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Preparation and characterization of SnO₂-Li₄Ti₅O₁₂ composite by sol-gel technique

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Abstract: SnO_2 -Li₄Ti₅O₁₂ was prepared by sol-gel method using tin tetrachloride, lithium acetate, tetrabutylorthotitanate and aqueous ammonia as starting materials. The composite was characterized by thermogravimertric (TG) analysis and differential thermal analysis (DTA), X-ray diffractometry (XRD) and transmission electron microscopy (TEM) combined with electrochemical tests. The results show that SnO_2 -Li₄Ti₅O₁₂ composite derived by sol-gel technique is a nanocomposite with core-shell structure, and the amorphous Li₄Ti₅O₁₂ layer with 20–40 nm in thickness is coated on the surface of SnO_2 particles. Electrochemical tests show that SnO_2 -Li₄Ti₅O₁₂ composite delivers a reversible capacity of 688.7 mA·h/g at 0.1*C* and 93.4% of that is retained after 60 cycles at 0.2*C*. The amorphous Li₄Ti₅O₁₂ in composite can accommodate the volume change of SnO_2 electrode and prevent the small and active Sn particles from aggregating into larger and inactive Sn clusters during the cycling effectively, and enhance the cycling stability of SnO_2 electrode significantly.

Key words: SnO₂; Li₄Ti₅O₁₂; composite; sol-gel method; lithium ion batteries

1 Introduction

Since it was used as anode material for lithium-ion batteries in 1997[1], SnO₂ has been thought as the most promising anode material for lithium ion batteries due to its high capacity[2-7]. While SnO₂ is used as anode material for lithium ion batteries. Sn is the active component and the reversible capacity is delivered from the reversible formation and decomposition of Li-Sn alloys(LiSn, Li₇Sn₃, Li₅Sn₂, Li₃Sn₅, Li₇Sn₂ or $Li_{22}Sn_5$ [8–10]. In the first cycle, SnO₂ acts with Li to form amorphous Li₂O, which can be the buffer for tin aggregation. The formation of Li₂O results in the irreversible capacity in the first cycle as high as 47.6%, which is a shortcoming of $SnO_2[2-3]$. However, the most fatal problem to hinder the application of SnO₂ in lithium ion batteries is volume mismatch, which results in a rapid drop in reversible capacity upon cycling[2-3]. To improve the volume mismatch, many methods were used. LI et al[11] reported that nano-SnO₂ fiber may absorb the volume changes in cycling to keep good cyclability even

at high current rate. SnO₂ thin film was also used to decrease the volume change[9, 12]. Metal composite oxides $M_x Sn_y O_z$ (M=Ni, Ca, Fe, Sb, Cu, Mg, Zn, etc) were also proposed to improve cycling stability of SnO₂[13–16]. By means of surface modification, such as coating a layer conductive materials on the surface of SnO₂ the cycling stability of SnO₂ can be also improved[17–19]. So far, coating Li₄Ti₅O₁₂ on surface of SnO₂ to improve its cycling stability has not been reported yet. SnO₂-Li₄Ti₅O₁₂ composite was prepared by sol-gel method and the electrochemical properties were studied here.

2 Experimental

2.1 Preparation of SnO₂-Li₄Ti₅O₁₂ composite

A certain quantity of tetrabutyl titanate (AR) was solved in ethanol absolute (AR) with the volume ratio of tetrabutyl titanate to ethanol absolute of 1:5. The solution of tetrabutyl titanate was added to an aqueous ethanol solution of lithium acetate (AR) under stirring strongly according to the stoichiometric ratio of $Li_4Ti_5O_{12}$ to get a

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clear yellow sol. A certain quantity of SnO₂ powder was dispersed uniformly in this sol with ultrasonic wave and stirrers. After stirring for 2-3 h, a gel was obtained. The gel was dried at 105 for 4 h in vacuum to get a precursor. The precursor was calcinated at 500 for 4 h to obtain SnO₂-Li₄Ti₅O₁₂ composite. In addition, Li₄Ti₅O₁₂ without SnO₂ was also prepared.

2.2 Characterization of SnO₂-Li₄Ti₅O₁₂ composite

The thermal behavior of the precursor was analyzed by thermal analysis apparatus (TGA/SDTA851^e, METTLER TOLEDO). Phase identification studies of the samples were carried out by an X-ray diffractometer (Rigaku D/MAX-gA) with Cu K_{α} radiation. The surface morphology analyses of SnO₂-Li₄Ti₅O₁₂ composite were done by scanning electron microscope (JSM 5600LV).

A slurry containing 80% SnO₂-Li₄Ti₅O₁₂ composite, 10% acetylene black and 10% PVDF (polyvinylidene fluoride) was made using *N*-methylprrolidinone (NMP) as the solvent. Electrodes with an area of 1 cm² for the measurements of electrochemical characterization were prepared by coating slurries (about 100 μ m in thickness) on copper foils followed by drying in vacuum at 60 for 12 h. Electrochemical tests were conducted using a conventional coin-type cell, employing lithium foil as a counter electrode and utilizing 1.0 mol/L LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (with an volume ratio of EC to DMC of 1:1) as the electrolyte. The assembly was carried out in an Ar-filled glove box. The electrochemical analyses were carried out with an electrochemical analysis system.

3 Results and discussion

3.1 Thermal analysis

Fig.1 shows the thermogravimertric (TG) analysis and differential thermal analysis (DTA) of dry gel precursor. From the TG curve, it can be seen that almost all mass loss takes place before 400 . The mass loss is



Fig.1 Thermal analysis curves of precursor of SnO₂-Li₄Ti₅O₁₂

due to the loss of physical absorbed water on surface of the precursor and the decomposition of $Li_4Ti_5O_{12}$. Specific mass loss stages can not be found from the TG curve, suggesting that the mass loss is a continuous process. Above 500 , there is no mass loss at TG curve, indicating that the decomposition of the precursor is complete. Accordingly, an endothermic peak at 400 appears on the DTA curve, which may be caused by the crystal shape due to the decomposition of the precursor and formation of SnO_2 -Li₄Ti₅O₁₂.

3.2 XRD analysis

Fig.2 shows XRD patterns of $SnO_2-Li_4Ti_5O_{12}$ composites. All peaks in Fig.2(a) agree well with the standard peaks of JCPDS card No.26-1198, indicating that $Li_4Ti_5O_{12}$ shares a face centered cubic structure with a space group of Fd3m[20]. The peaks in Fig.2(b) agree well with the standard peaks of JCPDS card No.21-1250, indicating that the sample is SnO_2 with rutile structure. There are obvious peaks assigned to SnO_2 and very weak peaks assigned to $Li_4Ti_5O_{12}$ in Fig.2(c), suggesting that the amorphous $Li_4Ti_5O_{12}$ layer is coated on the surface of SnO_2 particles.

3.3 TEM analysis

Fig.3 shows the TEM images of SnO₂ and SnO₂-Li₄Ti₅O₁₂ composite. It is apparent that the morphology of SnO₂ is regular spherical shape. The TEM image shows homogeneous appearance with particle size of 30–50 nm. As shown in Fig.3(a), the surface morphology of as-received SnO₂ is smooth, but it becomes a little coarse after loading Li₄Ti₅O₁₂ (Fig.3(b)). The transmission electron micrographs show that amorphous Li₄Ti₅O₁₂ layer with 20–40 nm in thickness is uniformly distributed over the surface of SnO₂ to form SnO₂-Li₄Ti₅O₁₂ composite with core-shell structure. Therefore, it is expected that nano-Li₄Ti₅O₁₂ particle will act as bridge to result in good contact between SnO₂ and Li₄Ti₅O₁₂.

3.4 Electrochemical properties

Fig.4 shows the initial charge-discharge curves of SnO_2 and SnO_2 -Li₄Ti₅O₁₂ as anodes for lithium-ion batteries at a constant current rate of 0.1C in the range of 0-1.0 V. The profiles of the charge and discharge curves were very similar, indicating that SnO_2 and SnO_2 - $Li_4Ti_5O_{12}$ have the same electrochemical mechanism. The first discharge capacities of SnO₂ and SnO₂-Li₄Ti₅O₁₂ are 1 640.5 mA·h/g and 1 565.2 mA·h/g, and the first charge capacities of SnO2 and SnO₂-Li₄Ti₅O₁₂ are 689.8 mA·h/g and 688.7 mA·h/g, respectively. Obviously, after loading amorphous Li₄Ti₅O₁₂ layer on SnO₂, the first discharge capacity and charge capacity of SnO₂ decrease. This may be due to



Fig.2 XRD patterns of samples: (a) $Li_4Ti_5O_{12}$; (b) SnO_2 ; (c) SnO_2 - $Li_4Ti_5O_{12}$



Fig.3 TEM images of SnO₂(a) and SnO₂-Li₄Ti₅O₁₂(b)

two reasons: On the one hand, the theoretical capacity of $Li_4Ti_5O_{12}$ (168 mA·h/g) is lower than that of SnO_2 (782 mA·h/g), resulting in lower capacity of composite electrode after SnO_2 being substituted by $Li_4Ti_5O_{12}$. On the other hand, due to that the discharge-charge plateau is 1.5 V[21], the capacity can not be utilized when the charge-discharge voltage is chosen to be 0-1.0 V.

Fig.5 shows the comparison of cycling performance of SnO₂ and SnO₂-Li₄Ti₅O₁₂ at current rate of 0.2*C*. From Fig.5, it can be seen that the discharge capacity of SnO₂ at the second cycle is 688.1 mA·h/g, and the discharge capacity after 60 cycles is 587.8 mA·h/g. So, the capacity retention of SnO₂ is 85.4%. Under the same conditions, the discharge capacity of SnO₂-Li₄Ti₅O₁₂ at the second cycle is 687.6 mA·h/g, and the discharge capacity after 60 cycles is 642.1 mA·h/g. So, the capacity retention of SnO_2 -Li₄Ti₅O₁₂ is more than 94.3%. It is apparent that the cycling stability of SnO_2 is improved effectively after being loaded a layer of amorphous Li₄Ti₅O₁₂. As is known, Li₄Ti₅O₁₂ is regarded as a "zero strain" insertion material[21]. The amorphous Li₄Ti₅O₁₂ layer on SnO_2 can avoid structural damage due to expansion and contraction of the electrode materials at the insertion material/solid electrolyte interfaces during the charge and discharge process and prevent the



Fig.4 Initial charge-discharge curves of SnO_2 (a) and SnO_2 -Li₄Ti₅O₁₂ (b)



Fig.5 Cycling performance of SnO₂ and SnO₂-Li₄Ti₅O₁₂

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aggregation of Sn particles, resulting in the improvement of cycling performance of SnO₂.

4 Conclusions

1) $SnO_2-Li_4Ti_5O_{12}$ composite was prepared by sol-gel method. The amorphous $Li_4Ti_5O_{12}$ layer with 20–40 nm in thickness is coated on the surface of SnO_2 particles to form $SnO_2-Li_4Ti_5O_{12}$ composite with core-shell structure.

2) SnO₂-Li₄Ti₅O₁₂ composite delivers a reversible capacity of 688.7 mA·h/g at 0.1*C*, and 93.4% of that is retained after 60 cycles at 0.2*C*. The amorphous Li₄Ti₅O₁₂ in composite can accommodate the volume change of SnO₂ electrode and prevent the small and active Sn particles from aggregating into larger and inactive Sn clusters during cycling effectively, and enhance the cycling stability of SnO₂ electrode significantly.

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