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TiS$_2$ nanotubes as the cathode materials of Mg-ion batteries

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Titanium disulfide (TiS$_2$) nanotubes were used as the cathode materials of rechargeable magnesium-ion batteries, showing potential low-cost, high-capacity, and good-reversibility properties.

There is an urgent demand for the research and development of additional rechargeable battery systems that will be made of cheap and environmentally friendly materials. Currently it seems that the rechargeable magnesium-ion battery is one of the systems of choice because Mg resources are highly abundant in the earth and are environmentally friendly.[1] Mg-ion batteries rely on the intercalation of Mg ions into the designed cathode.[2] It has been reported that the inorganic transition-metal chalcogenides such as TiS$_2$ have been used as the cathode materials of rechargeable lithium-ion batteries.[3] An average discharge voltage of 2.1 V, an almost 100% TiS$_2$ utilization, and a single homogeneous phase of intercalation with only 10% lattice expansion in the entire intercalation range of up to $x = 1$ in Li$_x$TiS$_2$ are the characteristics of TiS$_2$.[4] Recently, one-dimensional TiS$_2$ microtubules[5] and nanotubes[6,7] have been prepared and these tubular structures have shown potential applications in fields of energy storage such as Li-ion intercalation and hydrogen storage.[8,9] We here show that TiS$_2$ nanotubes can reversibly intercalate and deintercalate large amounts of Mg ions in the channels held by van der Waals interactions. The result indicates that TiS$_2$ nanotubes are attractive materials for the cathode of rechargeable Mg-ion batteries.

The TiS$_2$ nanotubes, prepared by a low-temperature gas reaction,[7] were mixed with carbon black (15%) and polytetrafluoroethylene (5%). This mixture was pasted into nickel foam and compressed by an oil machine at 150 MPa to fabricate the working electrode (Φ 10 mm × 0.1 mm). Electrochemical measurements were carried out by using two-electrode cells with Mg foil as the counter and reference electrode. The cell installation was performed in a glove box filled with pure argon (99.999%) in the presence of an oxygen scavenger and a sodium-drying agent. The electrolyte solution was 1 M Mg(ClO$_4$)$_2$ dissolved in acetonitrile. For parallel comparison, TiS$_2$ polycrystalline powder with an average particle size of about 20 μm was also prepared as the working electrode with the same experimental conditions. Brunauer–Emmett–Teller (BET) measurements by the nitrogen adsorption/desorption[10] showed that the specific surface areas of the TiS$_2$ nanotubes and polycrystallites are 28.5 and 2.6 m^2 g^{-1}, respectively. The electrochemical performance was investigated by means of a Solartron SI 1260 Potentionstat Analyzer with 1287 Interface and an Arbin charge-discharge unit. The discharge capacity in any electrode was based on the amount of the active material (TiS$_2$) not including the weight of the additives in the electrode.

Fig. 1 shows the cyclic voltammograms of the two TiS$_2$ electrodes for the first Mg intercalation ($Mg^{2+} + 2e^- \rightarrow Mg$) and deintercalation ($Mg \rightarrow Mg^{2+} + 2e^-$) at 20 °C. Similarly shaped voltammograms were also obtained for the coming five cathodic and anodic cycling. Since reversible peaks were observed, it can be judged that the TiS$_2$ nanotubes and polycrystallites can, indeed, reversibly intercalate and deintercalate Mg, but their characteristics are different. An interpretation of this figure follows. First, when the electrodes were scanned cathodically, a peak appeared with the peak position at about 0.98 V *versus* Mg, being attributed to Mg intercalation in the TiS$_2$. During the following anodic polarization, a peak was observed at 1.2 V *vs.* Mg, assigned to Mg deintercalation. Second, the values of peak currents of Mg intercalation and deintercalation for TiS$_2$ nanotubes were much larger than that of the polycrystalline TiS$_2$ electrode, revealing higher Mg intercalation/deintercalation capacity in the nanotube electrode. Third, the peak similarity between the cathodic and anodic cycling suggests that the electrochemical Mg intercalation/deintercalation proceeds reversibly, showing a desirable characteristic of rechargeable batteries. Consequently, it demonstrates that Mg can be reversibly intercalated and deintercalated in TiS$_2$, but the processes for the intercalation and deintercalation are much more effective in the nanotube electrode.

Fig. 2 shows typical discharge curves of the TiS$_2$ nanotube and polycrystalline electrodes at different discharge current densities. A maximum discharge capacity of 236 mAh g^{-1}, which corresponds to an intercalation of about 0.49 Mg per formula unit ($\sim$Mg$_{0.49}$TiS$_2$),[11] is achieved at 10 mA g^{-1} and in the range of 2.0–0.5 V. In addition, the discharge capacities of 193 mAh g^{-1} ($x = 0.4$) and 140 mAh g^{-1} ($x = 0.29$) were optimized at the current densities of 20 and 40 mA g^{-1}, respectively. As a comparison, the discharge capacity of polycrystalline TiS$_2$ powder at 10 mA g^{-1} was only about 96 mAh g^{-1} ($\sim$Mg$_{0.2}$TiS$_2$), while the

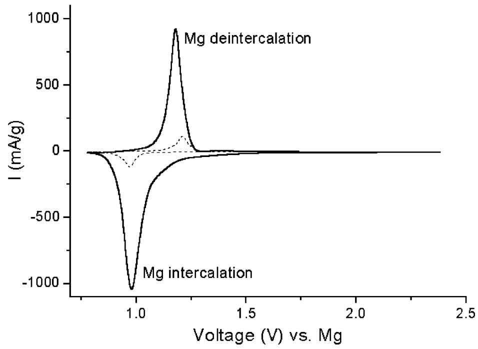

Fig. 1 Cyclic voltammograms of TiS$_2$ nanotube (solid) and polycrystalline powder (dots) electrodes at the temperature of 20 °C and the scan rate of 0.5 mV s^{-1}.

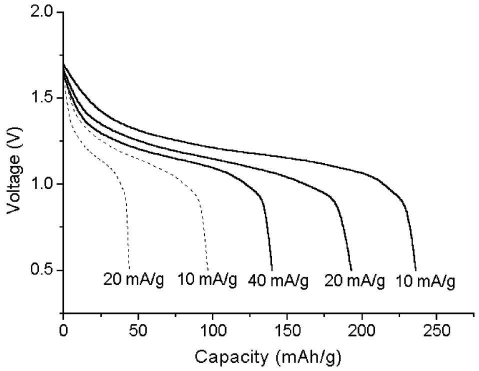

Fig. 2 Discharge curves of TiS$_2$ nanotube (solid) and polycrystalline (dots) electrodes at various discharge current densities and 20 °C.

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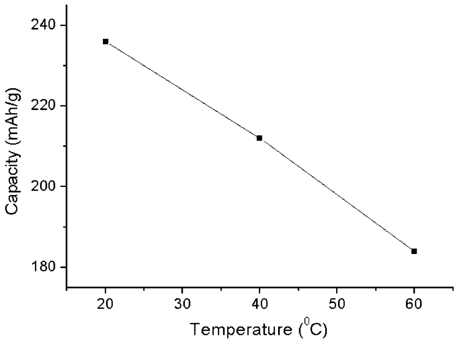

Fig. 3 Discharge capacity of TiS_2 nanotube electrode at the working temperature of 20, 40, and 60 °C.

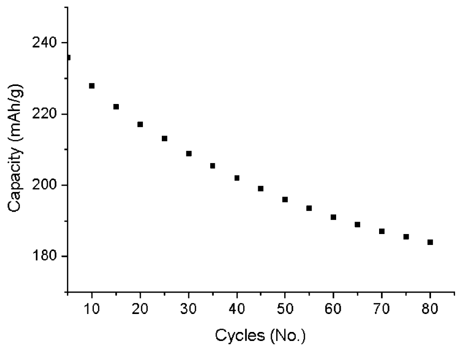

Fig. 4 Variation of discharge capacity of TiS_2 nanotube electrode with the numbers of discharging and charging at 20 °C.

capacity decreased to 45 mAh g^{-1} ($\sim Mg_{0.1}TiS_2$) at 20 mA g^{-1}. Therefore, the TiS_2 nanotube electrode exhibits quite different properties from those of its polycrystalline analogues. In particular, the reversible Mg intercalation with much higher capacity and better high-rate discharge ability has been achieved in TiS_2 nanotube electrodes due to their tubular structure with higher specific surface areas.

Fig. 3 shows the relationship between the discharge capacity and the working temperature of the TiS_2 nanotube electrode. From which, it can be seen that the discharge capacity of this electrode decreases only slightly with increase in the working temperature. For example, the electrode still kept 184 mAh g^{-1} at 60 °C, which is about 78% of the capacity at 20 °C. This feature is of critical importance in rechargeable batteries for high-temperature tolerance.

Fig. 4 displays the plot of discharge capacity *vs.* cycle numbers for the TiS_2 nanotube electrode. A preliminary test of 80 cycles at 100% depth of discharge shows about 22% capacity fading, namely an average capacity loss of 0.65 mAh g^{-1} per cycle.

According to the present experimental results, a 0.49 : 1 ratio is established between the Mg and the TiS_2 nanotube after the intercalation process. This means that the molecular sheets in the multiwalled nanotubes are reactive. Then, the great challenge would be to understand the intercalation mechanism. The main question is how do the Mg ions diffuse to the reactive sites. In TiS_2 nanotubes, owing to their much more orderly structure arrangement than their polycrystalline counterparts, the van der Waals gap between the S–Ti–S/S–Ti–S layers can be fully utilized during the intercalation process. After discharging and charging for 80 cycles, the electrode in the discharged state was opened in a dry box, and the material was recovered and washed with acetonitrile before being loaded on the TEM grid. The TEM image as shown in Fig. 5 shows that agglomeration of the reaction product is aligned around the tube wall. This may indicate that there is an increasing proportion of active sites in the nanotubes. On the other hand, bulk TiS_2 with small grains, which consist of platelets, would be as good for this purpose as the nanotubes; and this is under investigation. Nevertheless, the ordered arrangement of nanotube structures contributes at least to the superior capacity of the electrode.

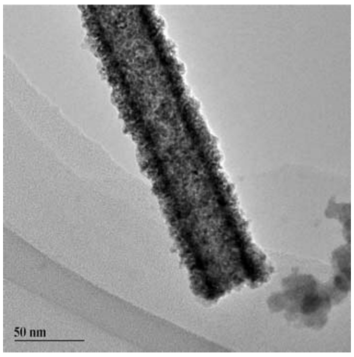

Fig. 5 TEM image of the TiS_2 nanotube electrode taken from the 80th cycle in the discharged state.

In summary, TiS_2 nanotubes can be used as the cathode materials of rechargeable Mg-ion batteries, showing important advantages in terms of environmental considerations, safety and relative high capacity. Further work on their applications and intercalation mechanism is in progress.

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11 The number of Mg atoms per formula unit (x) can be calculated from the discharge capacity (C_{dis}) by the Faraday equation, $x = 3600 (M_w \times C_{dis})/(2 \times 9.65 \times 10^7)$ where M_w is the molecular weight of TiS_2 and the units of C_{dis} are mAh g^{-1}.