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Synthesis of nanocrystalline transition metal and oxides for lithium storage

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Abstract

Nanosize silver and tin dioxide powders were synthesised by a novel reverse micelle technique. The reverse micelles were formed from a microemulsion of organic solvents, water based salts and surfactants. The spherical nanosize Ag powders were formed via in situ reduction. The tin hydroxide precipitates were formed in reverse micelles and converted to tin dioxide nanopowders after heat treatment. The Ag and SnO_2 powders have a particle size in the range of 20–50 nm. The as-prepared nanosize Ag and SnO_2 nanopowders were used in lithium-ion cells for lithium storage.
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1. Introduction

Tin based alloys and composite anode materials have recently attracted world-wide attentions due to their high lithium storage capacity [1–4]. This class of anode materials relies on the formation of Li_xSn alloys and de-alloying for reversible lithium storage. However, this alloying process is always accompanied by a significant volume change, which has detrimental effects on the electrode performance. Several strategic approaches have been developed to overcome this problem: (1) using nanosize tin based anode materials to reduce the volume change associated with the alloying and de-alloying process in the local domain, (2) embedding active tin based anode materials in an inactive matrix to buffer the volume variation.

Many techniques have been developed for preparing metallic or inorganic nanopowders, such as chemical vapour condensation (CVC) [5], sol–gel synthesis [6], high energy ball milling [7], spray conversion processing [8], etc. The grain size, morphology, and texture can be varied by suitably modifying/controlling the process parameters in each

method. A technique using a water-in-oil microemulsion solution, so called reverse micelles, is one efficient approach to synthesis of nanoparticles. This technique has been extensively used to prepare nanoparticles of various materials, including metals, oxides, hydroxides and some inorganic compounds [9–14]. In this study, we prepared nanosize Ag powders and SnO_2 powders via a reverse micelle synthesis technique. The physical and electrochemical properties of the as-prepared Ag and SnO_2 nanopowders were characterised.

2. Experimental

2.1. Preparation of Ag nanopowders

Reverse micelles A consists of 0.5 M $AgNO_3$ solution, cetyltrimethylammonium bromide (CTAB) as surfactant, 1-butanol as co-surfactant, and octane as organic matrix. The ratio of the ingredient chemicals in reverse micelles A is 0.5 M $AgNO_3$:CTAB:1-butanol:octane = 16:24:18:42 wt.%. Reverse micelles B consist of 1 M $NaBH_4$ solution, cetyltrimethylammonium bromide (CTAB) as surfactant, 1-butanol as co-surfactant, and octane as organic matrix. The

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ratio of the ingredient chemicals in reverse micelles B is 1 M $NaBH_4$:CTAB:1-butanol:octane = 16:24:18:42 wt.%.

The reverse micelles A and B were mixed by stirring the mixture solution, initially with a magnetic bar and then with high speed mechanical stirring, to achieve a homogeneous microemulsion. After that, the reverse micelles A and B were mixed together slowly with vigorous stirring. The colour of the solution changed from yellow to dark grey, indicating that Ag^+ ions were reduced to Ag inside the aqueous droplets. The reacted solution was then centrifuged at 4000 rpm for 60 min to precipitate the Ag nanopowders. The precipitates were then washed with methanol several times. The washed powders were dried in vacuum at 80 °C for 5 h.

2.2. Preparation of SnO₂ nanopowders

The reverse micelles contain 1 M $SnCl_4$ solution, 1 M $NH_3 \cdot H_2O$ solution, AOT ($C_2OH_{37}NaO_7S$) as surfactant and *n*-heptane (C_7H_{16}) as organic matrix. The ratio of the ingredient chemicals in the reverse micelles is 1 M $SnCl_4$:1 M $NH_3 \cdot H_2O$:AOT:*n*-heptane = 15:24:18:42 wt.%. The reverse micelles were formed by mixing the reactant chemicals together with magnetic stirring and high speed stirring. The reactant product $Sn(OH)_4$ was formed inside the reverse micelles. The reacted solution was then centrifuged at 4000 rpm for 60 min to precipitate $Sn(OH)_4$ powders. The precipitated product was washed using methanol four times and then dried in vacuum at 80 °C for 5 h. The dried $Sn(OH)_4$ powders were then sintered at 600 °C to convert them to SnO_2 nanopowders.

2.3. Physical and electrochemical characterisation of Ag and SnO₂ nanopowders

X-ray diffraction was performed on the prepared Ag and SnO_2 powders to determine the phase purity using Cu Kα radiation (MO3xHF22, MacScience, Japan). The morphology of the Ag and SnO_2 powders was studied using a high resolution transmission electron microscope (300 kV JEOL JEM-3000F with field emission).

The electrochemical evaluation of the synthesized Ag and SnO_2 powders was accomplished by assembling CR2032 coin cells. The Ag electrodes were made by dispersing 78 wt.% Ag nanopowders, 15 wt.% carbon black and 7 wt.% polyvinylidene fluoride (PVDF) binder in *n*-methyl pyrrolidone (NMP) solvent to form a homogeneous slurry. The SnO_2 electrodes were made by dispersing 60 wt.% SnO_2 nanopowders, 30 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder in *n*-methyl pyrrolidone (NMP) solvent to form a homogeneous slurry. The slurry was then spread onto a Cu foil. The coated electrodes were dried in a vacuum oven under a vacuum pressure of 30 Torr at 120 °C for 12 h. The electrodes were then pressed at a pressure of 1200 kg cm^{-2} to enhance the contact between the active materials and the conductive carbons. The 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 $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). The cells were galvanostatically charged and discharged over a voltage range of 0–1.5 V. Cyclic voltammetry (CV) measurements were performed using an EG & G Scanning Potentiostat (Model 362) at a scanning rate of 0.1 mV s^{-1}.

3. Results and discussion

When a water based solution is mixed with an organic matrix, two completely separated phases will be formed. However, if appropriate surfactant is added and mechanical stirring is applied, a dispersion system will be formed, in which water droplets will be dispersed in the organic matrix through microemulsion. They are also called reverse micelles. Fig. 1 shows a schematic of the reverse micelles. We used high speed mechanical stirring and ultrasonic treatment, so that nanosized water droplets were obtained. When two reverse micelles reacted with each other, Ag powders were generated with small particle size. In case of the preparation of SnO_2 powders, we obtained nanosize tin hydroxides through the reverse micelle process. When the tin hydroxides were sintered at 600 °C, they were converted to SnO_2. Because the sintering temperature is low, the tin dioxide remains nanocrystalline.

Fig. 2 shows an X-ray diffraction pattern of the as-prepared Ag powders. The Ag powders have very good crystallinity
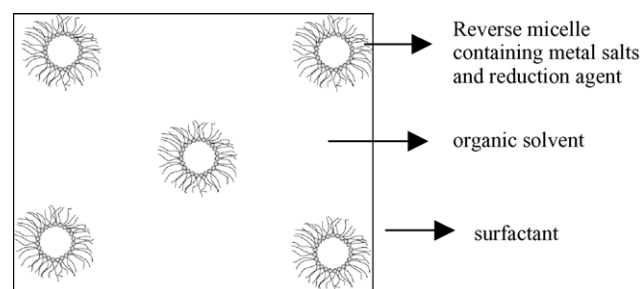

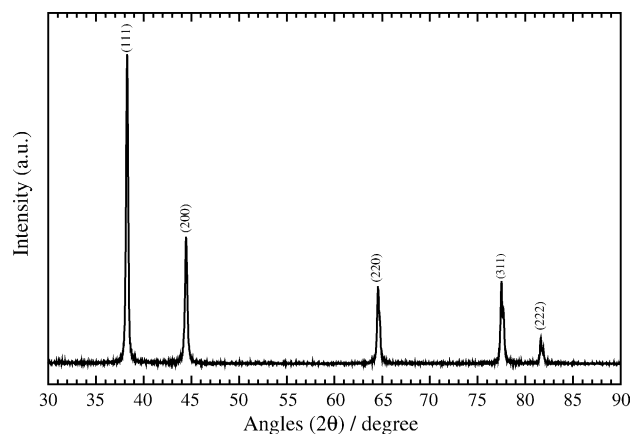Fig. 1. A schematic diagram of the reverse micelles.
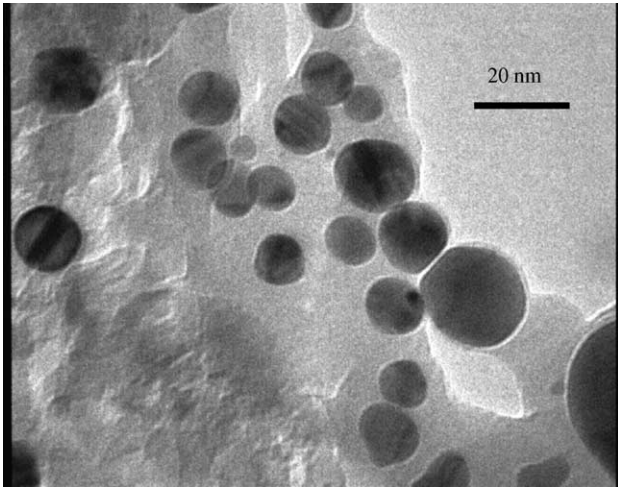

Fig. 2. X-ray diffraction pattern of nano Ag powders.

Fig. 3. TEM image of nano Ag powders.

Fig. 4. X-ray diffraction pattern of SnO$_2$ nanopowders.

and are phase pure. The surfactants and reductant have been thoroughly washed away. Therefore, we obtained pure Ag powders. A TEM image of the Ag powders is shown in Fig. 3. The Ag particles have a spherical shape with a particle size ranging from 5 to 20 nm. The individual Ag nanoparticles are very well separated. Through microemulsion, we successfully obtained nanosize Ag powders.

The X-ray diffraction pattern of the SnO$_2$ powders is shown in Fig. 4. All the diffraction lines are indexed to a tetragonal phase (S.G. *p42/mnm*). No impurity phase was detected by X-ray diffraction. Fig. 5 shows a TEM image of the SnO$_2$ powders. The as-prepared SnO$_2$ powders have a particle size of a few tens of nanometers. EDS trace element analysis was performed on the SnO$_2$ powders. Impurity
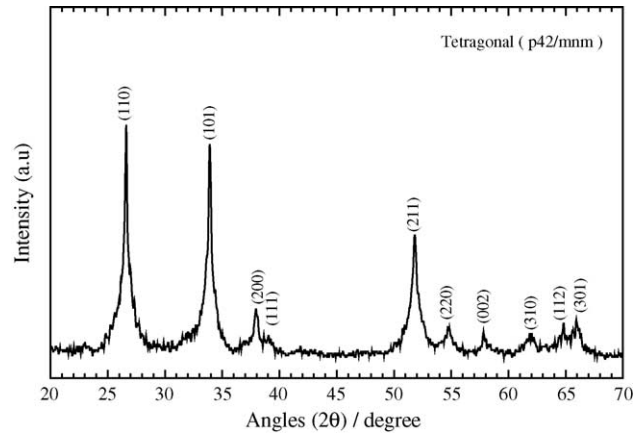
elements were not detected, indicating that the surfactant AOT had been eliminated during the repeated washing process. The individual SnO$_2$ nanoparticles stick together and form agglomerates.

The electrochemical properties of nano Ag powders as anodes in lithium-ion cells were measured via coin-cell testing. Ag has a theoretical capacity of 820 mAh g^{-1} when forming Li$_{3.3}$Ag alloys.

$$3.3\text{Li} + \text{Ag} \leftrightarrow \text{Li}_{3.3}\text{Ag} \tag{1}$$

This alloying reaction is reversible, but accompanied by substantial volume change. The reduced particle size can decrease volume expansion in the local domain when forming Li$_x$Ag alloys. The lithium storage capacity and cyclability of a nano Ag powder electrode is shown in Fig. 6. The Ag nanopowder electrode demonstrated an initial lithium storage
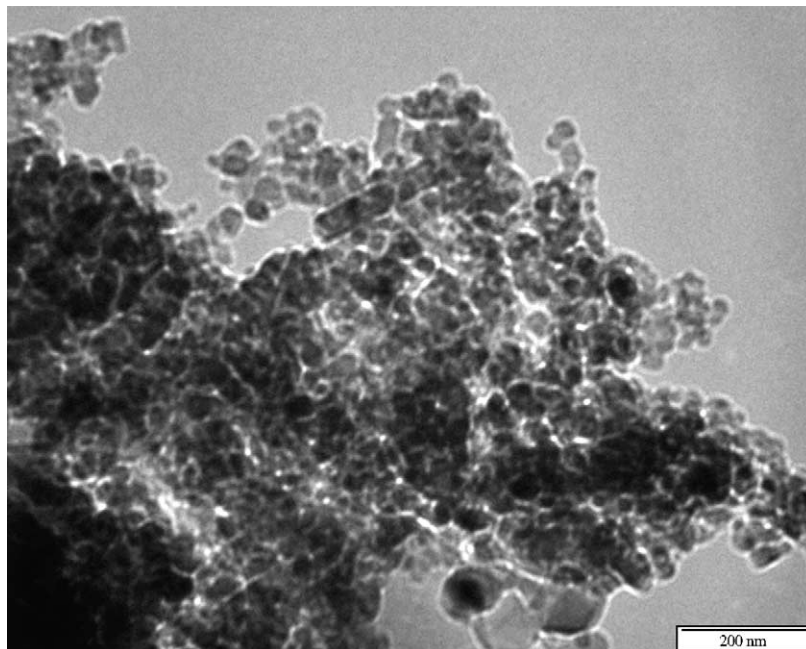

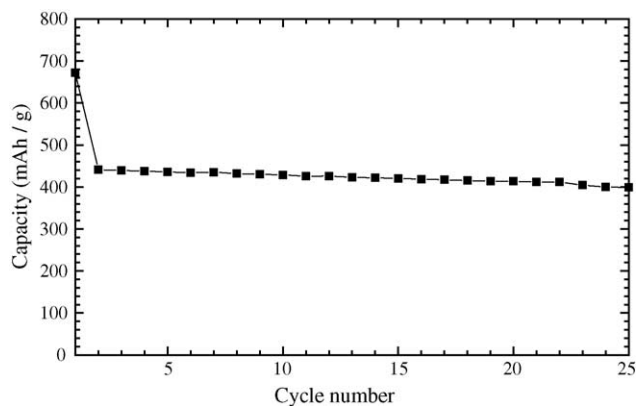Fig. 5. TEM image of SnO$_2$ nanopowders.

Fig. 6. The discharge capacity of Ag nanopowder electrode vs. cycle number.

capacity of $671 \, \text{mAh g}^{-1}$. However, its capacity decreased significantly in the first cycle. From the second cycle, the capacity became stabilized. Therefore, Ag nanopowder can not be used in a standalone situation. But it can be used as an additive in carbon anode materials to enhance lithium storage capacity and electronic conductivity.

Cyclic voltammetry measurements were performed on nanosized SnO_2 electrodes. Fig. 7 shows cyclic voltammograms of SnO_2 electrode. In the first scanning cycle, three lithiation peaks appear, which correspond to the formation of different Li_xSn alloys. From the second scanning cycle, only one pair of redox peaks occurs. The SnO_2 electrode reacted with lithium as follow:

$$SnO_2 + 8.4Li \leftrightarrow Li_{4.4}Sn + 2Li_2O \quad (2)$$

$$Li_{4.4}Sn \leftrightarrow Sn + 4.4Li \quad (3)$$
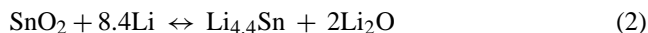
When forming $Li_{4.4}Sn$ alloys, there is a 300 vol.% increase. Therefore, it is a significant advantage to use nanosize SnO_2 powders to reduce the volume change in local sites. The Li_2O generated in the first cycle can act as a matrix to buffer such volume expansion. The cyclability of a nanosize SnO_2 electrode is shown in Fig. 8. In the first cycle, the SnO_2 electrode had a lithium storage capacity of about $1578 \, \text{mAh g}^{-1}$,
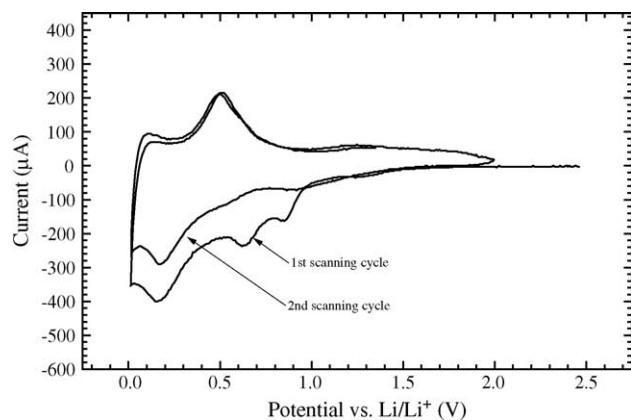

Fig. 7. Cyclic voltammograms of SnO_2 nanopowder electrode. Scanning rate: $0.1 \, \text{mV s}^{-1}$.
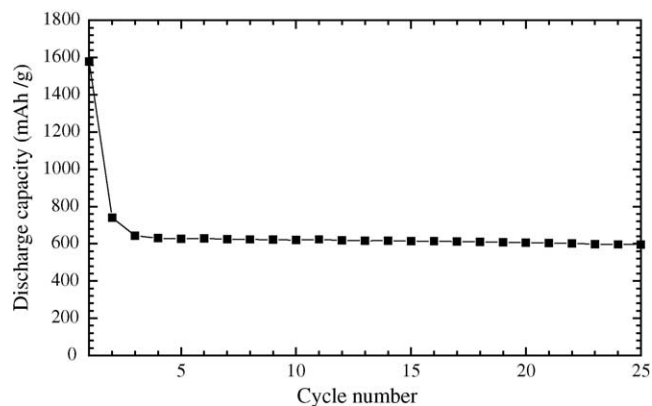

Fig. 8. Discharge capacity of SnO_2 nanopowder electrode vs. cycle number.

which exceeds the theoretical capacity of Eq. (2). Some of this capacity was used to form a passivation film due to the large surface area of the nanopowders. A stable reversible lithium storage capacity of about $630 \, \text{mAh g}^{-1}$ was achieved under repeated lithiation and de-lithiation cycling.

4. Conclusions

The reverse micelle synthesis technique is a universal approach for preparing nanocrystalline metals, oxides and inorganic compounds. Nanosize Ag and SnO_2 nanopowders were successfully synthesised by using the reverse micelle technique. The synthesised Ag powders are very strongly crystalline with a crystal size in the range of 5–20 nm. The SnO_2 powders have a particle size of a few tens of nanometers. The electrochemical performance of nano Ag and SnO_2 powders as anodes in lithium-ion cells was measured. These nanocrystalline anode materials could have significant applications for lithium energy storage and conversion.

Acknowledgements

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