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General synthesis of nano-M embedded $Li_4Ti_5O_{12}$/C composites (M = Sn, Sb and Bi) with high capacity and good cycle stability

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Nano-metal embedded $Li_4Ti_5O_{12}$/C composites ($Li_4Ti_5O_{12}$/M/C samples labeled as $Li_4Ti_5O_{12}$/Sn/C-L, $Li_4Ti_5O_{12}$/Sn/C-H, $Li_4Ti_5O_{12}$/Sb/C-L, $Li_4Ti_5O_{12}$/Sb/C-H, $Li_4Ti_5O_{12}$/Bi/C-L and $Li_4Ti_5O_{12}$/Bi/C-H, respectively) as high capacity anode were synthesized by sol-gel and high temperature solid state reaction methods. The physical properties of $Li_4Ti_5O_{12}$/M/C were detected by X-ray diffraction (XRD), scanning microscopy (SEM), transmission electron microscopy (TEM) and elemental analysis. All composites were completely coated by a thin carbon layer. Besides the $Li_4Ti_5O_{12}$/Bi/C-L, other $Li_4Ti_5O_{12}$/M/C samples were composed of spherical-like aggregate particles. Nano-M was embedded between inner $Li_4Ti_5O_{12}$ and outer carbon layer. Their electrochemical performances were studied by galvanostatic cycle and cyclic voltammograms (CVs). These analyses show that $Li_4Ti_5O_{12}$/Sn/C-L, $Li_4Ti_5O_{12}$/Sn/C-H, $Li_4Ti_5O_{12}$/Sb/C-H, $Li_4Ti_5O_{12}$/Bi/C-H delivered a reversible capacity of 231.9, 308.1, 235.9 and 213.5 mAh g^{-1} at 500th cycle on current density of 200 mA g^{-1}, respectively, while $Li_4Ti_5O_{12}$/C composite only delivered a capacity of 197.6 mAh g^{-1} at the same conditions. The results demonstrated that metal M can play an important role on high capacity performance of $Li_4Ti_5O_{12}$-based anode when it was embedded between inner "zero-strain" $Li_4Ti_5O_{12}$ and outer carbon coating layer. Their stable cycle performance owning to the co-effect of $Li_4Ti_5O_{12}$ as the structural stabilizer and carbon layer as the volume change buffer for preventing the volume change caused by M during cycling. This work provides an effective way to improve the discharge capacity of $Li_4Ti_5O_{12}$-based anodes.

1. Introduction

Li-ion batteries with high safety and excellent cycleability properties are promising power sources for electric devices, especially for electric vehicles (EVs) and other portable electric devices [1–3]. Graphite/carbon, as the commercial anode, suffers from safety and poor cycleability issues. In recent years, it has been extensively attempted to explore a new anode material with higher safety and excellent cycleability compared to commercial graphite/carbon. $Li_4Ti_5O_{12}$ has been considered as a safe and stable anode due to its "zero strain" structure [4–8]. However, the specific capacity of $Li_4Ti_5O_{12}$ is lower as 175 mAh g^{-1} at voltage range from 1 to 3 V vs. Li^+/Li. Although some research on $Li_4Ti_5O_{12}$ have reported including controlling its size to reduce the polarization [9], coating conductive carbon materials or adding metal to enhance its electronic conductivity [10–14], constructing specific morphology to improve its rate capability [15–20], those studies can not increase its specific capacity. Therefore, some researchers took a broad cycle voltage window from ~0 to ~2.5 V in order to obtain a higher specific capacity [21–23]. Compared to the capacity of commercial graphite/carbon, the specific capacity of $Li_4Ti_5O_{12}$-based anodes is still need to be improved further.

To increase the specific capacity of $Li_4Ti_5O_{12}$-based anodes, some reports took Si as a doping material to reach higher specific capacity, but the cycle performance was poor. Chen et al. [24] prepared $Li_4Ti_5O_{12}$/Si/Poly(acrylic acid)/Super P electrode. The electrode delivered a higher capacity of 1004 mAh g^{-1} at 10th cycle under 0.1C, but the capacity was lower as 10 mAh g^{-1} at 60th cycle under 2C. Nithya et al. [25] prepared 5%Si/95%$Li_4Ti_5O_{12}$ powder as an anode. The anode showed a discharge capacity of 200 mAh g^{-1} at a current density of 0.1 mA cm^{-2}. The electrodes in Ref. 24 and Ref. 25 exhibited a reversible capacity lower than the capacity of $Li_4Ti_5O_{12}$. The unsatisfactory electrochemical performances were caused by large volume expansion from Si to $Li_{4.4}Si$ (about 400%), leading to obvious electrode pulverization. To solve such a problem, one strategy is to use carbon as a coating layer to hind the volume expansion. The other is to add less volume expansion materials as composite components to fabricate a useful electrode.

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Due to higher specific capacity, Sn was chosen as a component to obtain Sn/$Li_4Ti_5O_{12}$ composite anode [26,27]. However, the electrochemical performances of those Sn/$Li_4Ti_5O_{12}$ composites are not satisfying, which should be improved further. It is well-known that in periodic table of elements, Sb is located at same period with Sn, and Bi belongs to same family with Sb, which implies their similar electrochemical properties. As similar as Sn, the lithium/delithium voltage on Sb and Bi is lower than 1.2 V. Some researchers fabricated TiO_2/Sb/C [28] and Bi@C[29]anodes. In ref. 28, Sb can improve the discharge capacity of rutile TiO_2/C anode higher to ~65% at 30th cycle on 100 mA g^{-1} when the mass ratio of Sb, TiO_2 and C ratio was 40.2%, 19.8 and 40%, respectively. In ref. 29, the Bi@C had a discharge capacity of 408 mAh g^{-1} after 100 cycles on 100 mA g^{-1}. These results indicated that the composite anodes composed of $Li_4Ti_5O_{12}$ and Sb or Bi maybe have a higher specific capacity.

In this paper, $Li_4Ti_5O_{12}$/M/C composites were prepared by simple sol-gel and solid state reaction methods. The outer carbon layer acts as an electronic conductor to weaken the volume expansion of M during cycling. The inner $Li_4Ti_5O_{12}$ acts as a "zero-strain" core to maintain the structure stability. The M acts as a capacity component providing high capacity for the electrodes. The fabricated $Li_4Ti_5O_{12}$/M/C has reasonable electrochemical properties due to the outer carbon layer as electronic conductor and the embedded M as high capacity material.

2. Experimental section

2.1. Materials

All synthesis processes were illustrated in Fig. 1. $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}$/C were synthesized firstly as intermediate product and counterpart, respectively. In a typical synthesis, TiO_2 spheres were first prepared by a reported sol-gel method with a slight modification [30]. Firstly, 80 mg heptanoic acid, 265 mg tetrabutyl titanate and 30 mL absolute ethanol were mixed and stirred, then 4.53 mL deinonized water was added and stirred to form a white gel. Subsequently, the gel was put into a 100 mL Teflon-lined stainless autoclave and heated at 150 °C for 12 h. After being isolated using centrifugation, washed with deinonized water and absolute ethanol, dried in vacuum, TiO_2 spheres were obtained. For synthesizing $Li_4Ti_5O_{12}$, as-prepared TiO_2 spheres were mixed with Li_2CO_3 under 5% lithium atom excess, and then the mixture was calcined at 800 °C in air for 20 h to obtain $Li_4Ti_5O_{12}$. For fabricating $Li_4Ti_5O_{12}$/C, 1.00 g $Li_4Ti_5O_{12}$ was added into 145 mL deinonized water under stirring, then ultrasonic dispersed for 30 min and water bath on 50 °C. Subsequently, 5 mL 0.01 M hexadecyl trimethyl ammonium bromide, 0.50 mL 14.7 M ammonium hydroxide, 0.48 g m-dihydroxybenzene and 0.66 mL 14.4 M formaldehyde were added, respectively. The solution was stirred for 2 h, isolated by centrifugation, washed with deinonized water and absolute ethanol respectively. The brown slurry precursor was dried under 80 °C in air and annealed at 550 °C for 4 h.

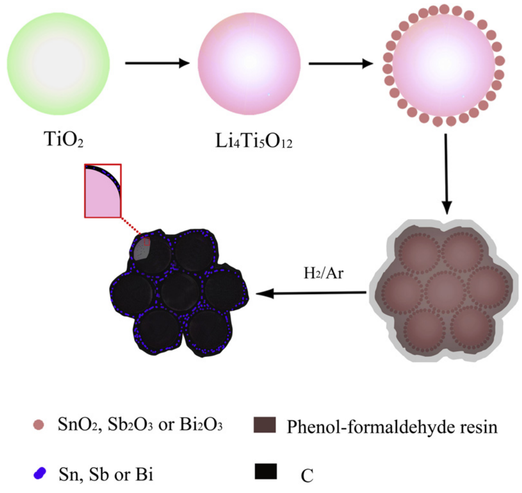

Fig. 1. Schematic illustration of samples preparation.

Synthesis of $Li_4Ti_5O_{12}$/Sn/C: 0.50 g $Li_4Ti_5O_{12}$ was dispersed into 15 mL absolute alcohol, and 0.50 mL 14.7 M ammonium hydroxide was added subsequently, then 15 mL 0.050 M (corresponding to $Li_4Ti_5O_{12}$/Sn/C-L) or 0.121 M (corresponding to $Li_4Ti_5O_{12}$/Sn/C-H) Tin(IV) chloride pentahydrate alcohol solution was added using a syringe pump at a rate of 1.0 mL min^{-1} and kept stirring for another 6 h. The precipitate was isolated using centrifugation, washed with deinonized water and ethanol to obtain $Li_4Ti_5O_{12}/SnO_2$ particles. Then $Li_4Ti_5O_{12}/SnO_2$ was coated by phenol-formaldehyde resin using the coating method of $Li_4Ti_5O_{12}$/C. Finally, the resin coated $Li_4Ti_5O_{12}/SnO_2$ was heat-treated on 700 °C for 4 h under H_2/Ar (volume ratio of 1/19).

Synthesis of $Li_4Ti_5O_{12}$/Sb/C: Before 0.50 g $Li_4Ti_5O_{12}$ was dispersed by ultrasonic dispersion, 0.50 mL 14.7 M ammonium hydroxide and 0.50 mL macrogol-600 were added into 15 mL absolute alcohol. Then 15 mL 0.048 M (corresponding to $Li_4Ti_5O_{12}$/Sb/C-L) or 0.118 M (corresponding to $Li_4Ti_5O_{12}$/Sb/C-H) antimony (III)chloride was added using a syringe pump at a rate of 1.0 mL min^{-1} and kept stirring for another 6 h. After that, the white gel was isolated using centrifugation, washed by deinonized water and absolute alcohol respectively, for obtaining $Li_4Ti_5O_{12}/Sb_2O_3$ particles. Finally, $Li_4Ti_5O_{12}/Sb_2O_3$ precursor was coated by phenol-formaldehyde resin and heat-treated as similar as the synthesis of $Li_4Ti_5O_{12}$/Sn/C, but the heat treatment temperature was on 550 °C.

Synthesis of $Li_4Ti_5O_{12}$/Bi/C: 0.5000 g $Li_4Ti_5O_{12}$ and 0.2900 g (corresponding to $Li_4Ti_5O_{12}$/Bi/C-L) or 0.6250 g (corresponding to $Li_4Ti_5O_{12}$/Bi/C-H) bismuth nitrate pentahydrate were dispersed into mixed solution of 17 mL ethylene glycol and 34 mL absolute alcohol under vigorous stirring and kept stirring for another 30 min. Afterwards, the solution was poured into a 100 mL Teflon-lined stainless autoclave and heated at 160 °C for 5 h. Then the precipitate was washed by deinonized water and absolute alcohol respectively, to obtain $Li_4Ti_5O_{12}/Bi_2O_3$. Finally, the $Li_4Ti_5O_{12}/Bi_2O_3$ was coated by phenol-formaldehyde resin and heat-treated as similar as the synthesis of $Li_4Ti_5O_{12}$/Sn/C, but heat treated temperature was on 600 °C.

Synthesis of pyrolytic carbon: 20 mL 0.01 M hexadecyl trimethyl ammonium bromide and 2.0 mL 14.7 M ammonium hydroxide were added into 145 mL deinonized water under stirring at 50 °C. Subsequently, 2.0 g m-dihydroxybenzene and 2.8 mL 14.4 M formaldehyde were added, respectively. The solution was kept stirring for 2 h, isolated by centrifugation, washed with deinonized water and absolute ethanol respectively. The brown slurry precursor was dried under 80 °C in air and annealed at 700 °C for 30 min under N_2.

2.2. Methods of materials characterization

XRD patterns were collected on a Shimadzu-XRD-7000S X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.54056$ Å) at a voltage of 40 kV and a current of 40 mA. SEM images were acquired on FEI Quanta 450 and S4800 microscopes. TEM images were taken on FEI Tecnai G20 microscopes. Carbon content was analyzed by using vario EL Elemental Analyzer.