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An investigation on electrochemical behavior of nanosize zinc sulfide electrode in lithium-ion cells

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Abstract Nanosize zinc sulfides were synthesized through the chemical reaction method. The as-prepared zinc sulfide nanopowders were characterized by X-ray diffraction, transmission electron microscopy and electrochemical testing. The results revealed that zinc sulfide electrodes exhibited a reversible lithium storage capacity of about 400 mAh/g with stable cyclability. Zinc sulfide nanopowders show promise as anode materials for lithium-ion batteries.

Keywords Lithium-ion battery · Anode · Zinc sulfide · Nanoparticles

Introduction

Recently, various lithium-based composite materials including metal, metal oxides and metal sulfides have been studied extensively as alternatives to replace current commercial carbonaceous anode material for lithium-ion batteries [1–3] because they show higher capacities than carbonaceous materials. However, the capacities fade on rapid cycling due to large volume changes during cycling [4–5]. An effective way to improve the cycling stability of metal alloy, metal oxide and sulfide electrodes is to modify their morphology by reducing their particle size to a few nanometers or by designing special nanostructures [6–8]. Indeed, this strategy is expected to have two effects on the performance of the electrodes. Firstly, improvement in cycling stability, since small particles enable easier accommodation of the mechanical strains (the absolute volume changes are smaller than for large particles, although the relative changes are the same). Secondly, enhancement

of power due to the reaction of the lithium ion diffusion length. The validity of this strategy has been confirmed by various authors [9–10].

In this paper, we report the preparation of zinc sulfide nanosize powders by one-step chemical reaction. The possibility of using zinc sulfide nanopowders as anode materials for lithium-ion batteries is examined.

Experimental

Zinc sulfide nanopowders were prepared by a chemical method, taking advantage of the small solubility of these materials in water [11]. Nanoparticles of zinc sulfide were prepared at room temperature by simultaneously dropping 20 ml of 1 M zinc sulfate (99.9%, Aldrich) solution and 1 M sodium sulfide (99.9%, Aldrich) solution into distilled water containing 0.1 M ethylene diamine tetra acetic acid (EDTA, Aldrich). The mixture solution was vigorously stirred using a magnetic stirrer. The insolubility of the zinc sulfide formed from the chemical reaction caused the formation of a number of new nuclei while preventing the growth of the already existing ones, thus limiting the size of the particles. The role of EDTA was to stabilize the particles against aggregation, which may lead to an increase in the size of the particles. The suspension was centrifuged at 4,000 rev/min for 15 min, and the precipitate was washed using deionised water with the assistance of an ultrasonic disintegrator. This procedure was repeated three times to remove any adsorbed ions. The precipitate was finally dried at 100°C in a vacuum oven for 10 h. Some resultant powder was then annealed at 450°C to improve the crystallinity.

The powders produced were characterised by X-ray diffraction (XRD) on a Philips PW1730 diffractometer with Cu K α radiation. The as-prepared zinc sulfide powder was studied by transmission electron microscope (TEM, JEOL 2010). The electrochemical experiments were carried out using coin cells. The zinc sulfide electrodes were made by dispersing 80% active materials,

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10% carbon black, and 10% polyvinylidene fluoride (PVDF) binder in dimethyl phthalate (DMP) solvent to form homogeneous slurries. The slurries were spread on copper foil substrates. The coated electrodes were dried in a vacuum oven at 100°C for 20 h and then pressed to enhance the contact between the active materials and the conductive carbons. After drying, the zinc sulfide electrodes were cut into 1×1 cm² size. CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the zinc sulfide electrodes and the lithium foil 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 range of 0.01–2.00 V at a current density of 0.05 mA/cm². Cyclic voltammetry (CV) measurements were performed using a potentiostat (model M362, EG&G Princeton Applied Research, USA) at a scanning rate of 0.1 mV/s.

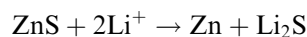
Results and discussion

The X-ray diffraction patterns of the as-prepared zinc sulfide and annealed powders are shown in Fig. 1. All diffraction lines are indexed to a cubic phase (S.G.: F-43 m). The X-ray diffraction peaks for as-prepared zinc sulfide powders are very broad, indicating their nanocrystalline nature. After annealing treatment, the intensities of diffraction peaks increase substantially, reflecting the increased crystallinity. The average crystal size of the zinc sulfide powders was determined by using the Traces Program and the Scherrer formula. The

crystal size is 3.41 nm for as-prepared zinc sulfide powders, and 11.12 nm for annealed powder.

Fig. 2 shows a TEM image of as-prepared zinc sulfide powders. The pristine crystals have an average crystal size of a few nanometers. The small crystals stick together, forming agglomerates. The electron diffraction pattern is shown in the inset of Fig. 2. We observed typical diffuse halo-rings, which are typical for nanocrystalline or amorphous materials.

Cyclic voltammograms of a zinc sulfide nanopowder electrode are shown in Fig. 3. In the first scanning cycle, a cathodic peak starts at 0.9 V with a maximum intensity at 0.6 V. This cathodic peak is attributed to the decomposition of zinc sulfide into metallic Zn and the formation of Li₂S:



Due to the nanocrystalline nature of zinc sulfide powders, part of the cathodic current was consumed in the formation of a passivation film (SEI) on the surface of the electrode.

There is a broad cathodic peak at 0.12 V in the first cycle, which corresponds to the formation of Li_xZn alloys.

From the second cycle, there are that can be clearly observed three anodic peaks that can be clearly observed at 0.30 V, 0.56 V and 0.70 V vs. Li/Li⁺, respectively. However, there are only two corresponding cathodic peaks that can be observed at 0.05 V and 0.45 V vs. Li/Li⁺. This may mean that two cathodic peaks have merged at 0.45 V vs. Li/Li⁺ [12]. The redox peaks in the low voltage range are related to the reversible formation and decomposition of lithium zinc alloys. It has been reported that lithium can form various Li_xZn alloys in the voltage range of 0.005–0.5 V versus Li/Li⁺ refer-

Fig. 1 X-ray diffraction patterns of zinc sulfide powders

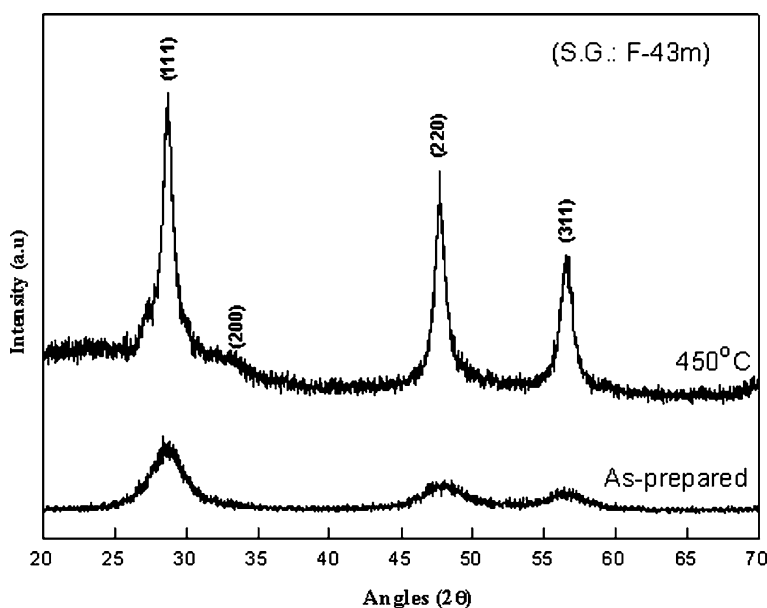


Fig. 2 TEM image of zinc sulfide nanocrystalline powders (inset: SAD electron diffraction pattern)

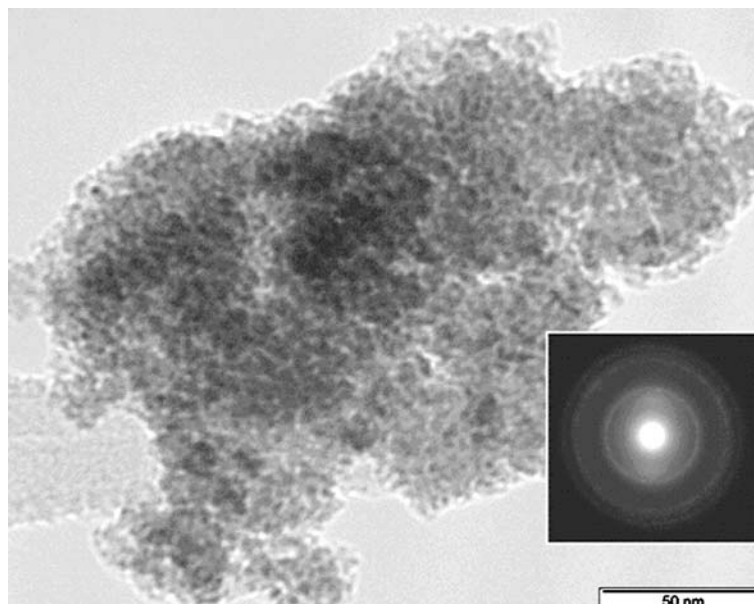
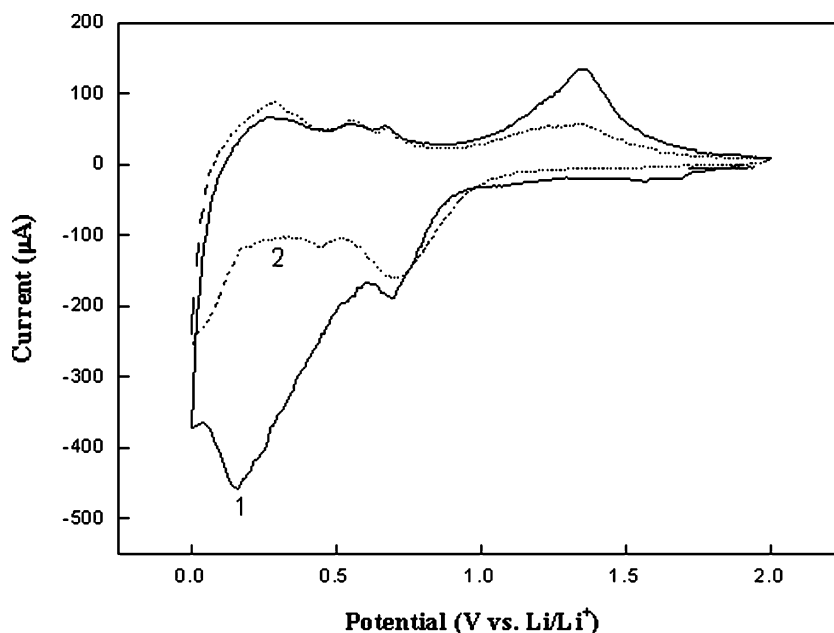
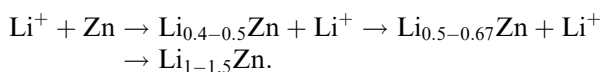


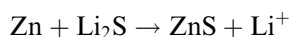
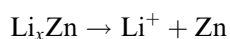
Fig. 3 Cyclic voltammograms of zinc sulfide electrode of as-prepared sample



ence electrode [13–14]. The reactions between Zn and Li^+ are:

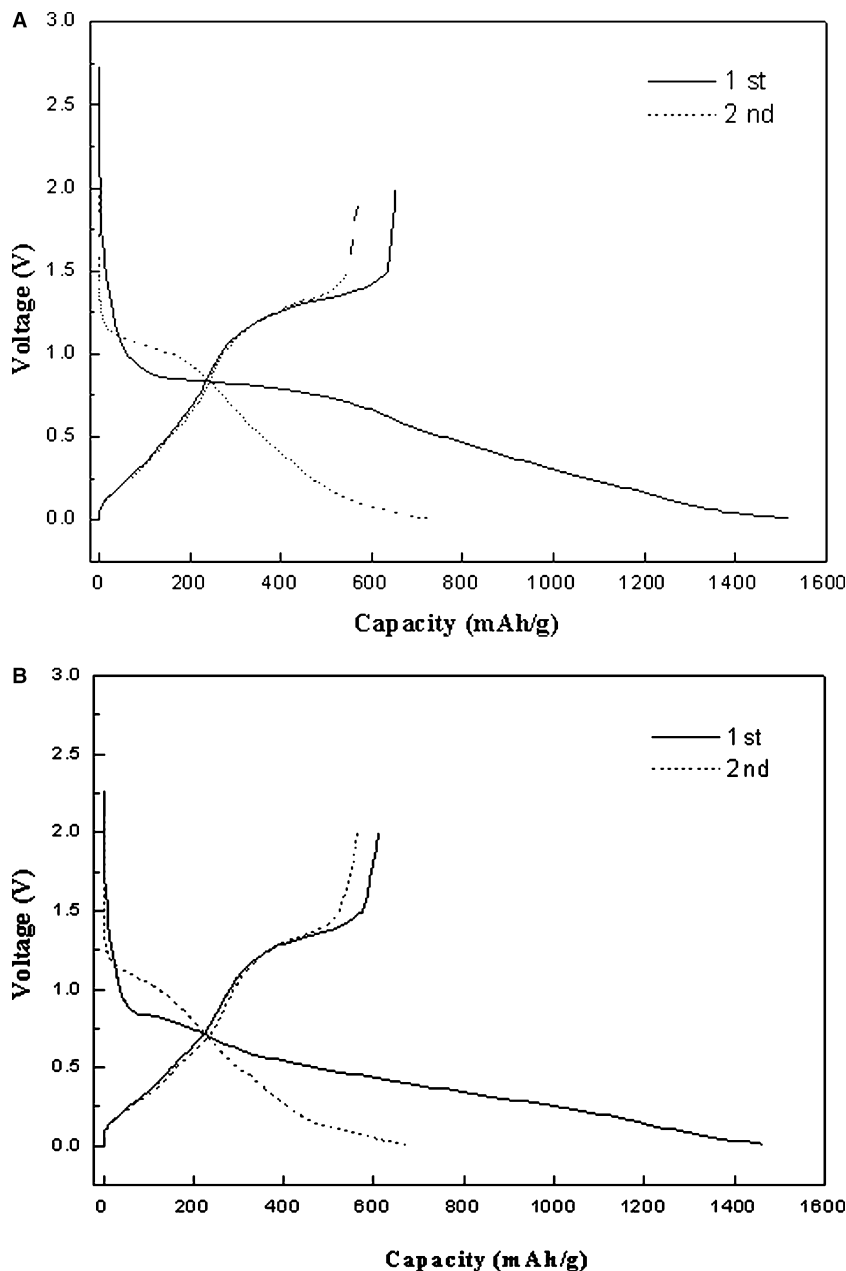


At the end of the cathodic scans, lithiation products of Li_xZn alloys and Li_2S are present. During the anodic scan, lithium ions are extracted from Li_xZn alloys to generate Li^+ and Zn in the low voltage range. With increasing scanning potential, ZnS is regenerated in a fully charged state, which is responsible for the anodic peak at 1.4 V. The reactions during the anodic scan can be expressed as [2, 3, 15]:



From CV results, it can be seen that the anodic peaks appeared in the range of 0.25–1.40 V versus Li/Li^+ , so the potential range of 0–2 V versus Li/Li^+ is enough for charge–discharge cycling. Fig. 4 shows the charge and discharge curves for zinc sulfide electrodes. The first cycle of both electrodes exhibits enormous irreversible capacity, which may be attributed to the irreversible reaction involved in the formation of the SEI layer. The irreversible capacity of the annealed sample was slightly

Fig. 4 The charge/discharge profiles of zinc sulfide electrodes: **a** As-prepared sample, **b** Annealed sample



smaller than that of the as-prepared zinc sulfide sample. During the subsequent cycle, the potential of the discharge plateaus is between 0.8 V and 0.0 V versus Li/Li^+ , which is suitable for anode materials for lithium-ion batteries. The potential of the charge plateaus is in the range of 0–1.5 V. The charge and discharge curves of zinc sulfide electrodes exhibit several discharge and charge plateaus, which involve a series of different reactions as the CV measurement demonstrates.

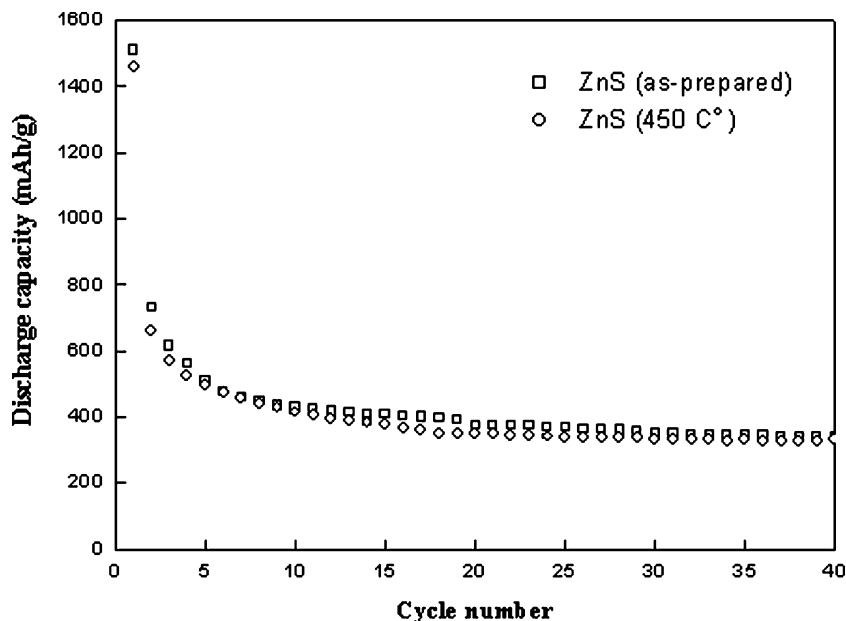
Fig. 5 shows the discharge capacity versus the cycle number for cells made from as-prepared and annealed samples. It can be seen that the initial discharge capacities of the two samples are both quite high, approximately 1,500 and 1,450 mAh/g for as-prepared and annealed samples, respectively. The capacity declined

rapidly to about 400 mAh/g after 15 cycles and maintained for more than 15 cycles.

Conclusions

Nanocrystalline zinc sulfide powders were prepared by chemical precipitation. TEM observation shows that zinc sulfide powders have a pristine crystal size in the range of a few nanometers. The possibility of using zinc sulfide powders as an electrode material in lithium ion cells was explored through electrochemical testing. Cyclic voltammetry measurements revealed that there are several electrochemical reactions during the lithiation and de-lithiation process. Zinc sulfide electrode

Fig. 5 Discharge capacities vs. cycle number. Current density 0.05 mA/cm²



demonstrated a reversible lithium storage capacity of 400 mAh/g.

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