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A carbon-free ruthenium oxide/mesoporous titanium dioxide electrode for lithium-oxygen batteries

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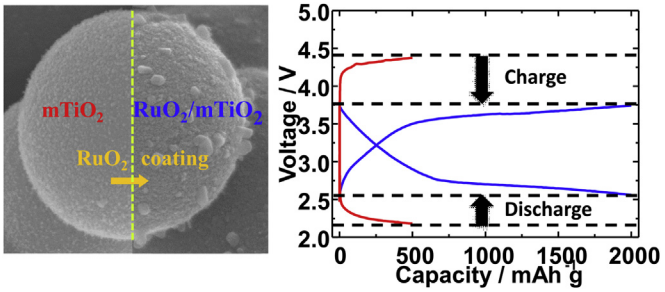
HIGHLIGHTS

- RuO_2 supported mesoporous TiO_2 materials were synthesized by hydrothermal method.
- The Li–O_2 cells using RuO_2/mTiO_2 cathode exhibited low polarization with high energy density.
- From the XRD and XPS results, we confirmed that TiO_2-based electrodes were stable in Li–O_2 batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous TiO_2 with well-distributed RuO_2 catalysts is considered in this paper as a carbon-free cathode material replacement. Benefiting from the highly-porous TiO_2 support structure and high catalytic activity of RuO_2, the Li–O_2 cells with composite RuO_2/mesoporous TiO_2 cathodes show low charge potentials with a high cell capacity. The stability of the TiO_2 materials was verified by investigating stable cell performance as well as through structural and chemical characterization via X-ray diffraction and X-ray photoelectron spectroscopy. This study demonstrates the possibility of achieving high energy at the cell level, free of carbon instability.

1. Introduction

Li–O_2 batteries offer the highest energy density among rechargeable batteries. This superb energy density makes the system one of the most attractive energy storage devices for electric vehicles (EV), energy storage systems (ESS), and other applications [1,2] where high energy density is the most important figure of merit. There remain many challenges, however, for the practical application of Li–O_2 batteries including low energy efficiency caused by the large energy loss during Li–O_2 electrochemical cycles. The widely-accepted theoretical reaction of Li–O_2 batteries is $2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$. The forward direction forming Li_2O_2 represents the discharge process and the reverse reaction of Li_2O_2 decomposition the charge process; however, many parasitic

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reactions have been reported, especially involving electrolyte and carbon materials [3–6]. These undesired side reactions significantly reduce the round-trip efficiency of Li–O_2 batteries. Carbon in particular, the most common material for air electrodes because of its high surface area and good electrical conductivity, may react to Li_2CO_3 in Li–O_2 cells that impede the reversible Li–O_2 reaction [3,6].

Some of the alternative cathode materials suggested recently include TiC [7], Ti_4O_7 [8], indium tin oxide (ITO) [9], MnO_2 [10,11], Co_3O_4 [12,13], and $(Co, Mn)_3O_4$ [14]. Bruce and his co-workers [7] ascribed the stability of TiC cathodes to the surface TiO_2 layer on TiC. The TiO_2 surface layer was stable from the attack of oxygen radicals during cycling. Recently, TiO_2 nanotubes have been explored as a support for electrocatalysts [15,16]. The resulting cells showed enhanced cycle life due to the higher stability of TiO_2 when compared with carbon materials. The Pt or RuO_2 catalyst-loaded TiO_2 nanotube exhibited an enhanced cyclability with low charge potentials, especially under high current density. Despite the high specific capacity in their research, however, the actual capacity of Li–O_2 batteries was not sufficient for practical application, since the specific capacity was calculated based on the catalyst loading mass, which is only 0.1 mg on a support with diameter of 15 mm. Li–O_2 batteries must be highly reversible with a high cell capacity for high energy applications.

An ITO is attractive material among the candidates of carbon-free cathode materials, because of their high electrical conductivity. But it is too hard to synthesize ITO materials with high surface area for large capacity of Li–O_2 batteries. TiO_2 is another candidate of carbon-free cathode materials. It has low electrical conductivity, though it is easy to synthesize the porous nano-structured TiO_2 materials for high capacity of Li–O_2 batteries. Here, we synthesized RuO_2/mesoporous TiO_2 composites, abbreviated as $RuO_2/mTiO_2$, and used as a cathode material for Li–O_2 batteries. A carbon-free electrode of $RuO_2/mTiO_2$ showed 2000 mAh/g of capacity with a low charge potential of under 4 V.

2. Experimental

2.1. Synthesis of mesoporous TiO_2

Mesoporous anatase TiO_2 (denoted as $mTiO_2$) sub-microspheres were synthesized via the urea-assisted hydrothermal method [17], wherein $TiCl_4$ was used as the starting material. A required amount of high-purity $TiCl_4$ (6.59 mL) was added dropwise to distilled

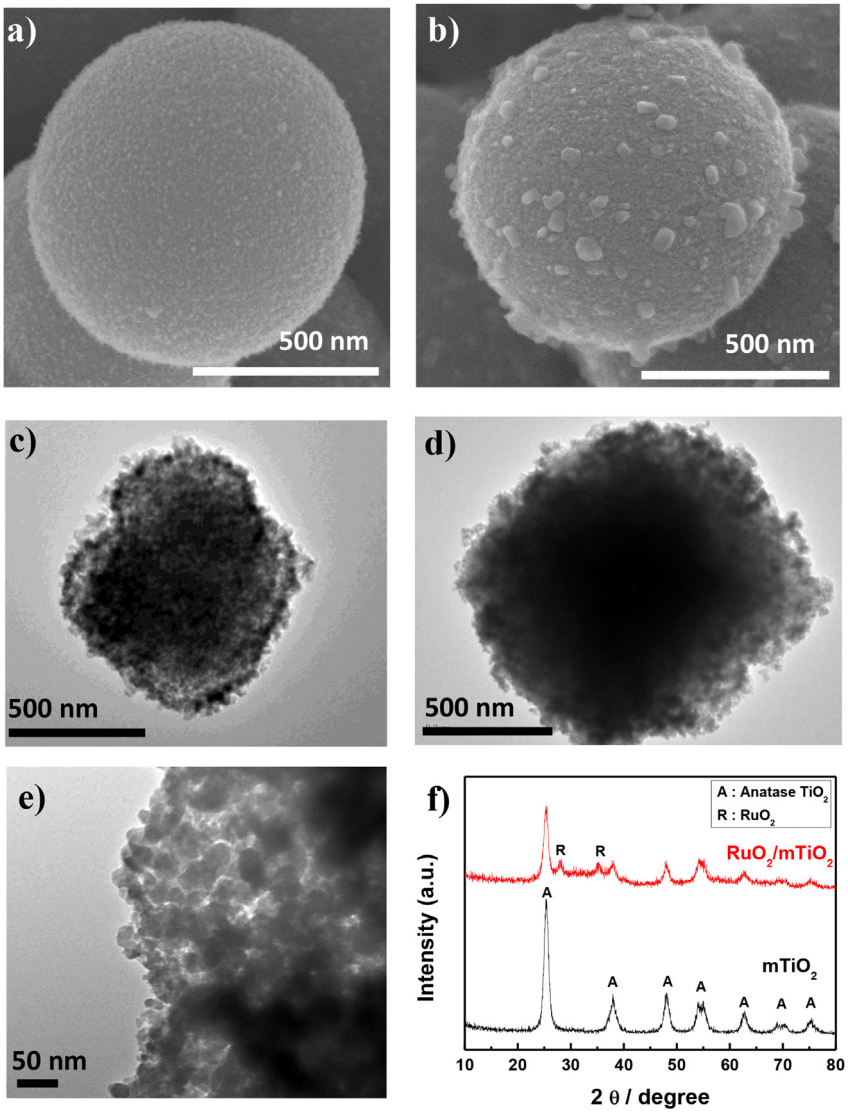

Fig. 1. SEM images of a) $mTiO_2$ and b) $RuO_2/mTiO_2$ particles. TEM images of c) $mTiO_2$ and d), e) $RuO_2/mTiO_2$ particles. f) XRD patterns of $mTiO_2$ and $RuO_2/mTiO_2$.