



Boosting the cyclability of commercial TiO₂ anode by introducing appropriate amount of Ti₉O₁₇ during coating carbon



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ABSTRACT

Resourceful TiO₂ is a potential alternative as anode material for Li-Ion batteries, but the low electrochemical performance of commercial TiO₂ (c-TiO₂) is the obstacle for its practical application. Herein, appropriate amount of Ti₉O₁₇ was introduced by simply coating carbon at 900 °C employing pitch as carbon precursor. The carbon-coated c-TiO₂ derived from 12 wt% pitch exhibited appreciable rate performance and cycling stability (retaining a reversible capacity of 155.8 mAh g⁻¹ after cycling at 500 mA g⁻¹ for 800 cycles). Combining the comparative experiments and systematic characterizations on the products, the appropriate amount of Ti₉O₁₇ introduced by controlling the pitch content during coating carbon contributes to meliorating the electronic and ionic conductivity of TiO₂, resulting in the boosted electrochemical performance.

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1. Introduction

Li-ion battery (LIB) is one of the most prevailing energy storage devices nowadays, and has been applied in diverse fields. The common anode materials for the current LIBs are graphite. However, graphite anode suffers from poor performance at low temperature and high current rate, as well as the safety problems resulted from lithium dendrites. Ti-based oxides, such Li₄Ti₅O₁₂ and TiO₂, behaving as anode could circumvent these problems. The fabrication of Li₄Ti₅O₁₂ consumes a lot of lithium which has no contribution to the capacity yet increases the price of Li₄Ti₅O₁₂, and the ratio of Li to Ti precursors should be well controlled with altering the calcinations temperature to obtain pure Li₄Ti₅O₁₂. TiO₂ with the similar theoretical specific capacity to Li₄Ti₅O₁₂ is resource-abundant and could be fabricated simply, thus exhibiting great predominance in price for practical application. Nevertheless, industrial TiO₂ reveals poor electrochemical performance because of the presence of various impurities. How to effectively improve the performance of commercial TiO₂ (c-TiO₂) is the major issue for its application in LIBs, but so far only several explorations are available [1–3].

Coating carbon is a general route to meliorate the poor electronic conductivity of TiO₂ [4–8]. However, the TiO₂ employed were mostly pure and derived from the precursors with high cost. In our recent research, the performance of c-TiO₂ was boosted by coating carbon employing pitch and glucose as carbon sources [2,3]. Particularly, it was found that the residual SO₄²⁻ radicals introduced in the fabrication process strongly affect the performance, but the negative effect could be effectively mitigated by sintering at temperatures above 750 °C due to the decomposition of the radicals [3]. Despite the improved performance by coating carbon at 750 °C, the cycling stability is still unsatisfactory, likely associating with the high carbon content in the products.

Comprehensively considering the currently available work concerning with c-TiO₂ anode, we fabricated carbon-coated c-TiO₂ with appropriate amount of Ti₉O₁₇ at a temperature of 900 °C by controlling pitch content, thus ameliorating the cyclability of c-TiO₂. The mechanism involved was explained by systematic characterizations.

2. Experimental

The c-TiO₂ employed is the same as that in our previous work [2]. The mass ratios of pitch powder to c-TiO₂ are 0.10, 0.12 and 0.135. The uniformly mixed c-TiO₂ and pitch in water were dried at

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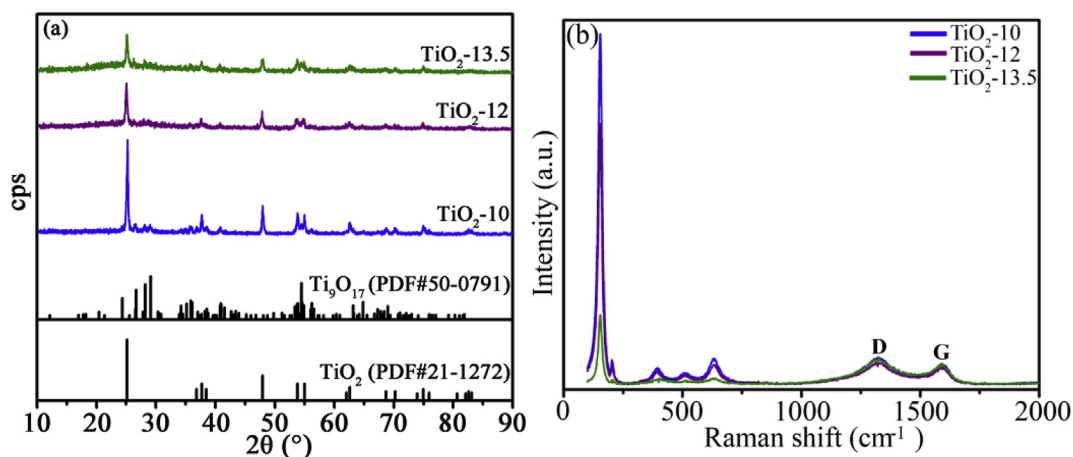


Fig. 1. XRD patterns (a) and Raman spectra (b) of TiO₂-10, TiO₂-12 and TiO₂-13.5.

105 °C thoroughly, and sintered at 900 °C for 3 h under N₂ atmosphere in a tube furnace. The products were assigned to TiO₂-10, TiO₂-12 and TiO₂-13.5 in terms of the mass ratio. For comparison, the samples without adding pitch and with a mass ratio of 0.08 for pitch to c-TiO₂ were also prepared under the same conditions, which were denoted as TiO₂-900, TiO₂-8, respectively.

The characterization techniques and performance measurements are similar to those in Ref. [2], and the details were provided in Supplemental File (SF).

3. Results and discussion

3.1. Structure and composition

The structure was firstly determined by X-ray diffraction (XRD) patterns. If the pristine c-TiO₂ was directly calcined at 900 °C for 3 h without the presence of pitch, part of the anatase c-TiO₂ transformed into rutile phase (Fig. S1), and the markedly narrowed diffraction peaks indicate the significantly coarsened grain size. Even in the presence of a low pitch content (say TiO₂-8), the rutile TiO₂ could also be detected in the XRD pattern, demonstrating that the carbon coating could hinder the transition from anatase to rutile phase to a certain degree [9]. When the mass ratio for pitch to c-TiO₂ is above 0.1, the transition from anatase to rutile phase hardly occurs, and the anatase TiO₂ is still the dominant phase

(Fig. 1a), but some changes are discernible with altering the pitch content. (1) A new phase of Ti₉O₁₇ could be detected in the carbon-coated products, the weak peaks demonstrate the low content of Ti₉O₁₇ due to the reduction of TiO₂ by the synchronously generated carbon. (2) The intensities of the diffraction peaks from anatase TiO₂ weaken gradually with increasing the pitch content, and the relative intensity of anatase TiO₂ to Ti₉O₁₇ decreases, indicative of the increment of the relative content of Ti₉O₁₇ in the products. (3) An amorphous peak becomes distinct around $2\theta = 25^\circ$, implying the increment of carbon content with increasing the pitch content. The presence of Ti₉O₁₇ means the formation of some Ti³⁺ in the carbon-coated TiO₂, and the coexistence of Ti⁴⁺ and Ti³⁺ is conducive to improving the electronic conductivity of TiO₂ [10–14].

The structure was also detected by Raman spectra (Fig. 1b). In the spectra, the peaks around 153, 202, 396, 513, and 635 cm⁻¹ result from the A_{1g} + 2B_{1g} + 3E_g modes of anatase TiO₂ [15], while those around 1329 and 1596 cm⁻¹ from the disordered carbon (D band) and graphitized carbon (G band) [16], respectively, confirming the coexistence of TiO₂ and carbon in the products. It is noted, the peak intensity of TiO₂ weakens greatly with increasing the pitch content, implying that the structural change resulted from the formation of Ti₉O₁₇ augments.

The presence of Ti₉O₁₇ could be determined by X-ray photoelectron spectroscopy (XPS) (Fig. 2a). Taking TiO₂-12 as an example, the deconvolution of the core level spectrum for Ti 2p yields four

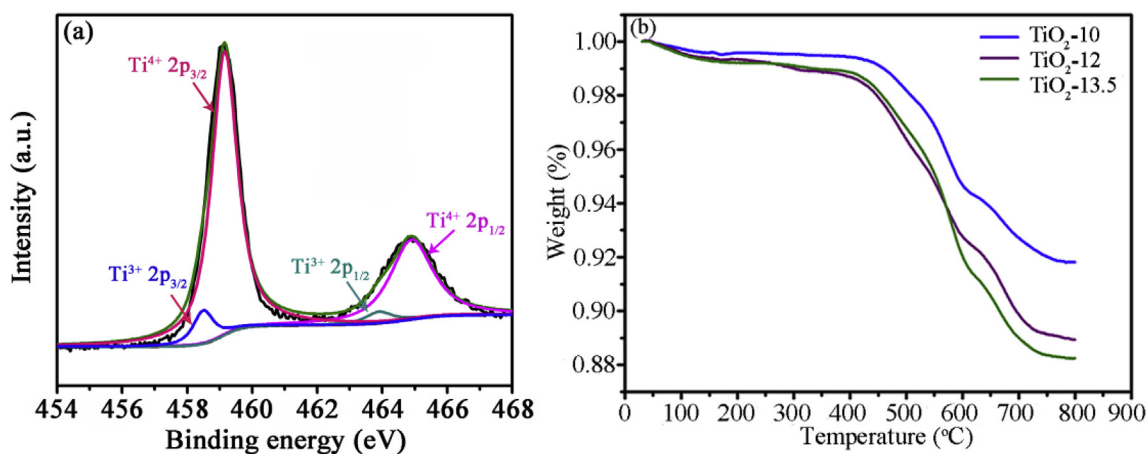


Fig. 2. (a) Core level spectrum of Ti 2p for TiO₂-12, and (b) TG curves of TiO₂-10, TiO₂-12 and TiO₂-13.5.

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