



Short communication

High catalytic activity of anatase titanium dioxide for decomposition of electrolyte solution in lithium ion battery



Ming Liu^{a, b}, Yan-Bing He^a, Wei Lv^a, Chen Zhang^c, Hongda Du^a, Baohua Li^{a, *},
Quan-Hong Yang^{a, c}, Feiyu Kang^{a, b, *}

^a Engineering Laboratory for Functionalized Carbon Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, China

^b Laboratory of Advanced Materials, Department of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China

^c School of Chemical Engineering and Technology, Tianjin University, Tianjin, 30072, China

HIGHLIGHTS

- Anatase TiO₂ possesses high reactivity to initiate the decarboxylation reaction of electrolyte solution.
- The ROLi species and the new phase of flake-like Li₂TiF₆ material are formed as the reaction products.
- The high reactivity restricts the applications of anatase TiO₂ anode in lithium ion battery.

ARTICLE INFO

Article history:

Received 24 March 2014

Received in revised form

6 May 2014

Accepted 12 June 2014

Available online 7 July 2014

Keywords:

Anatase titanium dioxide

Catalytic activity

Decomposition of solvents

Lithium ion battery

ABSTRACT

It has been indicated that anatase TiO₂ is a promising anode material for lithium ion power battery from many previous researches. Whereas, in this work, we find that the anatase TiO₂, when used as an anode for lithium ion battery, has high catalytic activity to initiate the decarboxylation reaction of electrolyte solution, resulting in the large generation of sole gaseous component, CO₂. The ROLi species and the new phase of flake-like Li₂TiF₆ material are the main reaction products between anatase TiO₂ and LiPF₆ based electrolyte solution. This work provides important and urgent information that the surface chemistry of anatase TiO₂ used as the anode material of lithium ion battery must be modified to suppress its catalytic activity for the decomposition of solvents.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Anatase titanium dioxide (TiO₂) has been widely investigated as an anode material of lithium ion battery because of its low cost, high stability, abundance and non-toxicity [1–4]. More importantly, the anatase crystal framework is free from volume variation as compared to other transition metal oxides during lithiation/delithiation process [5]. In addition, it is believed that a thermally unstable solid–electrolyte interface (SEI) film cannot be formed on the TiO₂ surface because the lithium ion insertion voltage of anatase TiO₂ is approximately 1.7 V versus Li⁺/Li and its cut-off discharge potential is 1.0 V, which is higher than the reduction potential of most electrolytes or solvents [6].

* Corresponding authors. Engineering Laboratory for Functionalized Carbon Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, China. Tel.: +86 755 26036118; fax: +86 755 26306118.

E-mail addresses: libh@mail.sz.tsinghua.edu.cn (B. Li), fykang@mail.tsinghua.edu.cn (F. Kang).

Unfortunately, the low electrical conductivity ($\sim 10^{-13}$ S cm⁻¹) of TiO₂ results in poor rate performance, which restricts its real applications in lithium ion battery [6]. Generally, two routes are proposed to improve its rate performance. The first one is to design and tune its microstructure and morphology, and quite many nanostructures, such as hierarchical and nanoporous structure [3], mesocrystals [4], nanospindles [2] and porous nanorods [1] have been reported. Another one is hybridization with carbon materials to obtain hybrid materials, including mesoporous TiO₂ nanospheres/graphene hybrids [7,8], sandwich-like graphene/TiO₂ nanosheets [6], hierarchical anatase TiO₂ nanosheets/carbon nanotube backbone [9], and self-assembled TiO₂/graphene hybrid nanostructures [10]. These aforementioned materials exhibit superior specific capacities, cycling stability and rate capability, promoting the real applications of anatase TiO₂.

Although the electrochemical performance is largely improved by the above efforts, there is another major challenge for the real application of anatase TiO₂, which is its high chemical reactivity. In

our previous work, we investigated the gassing behavior of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery and found that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has high reactivity with electrolyte solution along with generation of gases such as H_2 , CO_2 and CO [11]. It is well-known that the anatase TiO_2 has high photocatalytic activity for organic pollutant decomposition and hydrogen evolution [7,12]. The anatase TiO_2 may also have high catalytic activity for the decomposition of electrolyte solution of lithium ion battery. Unfortunately, to the best of our knowledge, there are no reports for the investigation of the catalytic reactions between anatase TiO_2 and electrolyte solution. In this communication, we, for the first time, report that the anatase TiO_2 has very high reactivity towards electrolyte solution, which contributes to the decarboxylation reaction of solvents along with a large amount of CO_2 generation.

2. Experimental

In this study, anatase TiO_2 was obtained by sintering the precursor amorphous TiO_2 at 450°C for 8 h. The details of the synthesis route of amorphous TiO_2 can be found elsewhere [13,14]. The reaction activity of TiO_2 towards the electrolyte was investigated as follows. 1.6 g of anatase TiO_2 powder was put into aluminum-plastic laminated film packages, and 4 ml solvent (diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene methyl carbonate (EMC)) or LiPF_6 -based electrolyte solution (1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$) was added into above packages before sealing of the packages in an argon-filled glove box. The packages were stored at 25 or 50°C for 3 months. The volumes of the packages before and after storage were monitored using the water displacement method. The gases generated under these conditions was extracted from the top of package by an injector and analyzed on a gas chromatograph (Agilent 7890A GC System) using the GB/T 9722-2006 method.

The anatase TiO_2 powder after soaking was washed using EMC to remove the electrolyte and solvents on the surface of the soaked TiO_2 samples and then dried them at 80°C . The X-ray diffraction (XRD) measurements of anatase TiO_2 samples before and after soaking in DEC and electrolyte of 1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$ at 50°C for 3 months were conducted using a diffractometer (Rigaku D/max 2500/PC) with $\text{Cu K}\alpha$ radiation. Microstructure and morphology of the TiO_2 before and after soaking were examined using field emission scanning electron microscopy (FE-SEM, HITACH S4800, HITACH Co., Japan) and transmission electron microscopy (TEM, JOEL JEM-2100F, Japan). In order to further confirm the reaction product, XPS measurements were conducted using Physical Electronics PHI5802 instrument with X-rays magnesium anode (monochromatic $\text{K}\alpha$ X-rays at 1253.6 eV) as the source. The C 1s region was used as a reference and was set at 284.8 eV. The Fourier transform infrared spectroscopy (FTIR) spectrometer (Bruker VERTEX 70) was applied to further investigate the residual products after reaction.

3. Results and discussion

Fig. 1a shows the detailed XRD patterns of anatase TiO_2 samples before and after soaking in DEC and electrolyte of 1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$ at 50°C for 3 months. It is exhibited that the diffraction peaks of the prepared TiO_2 are exclusively ascribed to TiO_2 crystal with the tetragonal anatase phase (JCPDS No. 21-1272). After the soaking in DEC, the XRD patterns of TiO_2 do not show any changes, indicating that the anatase TiO_2 can maintain its original structure. After soaking in electrolyte solution, the strong characteristic peaks of anatase TiO_2 can also be observed, indicating that the main phase of the reacted products is still the anatase TiO_2 and more interesting, a new phase of Li_2TiF_6 (JCPDS file of card No. 24-

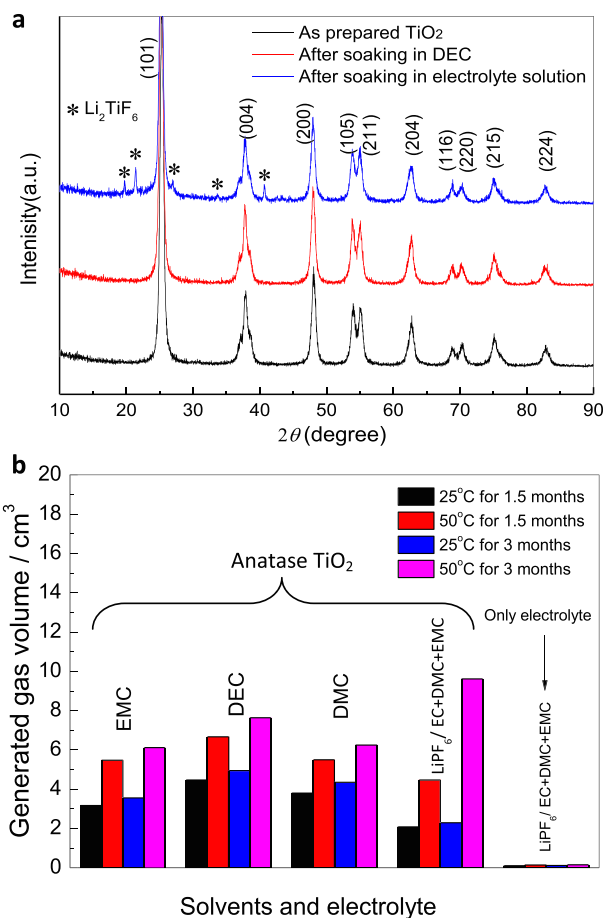


Fig. 1. XRD of the prepared TiO_2 before and after soaking in DEC and electrolyte solution of 1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$ at 50°C for 3 months (a) and gas generated volume when anatase TiO_2 is soaked in solvents and electrolyte solution for 1.5 and 3 months (b).

0662) is formed as a result of the reaction between HF and anatase TiO_2 (Fig. 1a) [15,16].

Severe gassing behavior occurs when the anatase TiO_2 is soaked in both solvents and electrolyte solution, whereas no obvious gassing behavior appeared when there is only electrolyte solution in the absence of TiO_2 . This difference can be clearly identified from the generated gas volume after reaction (Fig. 1b). The above results indicate that the gassing behaviors are intimately related to the anatase TiO_2 . In addition, the solvents of DMC, DEC, and EMC have different molecular structure, which results in their different reactivity with anatase TiO_2 . Therefore, different gas amount was generated when the anatase TiO_2 was soaked by solvents. In particular, up to 9.6 cm^3 of gas was generated after the anatase TiO_2 (1.6 g) was soaked in electrolyte solution (4 ml) at 50°C for 3 months, which is much larger than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rutile TiO_2 soaked in the same electrolyte at the same condition (0.67 and 0.25 cm^3) [11]. Above results clearly present that the anatase TiO_2 has much higher chemical activity than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rutile TiO_2 for the decomposition of solvents reported in our previous work. We also tested the volume of generated gases in packages after storage 1.5 months. Compared to that after storage 3 months, it is found that when the TiO_2 was soaked by single solvent, the generated gases only has minor increase with the storage time increasing from 1.5 to 3 months at both 25 and 50°C , while which has larger increase when the TiO_2 was soaked by electrolyte solution ($\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$) at 50°C . This may be because that the LiPF_6 in

Download English Version:

<https://daneshyari.com/en/article/7736278>

Download Persian Version:

<https://daneshyari.com/article/7736278>

[Daneshyari.com](https://daneshyari.com)