Yolk–shell MoS2 powders with a distinct configuration of MoS2@void@MoS2 were prepared for the first time by applying spray pyrolysis. The yolk–shell MoO3 powders prepared by spray pyrolysis were converted into MoS2 powders by a simple sulfidation process at 400 °C without altering the morphology. Dense structured MoS2 powders were also prepared by a similar process. The respective initial discharge capacities of the yolk–shell and dense structured MoS2 powders at a current density of 1000 mA g\(^{-1}\) were 651 and 490 mA h g\(^{-1}\), and the corresponding capacity retentions after 100 cycles measured from the second cycle were 100 and 72%.

**Introduction**

Recently, molybdenum disulfide (MoS2), which is one of the typical layered transition metal dichalcogenide compounds MX2 (M = Mo, Ti, W, X = S, Se) has received increasing attention in diverse applications including gas sensors, catalysts, hydrogen storage, and energy storage.\(^{1-17}\) In these applications, the morphology control of the MoS2 powders is one of the key issues. The structure of MoS2 is analogous to that of graphite, comprising three atom layers. The Mo atoms are sandwiched between two layers of S atoms by strong covalent bonding, whereas the triatomic layers are stacked together through weak van der Waals interactions.\(^{18-21}\) Due to the weak van der Waals interactions, Li-ions are readily inserted and extracted from this layered structure. MoS2 has a theoretical capacity higher than that of commercial graphite. Thus, MoS2 has been considered as a promising electrode material for Li-ion batteries (LIBs).\(^{22-32}\) However, the practical application of MoS2 in LIBs is still restricted due to the fast capacity fading and poor rate performance.

Fabrication of electrode materials with controlled morphology and size is an effective strategy for improving the electrochemical properties.\(^{33-38}\) Recently, yolk–shell structured electrode materials have attracted much attention due to their unique structure, comprising a hollow shell and movable core, which offers a large surface area, short Li-ion diffusion length, and buffering space for structural strain arising from Li-ion insertion/extraction.\(^{37-39}\) The preparation of MoS2 with diverse structures such as nanoflakes, nanowires, nanotubes, nanosheets, and nanoflowers has been widely attempted for LIBs.\(^{39-46}\) However, to the best of our knowledge, fabrication of MoS2 with a yolk–shell structure has not been reported.

The electrochemical properties of yolk–shell structured metal sulfide powders are scarcely studied due to the difficulty of preparation of these species. Recently, a simple, new process for preparing yolk–shell structured SnS powders for anode applications in LIBs has been introduced by our group.\(^{47}\) Herein, MoS2 yolk–shell powders are first synthesized and then applied as anode materials for LIBs. The electrochemical properties of the yolk–shell structured MoS2 powders are compared with those of the dense structured MoS2 powders.

**Results and discussion**

The crystal structure of the prepared MoS2 yolk–shell powders sulfidated at 400 °C for 6 h is shown in Fig. 1a. The XRD pattern of the sulfidated powders showed peaks associated with hexagonal MoS2 (JCPDS card no. 37-1492) without impurity peaks. The yolk–shell MoO3 powders were completely sulfidated to form MoS2 powders by means of a simple sulfidation process. The formation process of yolk–shell MoS2 powders is shown in Fig. S1.\(^{†}\) The XRD pattern of the MoS2 powder is compared with that of the MoO3 yolk–shell powder in Fig. S2.\(^{†}\) The intensity of the peaks observed in the XRD pattern of the MoS2 powder was low compared with the peak intensity of the MoO3 powder, indicating that the highly crystalline MoO3 powders were transformed into an amorphous-like MoS2 powders during the sulfidation process. The transformation of MoO3 into MoS2 by
The sulfidation process was confirmed by X-ray photoelectron spectroscopy (XPS) spectra. Fig. 1b and c show the Mo 3d region and S 2p region of the XPS spectrum for MoS2 yolk–shell powders, respectively. In the region of Mo 3d, the binding energies observed at 228.8 and 232.0 eV, which can be assigned to Mo 3d5/2 and Mo 3d3/2 binding energies of Mo4+.

The peaks at 161.5 and 162.7 eV can be attributed to S 2p3/2 and S 2p1/2 binding energies. The stoichiometric ratio of Mo : S estimated from the respective integrated peak area of XPS spectra is 2.2 suggesting that the structure is close to MoS2. The XPS results exhibited that the MoO3 powders were completely transformed into MoS2 powders after the sulfidation process.

Fig. 2 shows the morphologies of the MoS2 yolk–shell powders. The MoS2 powders were completely spherical without aggregation. The mean size of the MoS2 yolk–shell powders determined from the SEM images was 0.6 μm, which was similar to that of the yolk–shell MoO3 precursor powders shown in Fig. S2b. The low-resolution TEM image shown in Fig. 2b illustrates the clear yolk–shell structure of the prepared MoS2 powders. All of the powders shown in Fig. 2b had a spherical single core inside a single shell. The high-resolution TEM image shown in Fig. 2c and the selected area electron diffraction (SAED) pattern as an inset of Fig. 2c revealed the amorphous-like structure of the yolk–shell MoS2 powders. An interlayer distance of 0.62 nm was derived, which corresponds to the (002) plane of MoS2. The uniform distribution of molybdenum and sulfur in the shell and core regions shown by the dot-mapping images in Fig. 2d indicate that the yolk–shell MoO3 powders were fully transformed into yolk–shell MoS2 powders. The yolk–shell MoS2 powders had mesopores with a mean pore size of 7 nm as shown in Fig. S3. The BET surface area of the yolk–shell MoS2 powders was 4.1 m² g⁻¹.

The spherical MoS2 powders with dense structures were prepared by a two-step process. The as-prepared MoO3 powders obtained by spray pyrolysis from a spray solution containing the molybdenum precursor were sulfidated under the same conditions with the yolk–shell MoS2 powders for comparison of the electrochemical properties of these species with those of the yolk–shell powders. Precursor powders with dense structures were formed as a final product in the reactor maintained at 600 °C during spray pyrolysis. One powder was formed from one droplet by drying, decomposition, and crystallization even when the residence time of the powder inside the hot wall reactor was as short as 1.7 s. The as-prepared powders exhibited pure MoO3 structures without impurity as shown in Fig. S4. The morphologies and crystal structures of the spherical MoS2 powders with dense structures are shown in Fig. 3. The major peaks in the XRD pattern of the prepared powders were consistent with hexagonal MoS2. The MoS2 powders that were prepared by spray pyrolysis and a subsequent sulfidation process had a completely spherical shape and nonaggregation characteristics. The SEM image of the crushed powders and the TEM image of the MoS2 powders in Fig. 3d and e show the dense morphology of the MoS2 powders. The dot-mapping images of the dense MoS2 powders confirmed the uniform dispersion of Mo and S components all over the powder, as shown in Fig. 3f. The mean size of the MoS2 powders with dense structures was 0.8 μm.

The electrochemical properties of the yolk–shell and dense structured MoS2 powders are shown in Fig. 4. Fig. 4a shows the first three cyclic voltammograms (CVs) of the yolk–shell MoS2 powders. In the first discharge cycle, three main cathodic peaks were observed at around 1.34, 1.11, and 0.56 V. The cathodic peaks at ca. 1.34 and 1.11 V are attributed to the intercalation of Li-ions into the MoS2 lattice with phase transformation from 2H (trigonal prismatic) to 1T (octahedral) Li₁ₓMoS₂₄⁻ₓ. The peak at around 0.56 V corresponds to the conversion reaction process, in which Li₁ₓMoS₂ was decomposed into Mo nanocrystals embedded in a Li₂S matrix and formation of a gel-like polymeric layer, which resulted from electrochemically driven electrolyte degradation. In the first reverse scan, the two anodic peaks were observed at voltages of 1.47 V and 2.3 V, respectively.
which correspond to the conversion reaction of Mo and Li$_2$S to MoS$_2$.\textsuperscript{44-46} In the second and third cycles, the reduction peaks were observed at 1.94, 1.01, and 0.52 V, respectively, which are associated with the formation of S from Li$_2$S, and conversion of MoS$_2$ to Li$_x$MoS$_2$, and the decomposition of Li$_x$MoS$_2$ to Mo and Li$_2$S.\textsuperscript{45} The CV curves of the second and third cycles almost overlapped, indicating that the yolk–shell MoS$_2$ powders exhibited good electrochemical reversibility. Fig. 4b shows the discharge and charge voltage profiles of the yolk–shell MoS$_2$ powders for the first three cycles at a current density of 1000 mA g$^{-1}$. In the first discharge cycle, two plateaus were observed at 1.2 V and 0.6 V; the plateau at 0.6 V became less prominent in the subsequent discharge cycles, which is consistent with the CV results. Initial discharge and charge capacities of 791 and 651 mA h g$^{-1}$ respectively were measured for the yolk–shell MoS$_2$ powders, corresponding to a Coulombic efficiency of 82%. In contrast, the dense structured MoS$_2$ powders had initial discharge and charge capacities of 622 and 490 mA h g$^{-1}$, respectively, corresponding to a Coulombic efficiency of 79% (see Fig. S5†). The irreversible capacity losses of the MoS$_2$ powders in the initial cycles originated from the formation of a solid electrolyte interphase (SEI) layer irrespective of the morphologies of the powders.\textsuperscript{39} Fig. 4c shows the cycling performances of the yolk–shell and dense structured MoS$_2$ powders at a constant current density of 1000 mA g$^{-1}$. The discharge capacity of the dense structured MoS$_2$ powders was 362 mA h g$^{-1}$ after 100 cycles and the corresponding capacity retention was only 58% of the initial discharge capacity. In contrast, the yolk–shell MoS$_2$ powders exhibited a high discharge capacity of 687 mA h g$^{-1}$ after 100 cycles and the corresponding capacity retention was as high as 87% of the
MoS₂ powders was recovered when the current density returned above 99% from the 8th cycle as shown in Fig. 4c. The Coulombic efficiency of the yolk–shell MoS₂ powders was 805, 746, 712, 692, and 636 mA h g⁻¹ after 100 cycles measured from the second cycle, respectively. The Coulombic efficiency of the yolk–shell MoS₂ powders reached above 99% from the 8th cycle as shown in Fig. 4c.

The yolk–shell and dense structured MoS₂ powders were prepared by a similar process. Higher discharge and charge capacities and better cycling and rate performances were achieved with the yolk–shell MoS₂ powders relative to the dense structured MoS₂ powders. The unique structure of the yolk–shell MoS₂ powders with a distinct MoS₂@void@MoS₂ configuration improved their electrochemical properties even at high current densities. The yolk–shell MoS₂ powders prepared by this simple two-step protocol are prospectively applicable in various fields including energy storage.

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Notes and references


Conclusions

A simple process for preparation of single-shelled yolk–shell MoS₂ powders was introduced herein. Complete sulfidation of yolk–shell MoO₃ powders at 400 °C produced the yolk–shell MoS₂ powders with a uniform distribution of Mo and S throughout the shell and core. The electrochemical properties of the yolk–shell MoS₂ powders were compared to those of dense structured powders prepared by a similar process. Higher discharge and charge capacities and better cycling and rate performances were achieved with the yolk–shell MoS₂ powders relative to the dense structured MoS₂ powders. The unique structure of the yolk–shell MoS₂ powders with a distinct MoS₂@void@MoS₂ configuration improved their electrochemical properties even at high current densities. The yolk–shell MoS₂ powders prepared by this simple two-step protocol are prospectively applicable in various fields including energy storage.


