



## Short communication

# Ruthenium oxide modified titanium dioxide nanotube arrays as carbon and binder free lithium–air battery cathode catalyst



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## HIGHLIGHTS

- Carbon and binder free Li–O<sub>2</sub> battery cathodes constructed by a bottom-up method.
- RuO<sub>2</sub> catalyst on a stable TiO<sub>2</sub> nanotube array catalyst support.
- More than 100 cycle charge/discharge.

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## ABSTRACT

RuO<sub>2</sub> modified TiO<sub>2</sub> nanotube arrays, growing on Ti foams, are used as carbon and binder free cathodes for Li–O<sub>2</sub> batteries. The micrometer pores in Ti foams and nanometer pores in TiO<sub>2</sub> nanotubes supply facilitated transport channels for oxygen diffusing into/out of the catalysts in discharge and charge processes. The RuO<sub>2</sub> catalyst exhibits outstanding catalytic active toward oxygen evolution reaction (OER), which leads the charge voltage maintaining around 3.7 V all through the battery cycling. The stability of TiO<sub>2</sub>/Ti support, abundant oxygen transport path and favorable catalytic activity of RuO<sub>2</sub> toward OER enable the Li–O<sub>2</sub> batteries exhibiting 130 cycle discharge/charge.

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## 1. Introduction

RuO<sub>2</sub> has attracted great interest as cathode catalyst for Li–air batteries by its favorable electron conductivity and good catalytic activity towards oxygen evolution reaction (OER). Various carbon materials, such as reduced graphene [1], carbon black [2] and carbon nanotubes [3,4] supported RuO<sub>2</sub> were implemented as oxygen cathodes of Li–air batteries, which exhibited high round-trip efficiency and outstanding catalytic ability. The most attractive characteristic is the low charge voltages of these batteries, about 3.7 V vs. Li<sup>+</sup>/Li, much lower than those catalyzed by carbon materials only. The low charge voltage should be attributed to the strong catalytic ability of RuO<sub>2</sub> to OER. Ryung Byon and his coworkers [4] suggested that, RuO<sub>2</sub> contribute to the formation of poorly crystalline Li<sub>2</sub>O<sub>2</sub> coated over the catalyst with large contact area during

oxygen reduction reaction. Then this unique Li<sub>2</sub>O<sub>2</sub> structure could be smoothly decomposed at low potential upon OER by avoiding the energy loss associated with the decomposition of the more typical Li<sub>2</sub>O<sub>2</sub> structure with a large size, small contact area, and insulating crystals. However, all the studies mentioned above still used carbon materials as catalyst support and implemented conventional air cathode preparation approach, that mixing catalysts with conductive carbons and organic binders then pasting on the porous metal current collectors. Unfortunately, both carbon materials and organic binders have been reported degrading in Li–air batteries [5–11], which causes the instability of Li–air batteries' cathodes, harming batteries' rechargeability. Accordingly, the exploration of carbon and binder free cathodes is urgent for Li–air batteries [12–14].

TiO<sub>2</sub> is an attractive support material for catalyst, because it is stable, environmentally friendly and biocompatible [15–19]. Recently, Bruce and his co-workers [20] reported that, the stability of the TiO<sub>2</sub>-rich surface layer present on the Li–air batteries' cathodes is responsible for the stable and reversible Li<sub>2</sub>O<sub>2</sub> formation/decomposition. Therefore, TiO<sub>2</sub> is a good candidate for catalyst

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support of Li–air battery cathode. In various TiO<sub>2</sub> materials, nanotubes have drawn considerable attention, because of their large specific surface area and abundant mass transport channels. [21] The large surface area can supply abundant sites to accommodate Li<sub>2</sub>O<sub>2</sub> precipitate. Moreover, the straight channels in the nanotubes are beneficial for oxygen transport, enhancing rechargeability and cyclability of Li–air batteries. [22] In present study, we fabricate TiO<sub>2</sub> nanotube arrays on Ti foams, and use the foams as substrates for Li–O<sub>2</sub> battery cathodes. Then RuO<sub>2</sub> catalyst is deposited on TiO<sub>2</sub> support directly by electrodeposition, avoiding using any organic binder. The RuO<sub>2</sub>/TiO<sub>2</sub> cathodes exhibit good catalytic activity towards OER and enable the batteries exhibiting outstanding cycle performances.

## 2. Experimental

### 2.1. Sample preparation

The TiO<sub>2</sub> nanotube arrays were fabricated directly on circular titanium foam plates (thickness 0.5 mm, diameter 15 mm, 99.2% purity) using anodic oxidation. The Ti plates were initially sonicated in acetone, rinsed with pure water, and then etched in 5% HF for 2 min to remove any oxides from the surface. The etched Ti plate was then submerged in a two-electrode cell containing dimethyl sulfoxide (DMSO) + 2 wt% HF and was electrochemically treated via anodization at 20 V for 3 h. The as-anodized plates were washed with deionized water for depositing RuO<sub>2</sub>. RuO<sub>2</sub> was deposited on anodized Ti foams by electrodeposition, which was carried out by cyclic voltammogram (CV) in a potential window of –0.8–2.0 V (vs. SCE) with a scan rate of 50 mV s<sup>–1</sup> using a CHI 660 electrochemical analyzer. The anodized Ti foams were used as working electrode, a 1 cm × 1 cm Pt plate electrode was used as counter electrode, and SCE was used as reference electrode. The electrolyte for electrodeposition was consisted of 10 mM RuCl<sub>3</sub> and 1.2 mM HCl. In the CV process, Ru<sup>3+</sup> ions were reduced to metal Ru on the anodized Ti foams in cathodic process, and the Ru metal was oxidized to RuO<sub>2</sub> in the subsequent anodic process [23]. The generated RuO<sub>2</sub> could not be reduced in the following cathodic process. Therefore, the sweeping caused the RuO<sub>2</sub> growing on the anodized Ti foams [24]. The as-deposited plates were washed, dried and annealed in an oven at 650 °C for 3 h. The weights of the deposited product were measured on a micro-balance (Mettler Toledo) with an accuracy of 0.01 mg. The RuO<sub>2</sub> loading amount on a plate was about 0.1 mg. The RuO<sub>2</sub> modified TiO<sub>2</sub> nanotube array coated Ti foams in this study is abbreviated as “RTT” in the following text.

### 2.2. Instruments for characterization

Scanning electron microscope (SEM) images were obtained on a Hitachi Su-8100. The X-ray diffraction (XRD) patterns were

obtained on a PANalytical X'pert PRO X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). X-ray photoelectron spectra (XPS) were obtained with a K-Alpha electron spectrometer (ThermoFisher Scientific Company) using Al K $\alpha$  (1486.6 eV) radiation. The base pressure was about  $1 \times 10^{-8}$  mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

### 2.3. Li–O<sub>2</sub> battery tests

The Swagelok type Li–O<sub>2</sub> batteries were assembled inside an MBraun glove box. The cells were constructed by placing a 15 mm diameter Li disk on the bottom, covering it with a piece of glass fiber separator (20 mm diameter, Whatman), adding excessive electrolyte (1.0 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME)), placing an air electrode disk on the separator, and sealing the Swagelok cell. All the electrochemical measurements on the batteries were carried out in pure O<sub>2</sub> at 1 atm (99.99%). A BTS-2000 Neware Battery Testing System was employed for charge/discharge tests. For comparison, electrochemical measurements of super P carbon material were also studied as the Li–O<sub>2</sub> battery cathode catalyst. The battery assembling process was consistent with above, except the cathodes were prepared with a conventional carbon based air cathode preparation method. The details are mixing super P with the solution (10 wt%) of Polyvinylidene Fluoride (PVDF) containing N-methyl-2-pyrrolidone (NMP) in a weight ratio of carbon: PVDF = 4: 6, pasting the obtained homogeneous mixture on circular Cu foam plates (with diameter of 15 mm and thickness of 0.5 mm), drying the plates in a vacuum oven for 24 h on 120 °C. The dry plates were applied as the cathodes of Li–O<sub>2</sub> batteries.

## 3. Results and discussion

The SEM images of pristine Ti foams are shown in Fig. 1. The Ti foams are fabricated by hot briquetting from small Ti sands, and commonly used as the filtration devices for air/water treatment. The interspace between the Ti sands endows the Ti foams good gas/liquid permeability, which causes it attractive current collector for Li–O<sub>2</sub> batteries. Certainly, the outstanding stability of Ti metal compared with Al, Fe, Cu, Ni and the other common current collectors is another reason, that we choose it as the cathode substrate [25]. The SEM images of anodized Ti foams are shown in Fig. 2. Fig. 2(a) and (b) are the vertical views of the TiO<sub>2</sub> nanotube arrays, which demonstrate close packing of TiO<sub>2</sub> nanotubes, free-standing on the Ti substrates. The tube diameter is about 150 nm, and the tube wall is about 20 nm, as seen in Fig. 2(a). The bottom views of the films in Fig. 2(c) and (d) also exhibit close packing morphology of the nanotubes. Fig. 3(a) and (b) are the SEM images of the nanotube arrays deposited with RuO<sub>2</sub>, demonstrating the nanoparticle morphology with several decade nanometers on the tube

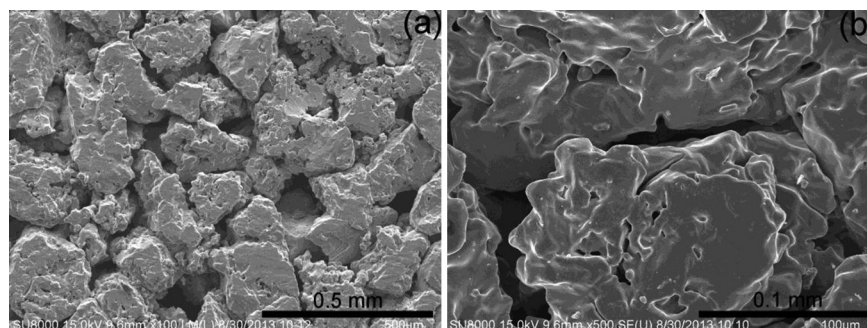


Fig. 1. SEM images of Ti foams.

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