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Improving the performance of a non-aqueous lithium-air battery by defective titanium dioxides with oxygen vacancies

Fang Wang, Haojun Li, Qixing Wu*, Jie Fang, Yang Huang, Chunli Yin, Yanghai Xu, Zhongkuan Luo

Shenzhen Key Laboratory of New Lithium-ion Batteries and Mesoporous Materials, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China

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ABSTRACT

In this work, we proposed using titanium dioxides (TiO_2) with oxygen vacancies (H-TiO_2) as cathode catalysts to improve the electrochemical performance of non-aqueous lithium-air batteries. Such H-TiO_2 catalysts were attained by a facile heat treatment of rutile TiO_2 and the existence of vacancies was confirmed by Raman spectra and X-ray photoelectron spectroscopy (XPS). It was demonstrated that due to the presence of defects which can facilitate the adsorption and dissociation of oxygen, the in-house lithium-air battery with H-TiO_2 can be discharged at the current densities of 0.3 and 0.5 mA cm^{-2} while maintaining the specific capacities of 3.2 and 2.8 mAh cm^{-2}, respectively, much higher than those of the batteries without catalysts or with pristine rutile TiO_2. In addition, the cycling test showed that the battery with H-TiO_2 can undergo 400 and 372 cycles, respectively, at the current densities of 0.3 and 0.5 mA cm^{-2} with a fixed specific capacity of 0.1 mAh cm^{-2} and a cutoff discharge voltage of 2.0 V.
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1. Introduction

Lithium-air (Li-air) batteries have been proposed as the next-generation power sources for portable electronic devices and electric vehicles due to their ultra-high theoretical energy density of 11,140 Wh kg^{-1} at charged state (neglecting oxygen) and 3,458 Wh kg^{-1} at discharged state (considering oxygen) [1–3]. Among various types of Li-air batteries, the one using a non-aqueous electrolyte has been of great interest [7] since the pioneered works by Abraham and Jiang [5]. Although promising, the non-aqueous Li-air battery is still far from practical applications. A number of scientific and practical issues [4–6] have impeded its development. One challenge is the sluggish kinetics of oxygen reduction reaction (ORR) on the cathode [7,8], which results in poor discharge performance and cyclability. Thus, the development of efficient electrocatalysts to accelerate the ORR kinetics is urgently needed.

Up to now, a variety of electrocatalysts, including carbon materials [9–11], noble metals [12,13], perovskites [14–17] and transition metal oxides [18–22] have been investigated in non-aqueous Li-air batteries. Among them, transition metal oxides have attracted considerable interests as promising catalysts for their defective structure, low cost and outstanding catalytic activity. Zhang et al. [23] synthesized porous δ-MnO_2 as catalyst for a Li-O_2 battery. They found that the δ-MnO_2 electrode exhibited a catalytic effect in the discharge process and delivered much higher specific capacities. Yan et al. [24] introduced Co_3O_4 as the cathode catalyst and the cell with the Co_3O_4/carbon (80 wt. % carbon) electrode showed a longer operating life and a higher discharge capacity than did the cells without Co_3O_4. In addition to MnO_2 and Co_3O_4, TiO_2 is also a commonly used metal oxide and its wide application has been demonstrated in the fields of water splitting [25], dye sensitized solar cells [26], sodium-ion [27] batteries and lithium-ion batteries [28]. Recently, TiO_2 were reported as catalyst substrates [29–31] and effective catalysts [32–34] for Li-air batteries due to its superior physicochemical properties and excellent chemical stability. Zhao et al. [29–31] investigated TiO_2 nanotubes as a support for electrocatalysts (RuO_2 and Pt). They proved that TiO_2 could reduce the side reactions and electrolyte decomposition to enhance cycle life of a Li-air battery. Agyeman et al. [32] reported that the catalytic activity of TiO_2 (anatase) was enhanced by nitrogen doping. They attributed the promoted round-trip efficiency and cyclic retention to the improved Li^+ chemisorption and conductivity, which resulted from the presence of the localized states on the surface of nitrogen-doped TiO_2. Kang et al. [33] compared the catalytic activity of two different TiO_2

* Corresponding author. Tel.: +86 755 26557393; fax: +86 755 26536141.
E-mail address: qxwu@szu.edu.cn (Q. Wu).

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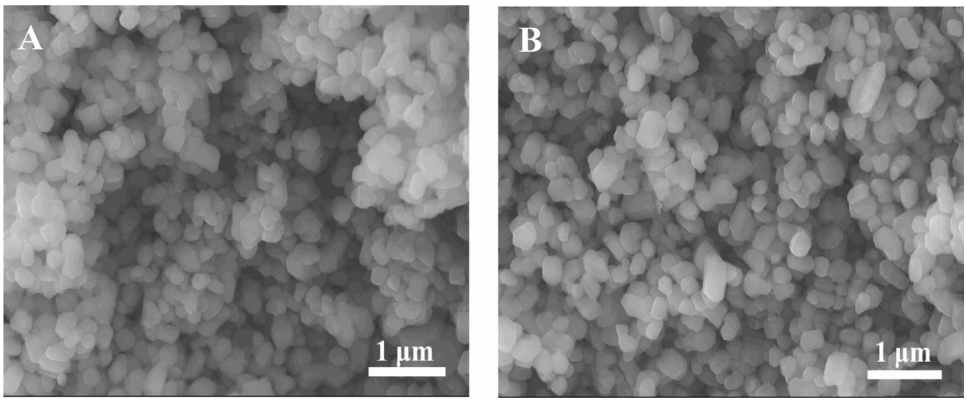

Fig. 1. FESEM images of (A) TiO_2 and (B) H-TiO_2 particles.

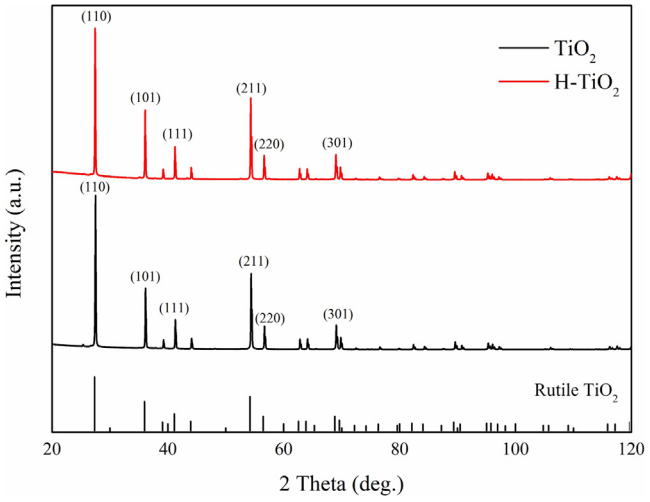

Fig. 2. XRD patterns of TiO_2 and H-TiO_2.

polymorphs (anatase and rutile). They found that rutile TiO_2 exhibited a better catalytic activity in Li–O_2 batteries, owing to its intrinsic electronic structure and surface oxidation state. Geng et al. [35] used density functional theory calculations to study the Li_2O_2 deposition on rutile TiO_2(110) surfaces and found that Li_2O_2 would probably wet the oxides to form amorphous thin films instead of particles, which may facilitate the transport of charge and ions.

In the field of photocatalysis, TiO_2 has been widely used due to its excellent adsorption ability of oxygen [36–38], arising from the presence of oxygen vacancies. Hence, alerting the surface oxidation state of rutile TiO_2 by producing oxygen vacancies may be one way to create more active sites for ORR process, which is of particular interest in a non-aqueous Li-air battery. In the present work, rutile TiO_2 with oxygen vacancies was synthesized by a facile heat treatment method and its physical and chemical characteristics as well as the electrochemical performance in non-aqueous Li–air batteries were studied systematically.

2. Experimental

2.1. Preparation of TiO_2 with oxygen vacancies

To create oxygen vacancies in the TiO_2, rutile TiO_2 (Aladdin Industrial Inc) with particle sizes of about 100 nm was heated at 450 °C for 2 h and followed by annealing in a furnace with argon flow from 450 °C to 1000 °C at a heating rate of 5 °C min^{-1}. The TiO_2 particles after heat treatment were termed as H-TiO_2 hereafter.

2.2. Preparation of cathode and cell assembly

To prepare the cathode slurry, the nitrogen doped carbon nanotubes (NCNTs, Beijing DK Nano Technology), as-prepared

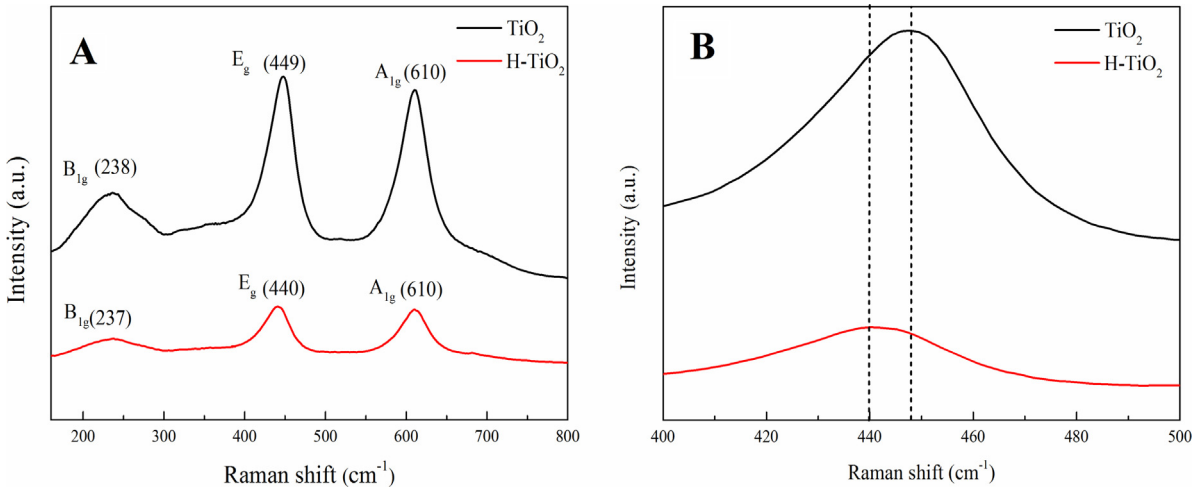

Fig. 3. (A) Raman spectra of TiO_2 and H-TiO_2 at an excitation wavelength of 532 nm; (B) the high-resolution E_g mode of TiO_2 and H-TiO_2.

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