process of ZB-MnS. In the upcoming cycles, the reduction peak at 1.41 V shifts to 1.49 V. During the first anodic process, the ZB-MnS shows three oxidation peaks at 1.08 V, 1.96 V and 2.36 V, respectively. The CV behavior indicates that most related CV peaks on RS-MnS curve can also be observed for the case of ZB-MnS. In Fig. 3c, two major reduction peaks at 1.41 V and 1.61 V can be observed during the first cathodic process of WZ-MnS. These two reduction peaks transformed to one peak at 1.46 V in the following cycles. Meanwhile, several minor peaks can be observed in the low potential region (0.01 - 1.0 V), indicating the complex conversion process of WZ-MnS along with the formation of SEI in the first cycle. Similar to RS-MnS, four oxidation peaks at 1.08 V, 1.36 V, 1.96 V and 2.38 V can be observed from the first anodic process of WZ-MnS. The peak at 1.96 V shifts to 1.91 V on the second cycle. Consequently, for the three kinds of MnS electrodes, more or less, there are some peak shifts after the first cycle. One possible reason to explain the peak shift

could be the change of reaction kinetics due to the SEI formation [40]. It has to be noted that some reduction (e.g., RS 1.59 V and ZB 1.41 V) and oxidation (e.g., RS 1.42 V and WZ 1.36 V) peaks are not always obvious in all three different phases, indicating the reaction kinetics at different growth sectors might be slightly varied. In the subsequent cycles after the first cycle, the reduction and oxidation peaks most likely remain at the same position. However, the intensities gradually decrease, indicating the weakening of the redox reaction. The CV results seem to be in good agreement with the proposed electrochemical reaction process of MnS based on the conversion mechanism with intermediate Li_xMnS phase [28, 38]:

Fig. 3d-f present the galvanostatic discharge/charge profiles of RS-MnS, ZB-MnS and WZ-MnS samples as working electrodes in LIBs. As shown in Fig. 3d, the first reduction plateau can be observed at 1.5 V on the first discharge curve of RS-MnS, which may be attributed to Li^+ insertion into MnS lattice to form Li_xMnS [14]. With voltage decreasing, the second reduction plateau is observed at 0.75-0.5 V attributed to conversion reaction of Mn^{2+} to Mn and the formation of SEI process [41]. Furthermore, there is no obvious plateau shown up on the RS-MnS charge curve of the first cycle. On the following discharge/charge curves of the 2nd, 50th, 200th, 400th and 600th cycles, there are no obvious plateaus observed. This implies that the formation of SEI layer mainly takes place in the first cycle, which is in good agreement with the CV results. From Fig. 3e, it can be seen that the discharge behavior of the ZB-MnS in the first cycle is similar to RS-MnS with the reduction plateaus at around 1.5 V and 0.75 V. There is an oxidation plateau at around 1.0 V on the first charge curve, which is corresponding to the first oxidation peak on the CV curve of ZB-MnS in Fig. 3b. In Fig. 3f, it shows that there are two

reduction plateaus at around 1.5 V and 0.5 V on the discharge curve of WZ-MnS in the first cycle. There is an oxidation plateau at around 2.3 V on the first charge curve, which may represent the Li^+ extraction from WZ-MnS lattice process [28]. In following cycles up to at the 600th cycle, small plateaus on the discharge/charge curves can still be observed for WZ-MnS, indicating the similar lithiation/delithiation process as occurred in the first cycle. With the voltage decreasing to 0.01 V, The RS-MnS, ZB-MnS and WZ-MnS electrodes deliver the first discharge capacities of 438.8 mAh g^{-1} , 1545.1 mAh g^{-1} and 463 mAh g^{-1} , respectively. The first charge capacities of RS-MnS, ZB-MnS and WZ-MnS are 80.5 mAh g^{-1} , 430.6 mAh g^{-1} and 144.7 mAh g^{-1} , respectively. Capacity loss ranging from ~30% to ~50% of MnS or MnS/carbon composites as electrodes were reported in studies [28, 32, 34, 38]. The irreversible capacity loss may be attributed to the formation of SEI on the surface of MnS particles [41]. The comparison of charge-discharge behavior of MnS at the 1st and 400th cycles is shown in Fig. S2. It can be seen that the plateaus are more and more difficult to identify, especially after long cycling. Since our test current of 0.1 A g^{-1} is not fairly high, the extra capacity should not simply from capacitance contribution. We believe the contribution from charge storage due to reaction of Li ion with MnS cannot be excluded at such current rate. In fact, sloping charge-discharge curve is pretty common phenomenon, which has been discussed and debated by many authors. For example, in M. Rosa Palacin et al.'s review work of electrode materials through conversion reaction [42], extra capacity is a sloping curve after conversion plateau at low potentials. Two mechanisms for the origin of extra capacity has been proposed, one is electrolyte decomposition that leads to gel-like polymeric layer. This layer enables additional lithium storage in a capacitive way. The other one is interfacial storage that based on two-phase capacitive behavior, it allows for the storage of Li ion. In addition, Maier et al. [43] attributed the extra charge storage

to high surface area introducing interfacial storage. In our case, we believe these mechanisms could be used to explain the extra capacity of MnS.

Fig. 4. (a) Cycling performance of RS-, ZB- and WZ-MnS electrodes at a current density of 0.1 A g⁻¹, respectively; (b) Nyquist plots of fresh cell and cell after cyclability test with ZB-MnS as anode in LIBs. Figure insets give equivalent circuit model for the fitting of the Nyquist plots and enlarged semicircles in high frequency range (below).

Fig. 4a shows the galvanostatic cycling performance of MnS electrodes with different phases. The capacity trend with cycling exhibits two distinctive stages. First stage is an abrupt drop in capacities with increased cycle numbers during the first ~40 cycles. The discharge capacities of RS-MnS, ZB-MnS and WZ-MnS decrease to the lowest values of 11.4 mAh g⁻¹, 146.2 mAh g⁻¹ and 8.1 mAh g⁻¹ at around the 40th cycle, respectively. In contrast, the second stage shows a gradual increase of discharge capacity during the following cycles. At the 600th cycle, the discharge capacities of RS-MnS, ZB-MnS and WZ-MnS cells reach to 232.5 mAh g⁻¹, 287.9 mAh g⁻¹ and 79.8 mAh g⁻¹, respectively. The ratio of discharge capacities of RS-, ZB- and WZ-MnS at the 600th cycles compared to their first cycles are 53%, 18.6% and 17.2%. Further

effort needs to be done to understand this unusual capacity increase phenomenon.

To provide insights on the change of charge transfer resistance and Li^+ diffusion kinetics during cyclability test, EIS has been conducted on the three kinds of MnS before and after cycling. Fig. 4b shows the Nyquist plots of the ZB-MnS electrodes, which are fitted by an equivalent circuit (Fig. 4b inset). Fitting results of RS, ZB and WZ-MnS are summarized in Table S1. In Fig. 4b, it can be seen that both Nyquist plots consist of one semicircle in the high-frequency region and a linear straight line in the low frequency region. Obviously, the semicircle's diameter of ZB-MnS after cycling is smaller than that of ZB-MnS fresh cell, indicating an enhanced charge-transfer process after cycling. The slopes of the linear straight lines show almost the same value of $\sim 60^\circ$ (angle of linear line to x axis), indicating a retaining of similar Li^+ diffusion behavior in the MnS electrode [44]. In the equivalent circuit, where R_e denotes the electrolyte resistance, R_f denotes the surface related resistance, R_{ct} denotes the charge transfer resistance, Q_1 and Q_2 represent related constant phase elements, and Z_w is the Warburg element [45]. It has to be noted that R_f after cycling is mainly associated with SEI layer at the surface of electrode materials. From the summarized fitting results (Table S1), the values of R_e , R_f and R_{ct} of ZB-MnS after cycling are 6.6 Ω , 63.9 Ω and 4.8 Ω , which are smaller than the corresponding values of 7.0 Ω , 144.9 Ω and 197.2 Ω for the fresh ZB-MnS cell, indicating a lower charge transfer resistance and Li^+ diffusion resistance after cycling. This gives evidence that ZB-MnS electrode exhibits better electrical conductivity after cycling which may enhance the kinetics of Li^+ insertion/extraction process, leading to the capacity increase.

To further understand the capacity increase mechanism after 40 cycles, three coin cells were fully charged to 3.0 V after cycling and then disassembled in the glovebox. Next, the electrodes were rinsed with diethyl carbonate and dried under vacuum at room temperature. Fig.

5a-f show the TEM and HRTEM images of the disassembled electrodes (RS, ZB and WZ-MnS in Fig. 5a-b, 5c-d and 5e-f, respectively). From the low resolution TEM images (Fig. 5a, 5c and 5e), it can be found that MnS NCs are surrounded by amorphous structure materials. These materials might be carbon black and binder PVDF or amorphous MnS which are the MnS nanocrystals losing their crystallinity during cycling. The morphologies of disassembled MnS have significantly changed, compared to those of as-synthesized MnS NCs (e.g., nanocube and nanorod) in Fig. 2. As shown in HRTEM images (Fig. 5b, 5d and 5f), **all three kinds of MnS NCs break down to small NCs after 600 cycles with average size of ~5 nm, which is smaller compared to the samples before cycling (Fig. 2) and RS-MnS after 40 cycles (Fig. S3b).** It has been found that lattice fringes with interplanar spacing remain the same as various initial MnS samples (RS-MnS with 2.61 Å, ZB-MnS with 3.23 Å and WZ-MnS with 3.22 Å). As we observed from the TEM/HRTEM investigation, different from commonly observed Si case where crystalline Si changes to amorphous Si after cycling, different phases of MnS showed original type of crystalline structure with reduced particle sizes after cycling. In the case of Si, direct evidence has been reported. For example, in Yetming Chiang et al. and Yi Cui et al.'s work [46, 47], phase transformation of Si from crystalline to amorphous has been detected by TEM. The phase transformation mechanism is proposed that the amorphization occurs when alloying is electrochemically driven. From our knowledge, this is the first work of detailed study on the relationship of phase and electrochemical performance for MnS NCs. As compare to Si, it has to be mentioned that the lithiation mechanisms of MnS is different. For Si, it is alloying mechanism, but for MnS, the proposed mechanisms are insertion and conversion. In Fig 5, it can be observed that crystalline MnS particles are randomly embedded in amorphous matrix without uniform amorphous coating, however, it cannot be confirmed that those amorphous matrix

belongs to MnS. Herein, there are two possibilities that might occur during cycling, first one is that different phases of MnS keep their crystal structures during cycling with reduced particle sizes. The second possibility is partially transformation of crystalline to amorphous structure with the crystalline core due to incomplete lithation/delithiation. More detailed study will be conducted in our future work.

Fig. 5. TEM and HRTEM images of disassembled (a,b) RS-MnS, (c,d) ZB-MnS and (e,f) WZ-MnS electrode materials after 600 cycles (charged to 3 V).

Similar phenomenon of two stage capacity change with cycling has been reported with other electrode materials as well, such as carbon materials [48, 49], transition metal oxide [50-52] and transition metal sulfide [1, 24, 53, 54]. Typically, the capacity drop in typical batteries involved with insertion and conversion mechanisms could be due to several factors, such as: the SEI formation [44, 51], volumetric expansion and contraction introducing loss of active materials [51, 55, 56], metal nanoparticle aggregation [51, 57], structure degradation [58-60], impedance change at the interface [61], as well as incomplete insertion/conversion reaction [51, 62]. In this work, EIS result of RS-MnS (Fig. S3a) reveals the increased Li^+ charge transfer resistance and decreased Li^+ diffusion kinetics during the initial 40 cycles. HRTEM image (Fig. S3b) shows the degraded morphology and continuously reduced particle size of RS-MnS at the 40th cycle. Both kinetics change at the interface and structure degradation could contribute to the fading of the capacity of RS-MnS in the first 40 cycles. For the second stage of capacity increase, the possible phenomenon and mechanisms have been reported, for example: 1) active materials partially lose crystallinity and transform to amorphous-like structure [50, 59], 2) gel-like polymeric film continual growth by catalytic activity of metal particles [44], 3) electrochemical milling effect during cycling [52, 63] and 4) interfacial Li storage [64]. The HRTEM results in Fig.5 show the continuous size milling effect during lithiation/delithiation cycles. This gradual electrochemical size milling could induce a gradual activation process which may contribute to improved Li^+ diffusion kinetics (Fig. 4b). Meanwhile, the reduced MnS particle size leads to the increase of interfacial surface area which could be beneficial for Li^+ /electron transport and interfacial charge storage. Besides, the nonuniform amorphous phase could also enhance the diffusion kinetic of Li^+ and lead to capacity increase. Further investigations using in-situ TEM need to be conducted to study the mechanism of two stage capacity change with cycling.

4. Conclusions

In summary, we have successfully synthesized RS-MnS, ZB-MnS and WZ-MnS NCs with different morphologies via a facile solvothermal approach. The structural and morphological characterizations indicate that the obtained products exhibited high purity and excellent crystallinity. When evaluated as anode materials in LIBs, RS-, ZB- and WZ-MnS have achieved the capacities of 232.5 mAh g⁻¹, 287.9 mAh g⁻¹ and 79.8 mAh g⁻¹ at the 600th cycle, respectively. Notably, all the MnS samples showed an anomalous cycling performance as the capacity increases with the increase of cycle numbers, which can be attributed to the better Li kinetics and enhanced interfacial charge storage. Moreover, ZB-MnS delivered better electrochemical performance compared to RS-MnS and WZ-MnS.

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