



Evaluation of the electrochemical characteristics of silicon/lithium titanate composite as anode material for lithium ion batteries



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ABSTRACT

Silicon/lithium titanate (Si/Li₂TiO₃) nanocomposite is successfully prepared through the combination of a sol–gel approach with a high-temperature treatment as well as a high energy ball milling process. The structure and morphology of the composite are characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) analysis reveals Si particles are coated by the uniform disordered Li₂TiO₃ layer with a thickness of about 5 nm. The investigation in cycling performances demonstrates that Si/Li₂TiO₃ exhibits the improved cycling stability, with specific capacity of 471.0 mA h g⁻¹ after 50 cycles and the capacity retention is 31.5%, much higher than pure Si. Compared with pure Si, Si/Li₂TiO₃ shows better rate-capability, a reversible capacity of 315.2 mA h g⁻¹ at 0.8 A g⁻¹ is maintained. The higher ionic conductivity of Li₂TiO₃ is responsible for the improved rate performance. In addition, the results derived from XRD, the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) indicate that lithium ions could react reversibly with Si, and electrochemically less active Li₂TiO₃ turns into the Li–Ti–O ternary phase, which acts as a buffer matrix in the Si/Li₂TiO₃ composite, thus improving the reversibility of electrode.

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1. Introduction

In the rapid development of portable electronic devices, lithium-ion batteries (LIBs) are strongly demanded in consideration of their high energy density, long cycle life and fast charge/discharge rates. Graphite, currently used as lithium-ion battery anode, is increasingly approaching its theoretical capacity limit of 372 mA h g⁻¹, however, it is far from meeting the demands of future electronic equipment [1]. Therefore, a variety of anode materials with improved storage capacity have been intensively explored for lithium-ion batteries in the last decade. Among these, silicon has aroused extensive attention for its numerous appealing features: it has the highest specific capacity of ~4200 mA h g⁻¹ [2] and is inexpensive, abundant, furthermore, the lithiation/delithiation potential of Si is slightly higher than that of lithium, resulting in the electrode with safe feature. However, there are two major problems of Si anode material: the low intrinsic electronic conductivity and huge volume expansion during Li insertion/extraction processes, resulting in cracking and crumbling of the electrode, which makes it retain poor cycling performance [3–5]. Tremendous efforts have been made to

overcome these drawbacks, including: 1) using nanotechnologies to synthesize different Si nano/micro-structures, such as nanoparticles [6,7], nanotubes [8,9], thin films [10] and mesoporous structures [11,12]; 2) coating with carbon (C) to form Si/C composites [13,14]; 3) combining with inactive/active materials [15,16], such as metal alloys [17,18] and metal oxides [19,20].

Among other alternative anode materials, Ti-based compounds are particularly attractive for their excellent structural stability during cycling and higher flat electrode reaction voltage. Lithium titanate has emerged as a good candidate as anode material for lithium-ion batteries with higher and flatter Li insertion reaction voltage, preventing the formation of Li dendrites and the decomposition of electrolyte [21–26]. Considering the merits emerged above, anodes made of silicon/lithium titanate composites can combine the advantageous properties of silicon (high lithium-storage capacity) and lithium titanate (excellent structural stability) to improve the overall electrochemical performance of the anode for lithium-ion batteries. There have also been some researches on the composites consisting of silicon and lithium titanate in the previous reports. For example, Si/LiTi₂O₄ composite film was synthesized by a sol–gel method in combination with a following heat-treatment process using nano-Si powder as the raw material. The composite exhibited excellent cycle performance (1100 mA h g⁻¹ remained after 50 cycles) but a low initial coulombic efficiency

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(only about 74.8%). It was reported that the improvement of electrochemical performance was mainly induced by the porous structure of the Si/Li₂TiO₃ nanocomposite film, which could offer convenient channels and provided a buffer interspace to alleviate the volume expansion of Si during the cycle process [27]. Yingbin Lin et al. [28] synthesized composite α -Si film/Li₄Ti₅O₁₂ via vacuum thermal evaporation technique, which shows better cycling performance than that of Li₄Ti₅O₁₂ in the voltage range of 1.0–3.0 V. However, the vacuum thermal evaporation technique is difficult to achieve from the point of view of large-scale commercial applications.

Li₂TiO₃ owns a cubic structure and can react with Li atoms to form zero-strain insertion materials. Moreover, Li₂TiO₃ has a three-dimensional path for Li⁺-ion diffusion, in which Li⁺-ion migration can take place in (0 0 3) plane and along c direction [29]. The structural stability and its better ionic conductivity make it act as ideal buffer to the Si powder. Besides, the introduction of carbon can further improve the electrical conductivity of the Si/Li₂TiO₃ composite.

In this paper, the synthesis of Si/Li₂TiO₃ composite is reported by dispersing micro-Si powder in Li₂TiO₃ matrix by a facile sol-gel method followed by a high-temperature solid-phase calcination process and high-energy ball-milling technique. According to our knowledge, there are few reports considering the effect of Li₂TiO₃ on the electrochemical performance of pure Si. In this work, the introduction of Li₂TiO₃ endows the Si/Li₂TiO₃ electrode with the excellent cycling stability and better rate-capability compared with pure Si. The improved electrochemical performance of the Si/Li₂TiO₃ electrode might be attributed to the buffer action of the Li₂TiO₃ matrix and the higher ionic conductivity of Li₂TiO₃.

2. Experimental

2.1. Preparation of Si/Li₂TiO₃ composite

For a typical synthesis of Si/Li₂TiO₃ composite, lithium acetate and tetrabutyl titanate with a molar ratio of 4:5 (Li:Ti) were dissolved in an ethanol solution. Then an appropriate amount of triethanolamine was added into the above solution, followed by an ethanol solution containing Si powder with a particle size of 1–20 μ m and the molar ratio of Si to Ti was 2:1. Subsequently, an aqueous solution of glucose (C₆H₁₂O₆·H₂O) with water to glucose molar ratio of 9:1, was added dropwise into the mixture under stirring. A suspension was achieved, then dried at 80 °C for 10 h to form a dry gel precursor. The resulting precursor was pressed into round slice under pressure of 10 MPa and then heated at 700 °C in argon atmosphere for 24 h. Finally, the obtained black powder was ball-milled at 400 rpm for 6 h in a 100 mL ceramic vial filled with ceramic balls and argon gas. The weight ratio of the ceramic balls to the material was maintained at 20:1.

2.2. Structural Characterization

The phase of the as-prepared powders were characterized by X-ray diffraction (XRD) using a Rigaku D/max-2500 X-ray diffractometer equipped with Cu-K α radiation. The morphologies and microstructures of the synthesized materials were characterized by a transmission electronic microscopy (TEM, FEI Tecnai20) and a scanning electron microscopy (SEM, Philips XL-30). The elementary composition was primarily determined by energy dispersive spectrum (EDS). The pyrolysis performance of the samples was studied by a thermal gravimetric analyzer (TG, SDTQ600).

2.3. Electrochemical characterization

Electrodes containing Si, or Si/Li₂TiO₃ active materials, polyvinylidene fluoride (PVDF) binder and carbon black at a weight ratio of 8:1:1, were prepared by coating the slurry of the electrode

ingredients dissolved in N-methyl pyrrolidone (NMP) onto copper foil and then dried at 80 °C under vacuum for 24 h. The working electrodes were assembled in 2032 coin cells using Celgard 2400 as the separator and lithium foil as the counter electrodes. 1 mol L⁻¹ LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume ratio) was employed as the electrolyte. The coin-type cells were assembled in an argon-filled glove box.

The cyclic voltammetry (CV) measurement was performed on a Solartron 1287 electrochemical workstation between 0 and 3.0 V at a scan rate of 0.1 mV s⁻¹, and the test temperature was kept at 25 °C. Electrochemical impedance spectroscopic (EIS) measurement was carried out by utilizing an AC voltage of 5 mV amplitude of in the frequency range of 10 kHz to 100 MHz using a Solartron 1250 impedance analyzer, and the test temperature was kept at 25 °C. The galvanostatic charge/discharge tests were conducted on a LAND CT2001A battery test system at 25 °C with the cut-off voltage of 0.02 and 3.0 V (vs. Li/Li⁺) at a specific current density of 80 mA g⁻¹. Especially, the rate test of pure Si and Si/Li₂TiO₃ composite at different current densities was in the voltage of 0.01 and 3.0 V (vs. Li/Li⁺).

3. Results and discussion

3.1. Structure characterization

Fig. 1 shows the TG-DTA curves of the glucose and the Si/Li₂TiO₃ precursor. It can be clearly seen that four main endothermic peaks are observed at around 74, 157, 220 and 313 °C in the DTA curve in

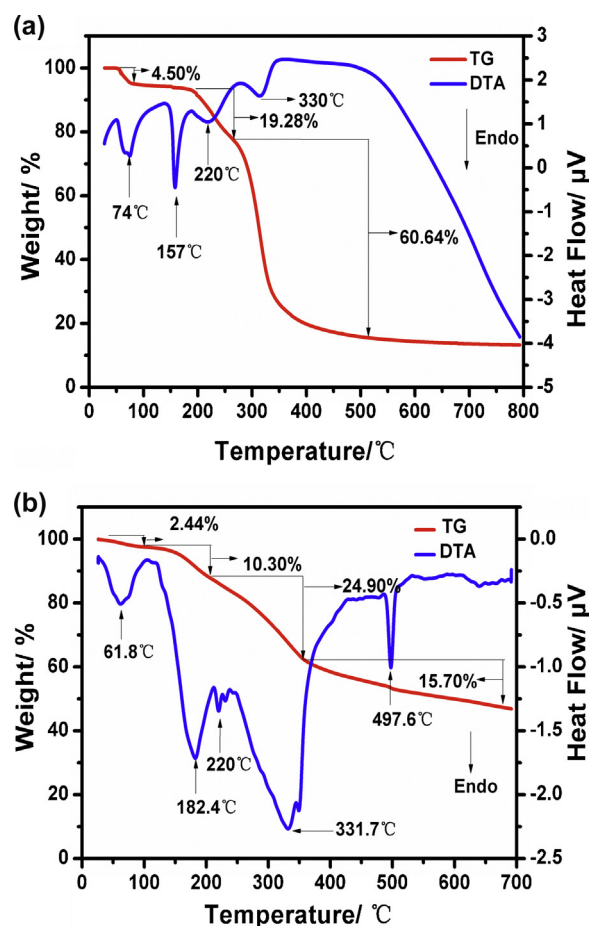


Fig. 1. TG-DTA curves of glucose (a) and the Si/Li₂TiO₃ precursor (b).

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