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Tungsten Disulfide Nanotubes for Lithium Storage

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WS₂ nanotubes were synthesized by sintering amorphous WS₃ at high temperature under flowing hydrogen. High-resolution transmission electron microscopy observation revealed that the as-prepared WS₂ nanotubes have an open end with an inner hollow core of about 4.6 nm. We studied the lithium intercalation behavior of WS₂ nanotubes. The WS₂ nanotubes demonstrated a stable cyclability in a wide voltage range (0.1-3.1 V vs. Li/Li⁺). The nanotubes could provide a new class of electrode materials for lithium-ion batteries.

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Since the discovery of WS₂ and MoS₂ nanotubes by Tenne and co-workers,¹⁻⁴ extensive investigations have been done on the synthesis and physical and structural characterization of metal dichalcogenide nanotubes. Tenne *et al.* synthesized WS₂ nanotubes by treating tungsten films in an atmosphere of hydrogen sulfide and fullerene-like MoS₂ nanotubes by gas-phase reaction between MoO₃ thin-films and H₂S at high temperature.^{1,4} Rao *et al.* employed hydrogen treatment of amorphous MoS₃ and WS₃ to produce MoS₂ and WS₂ nanotubes with a high rate of yield.⁵ These nanotubes have an average outer diameter of about 25 nm. MoS₂ and WS₂ nanotubes have also been synthesized by chemical transportation using iodine as the transport agent,⁶⁻⁸ by the activation method (acid treatment following by sonication),⁹ and by template synthesis.¹⁰ The yield of nanotubes usually is in the range of 15-20% by these approaches. Numerous new transition metal disulfide nanotubes such as TiS₂, NbS₂, and TaS₂ have also been prepared.^{11,12}

The one-dimensional (1D) nanotube materials have various potential applications ranging from quantum computers to nanoscale biomedical sensors.^{13,14} Carbon nanotubes have been proposed for hydrogen storage¹⁵ and for applications related to lithium-ion batteries and fuel cells.¹⁶ Thin films of fullerene-like MoS₂ nanoparticles have ultralow friction and wear.¹⁷ It has been reported that MoS₂ nanotubes have a moderate hydrogen storage capacity¹⁸ and MoS_{2-x}I_y nanotubes have demonstrated a reversible lithium intercalation capacity of 385 mAh/g.¹⁹ Lithium-ion batteries are the most advanced power sources for modern portable electronic devices. The development of next generation lithium-ion batteries with high energy relies on new electrode materials.²⁰ Here we report, for the first time, the lithium intercalation properties of WS₂ nanotubes in lithium-ion cells.

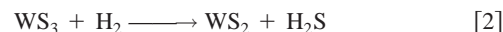
Experimental

WS₂ nanotubes were synthesized by high-temperature treatment of amorphous WS₃ in hydrogen. Amorphous WS₃ was obtained by decomposition of (NH₄)₂WS₄ at low temperature under flowing argon. The starting (NH₄)₂WS₄ powders were purchased from Sigma-Aldrich Chemical. The yield of WS₂ nanotubes is high, more than 80%. The as-prepared WS₂ nanotubes were studied using 300 kV JEOL JEM-3000F transmission electron microscope (TEM) with field emission. The electrochemical properties of WS₂ nanotubes were measured via coin cell testing. The WS₂ nanotube electrodes were made by dispersing 84 wt % active materials, 8 wt % carbon black, and 8 wt % polyvinylidene fluoride (PVDF) binder in dimethyl phthalate solvent to form a homogeneous slurry. The slurry was then spread on a copper foil. The coated electrodes were dried in a vacuum oven at 120°C for 12 h and then pressed to enhance the contact between the active materials and the conductive carbons. The CR2032 coin cells were assembled in an argon-filled glove box

(Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by Merck KgaA, Germany). The cells were galvanostatically discharged and charged in the voltage range of 0.01-3 V. Cyclic voltammetry (CV) measurements were performed on WS₂ nanotube electrodes using an EG&G scanning potentiostat (model 362) at a scanning rate of 0.1 mV/s.

Results and Discussion

Amorphous WS₃ powders were first synthesized by decomposing ammonium tetrathiotungstate [(NH₄)₂WS₄] at low temperature. WS₂ nanotubes were then prepared by sintering the as-obtained amorphous WS₃ at high temperature under flowing hydrogen. The two reaction steps involved are



The yield of WS₂ nanotubes is high, more than 80%. X-ray diffraction (XRD) was performed on the intermediate product WS₃ and the final product WS₂, which confirmed the amorphous nature of WS₃ and the hexagonal phase of WS₂. The WS₂ nanotubes were studied using JEOL-3000F transmission electron microscope with field emission. Figure 1a shows a TEM image of the as-prepared WS₂ nanotubes. The nanotubes in Fig. 1a have open tips, and some of them have a nearly rectangular tip shape. This is in contrast to a previous report,⁵ which demonstrated a closed tip. The outer diameters of these WS₂ tubes are about 30-40 nm with a wall thickness of 15 nm. The hollow core of the nanotubes is about 4.6 nm, which is indicated in Fig. 1a. These WS₂ nanotubes are also short in length (a few hundred nanometers), straight, and well dispersed. Some nest-shell nanoclusters are also presented in Fig. 1a. Figure 1b shows a more magnified TEM image of WS₂ nanotubes, which demonstrates that nanotubes stick together to form bundles. The

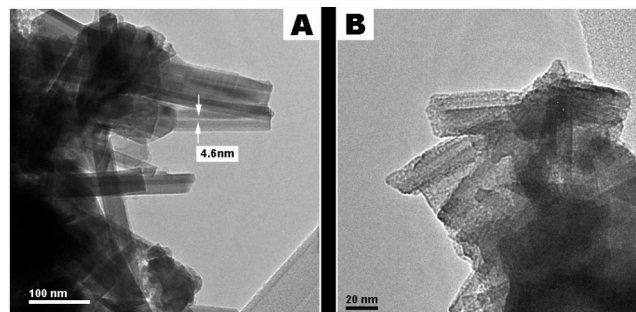


Figure 1. TEM images of WS₂ nanotubes.

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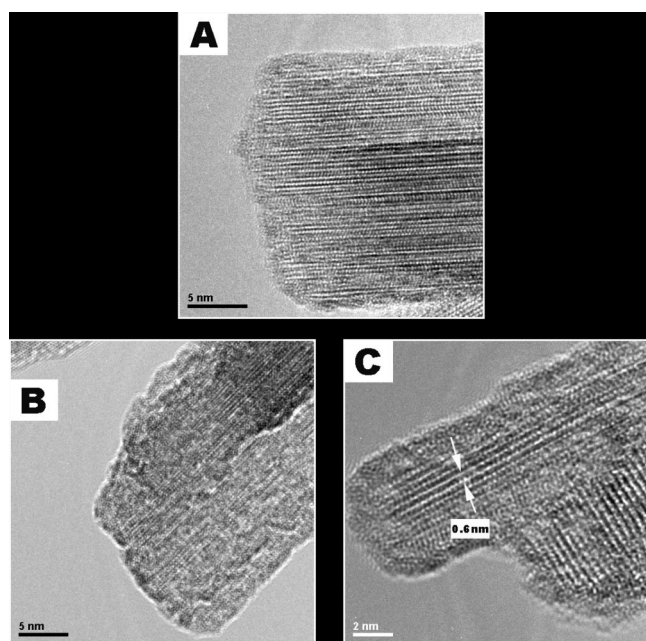


Figure 2. HRTEM images of WS₂ nanotubes.

outer diameter of the WS₂ nanotubes in Fig. 1b is about 25 nm. High-resolution TEM images of WS₂ nanotubes are shown in Fig. 2. Figure 2a shows the tip of a straight WS₂ nanotube with an outer diameter of ~20 nm. This nanotube has a nonspherical open tip and a clear-cut outside wall. Figure 2b shows the tip of another WS₂ nanotube, which has an onionlike cluster structure. A more magnified HRTEM image of a WS₂ nanotube is shown in Fig. 2c. The interlayer spacing is about 0.6 nm, corresponding to the (002) plane.

The electrochemical properties of WS₂ nanotubes were measured via coin cell testing. Figure 3a and b shows the cyclic voltammograms (CVs) of a WS₂ nanotube electrode in the first scanning cycle, the second and the third scanning cycles, respectively. In the first scanning cycle (Fig. 3a), the broad cathodic peak starts from 1.0 V and is centered at 0.5 V; whereas the anodic peak is located at 2.42 V. In the second scanning cycle, the cathodic peak at 0.5 V has disappeared, while instead, a new cathodic peak appears at 1.85 V. From the second cycle, the CV curves remain consistent and maintain a pair of redox peaks, representing the lithium intercalation plateau at ~1.85 V and the lithium deintercalation plateau at ~2.42 V.

The discharge/charge profiles of WS₂ nanotube electrode in the first and second cycles are presented in Fig. 4a and b. In the first cycle, the WS₂ nanotube electrode delivered a lithium insertion capacity of about 915 mAh/g, corresponding to 8.6 mol lithium per mole WS₂ nanotubes. This is much higher than for WS₂ powders (assuming the layered WS₂ host can accommodate the insertion of 1 mol Li⁺ per mol WS₂²¹). The high lithium insertion capacity of WS₂ nanotubes could be ascribed to their 1D structure. The HRTEM analysis has identified that WS₂ nanotubes have open ends and a hollow core of about 4.6 nm in diameter. The individual straight WS₂ nanotubes stick together to form bundles. Some WS₂ nanoclusters are also present. Therefore, there are four possibilities for lithium intercalation in the WS₂ nanotube electrode, (i) lithium ions intercalate into intratubular sites (the hollow core) through the open end, (ii) lithium ions intercalate into intertubular sites (the sites between individual nanotubes) through diffusion in the bundles, (iii) lithium ions intercalate into WS₂ nano clusters and (iv) lithium ions intercalate into layered WS₂ structures, including in

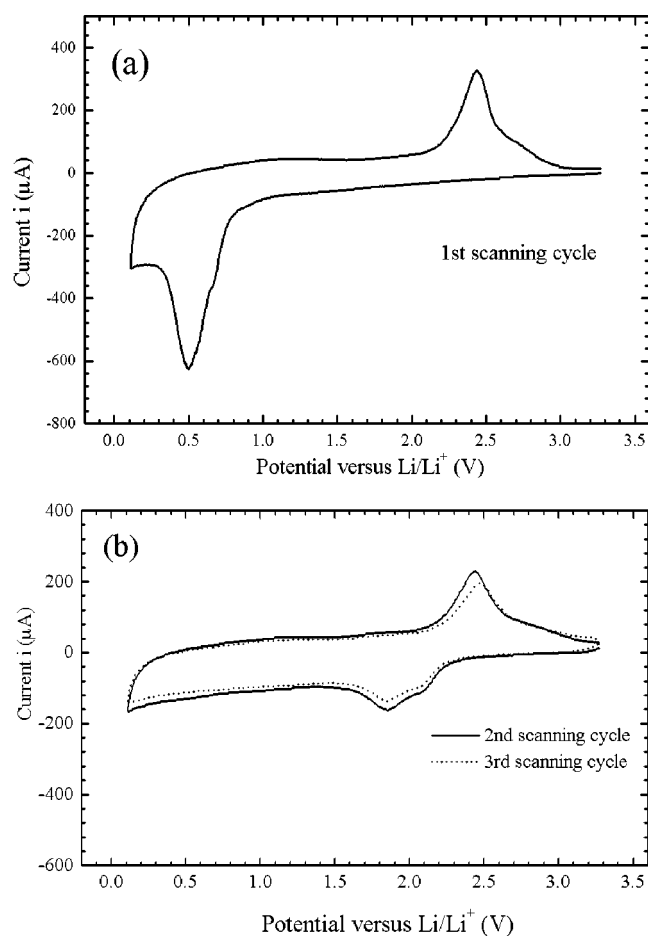


Figure 3. CVs of WS₂ nanotube electrode. (a) The first scanning cycle and (b) the second and the third scanning cycles.

nanotube structures and nanocluster structures. All these four possibilities may contribute to the high lithium insertion capacity of WS₂ nanotube electrodes.

We observed two lithium insertion plateaus at ~0.8 and ~0.6 V as well as a slope starting from 0.5 V down to the cutoff voltage of 0.1 V in the first cycle. Dominko *et al.*¹⁹ attributed the 0.8 V insertion plateau to the reaction between Li⁺ and interstitial iodine in MoS_{2-x}I_y nanotubes and the 0.6 V plateau to lithium insertion in MoS_{2-x}I_y bundles. Because our WS₂ nanotube sample does not contain iodine, we attribute both plateaus to lithium insertion in the WS₂ nanotube bundles (either intertubular or intratubular sites). Surprisingly, we found that the lithium extraction potential is located at a much higher voltage of 2.3 V vs. Li/Li⁺. From the second cycle, the discharge plateau is located at 2.0 V. (The discharge plateau at low potential observed in the first cycle disappeared.) The charge/discharge plateaus match very well with the anodic and cathodic peaks in the CV curves (Fig. 3). The significant difference between the first discharge and second discharge may be associated with the physical and structural changes after lithium intercalation into WS₂ nanotubes.

The electrochemical behavior of WS₂ nanotube is significantly different from that of crystalline WS₂ powders, which was described in a previous report.²² The lithium insertion capacity was only 0.6 mol Li⁺ per mole crystalline WS₂. We attribute this difference to the 1D topology of WS₂ nanotubes. The 1D WS₂ nanotubes have an open structure. We suggest that, in the first lithiation process, lithium ions predominantly intercalate into intratubular and intertubular sites in WS₂ nanotubes. Once these intra- and intertubular sites are satu-

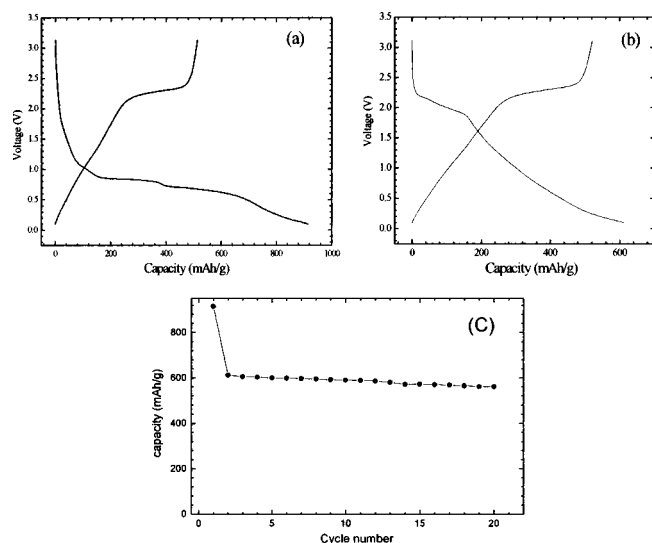


Figure 4. (a) Discharge/charge profiles of WS₂ nanotube electrode in the first cycle. (b) Discharge/charge profiles of WS₂ nanotube electrode in the second cycle. (c) Discharge capacity vs. cycle number for WS₂ nanotube electrode.

rated with Li⁺, lithium ions will then diffuse into WS₂ structure to form Li_xWS₂ intercalation compounds due to the high concentration of Li⁺ in these sites. During charging, a fraction of Li⁺ ions first deintercalate from the bundles of WS₂ nanotubes at low potentials (observed as the slope in the charging curve), and then deintercalate from Li_xWS₂ structures at high potentials (observed as the plateau on the charging curve). But the fraction of Li⁺ ions trapped in the intra- and intertubular sites induce irreversible capacity. The high irreversible capacity in the first cycle may also be caused by the decomposition of electrolyte on the surface of WS₂ nanotubes to form a passivation layer on the electrode. From the second cycle, lithium inserted into WS₂ structure at high potential and then inserted into the bundles of WS₂ nanotubes at low potential; vice versa for deintercalation process. So, after the first cycle, the intercalation reaction dominates the electrochemical process, which is evidenced by the plateau at 2.0 V in Fig. 4b. Compared to the charge capacity, the increased discharge capacity in Fig. 4b may be due to the use of a Li auxiliary electrode. The low cutting potential in the discharge probably causes the passivation of lithium on the electrode. It is claimed that the intercalation compound (Li_xWS₂) decomposed to a mixture of W and Li₂S for a high degree of Li insertion ($x > 1$) in crystalline WS₂ powders.²² Because the CV measurement does not detect any decomposition reactions, this process is unlikely to occur for WS₂ nanotubes. Figure 4c shows the lithium insertion capacity vs. the cycle number. After the first cycle, the WS₂ nanotube electrode exhibited stable cycling behavior in a wide voltage range of 0.1–3.1 V vs. Li/Li⁺.

Because the WS₂ nanotubes demonstrated a high discharge plateau at 2.0 V, they can be used as cathodes with a cutoff voltage of 1.5 V vs. Li/Li⁺. When WS₂ nanotube electrodes were cycled between 1.5 and 3.0 V from the second cycle, they had an approximate capacity of 200 mAh/g. Compared to the other high potential cathode materials such as LiCoO₂ (3.6 V), the energy density of WS₂ nanotubes is relatively lower. Whereas WS₂ nanotubes also demonstrated an interesting electrochemical behavior when cycled at low potential range. One WS₂ nanotube electrode was cycled between 0.1 and 1.5 V, and it showed a capacity of about 350 mAh/g.

Conclusion

We have synthesized and characterized WS₂ nanotubes. The WS₂ nanotubes demonstrated a significant different electrochemical properties compared to the crystalline WS₂ powders. The WS₂ nanotube electrodes show stable cyclability over a wide voltage range. Nanotube materials may provide a class of versatile electrode materials for lithium-ion batteries with improved electrochemical characteristics.

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