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Vertically aligned carbon nanotube-ruthenium dioxide core-shell cathode for non-aqueous lithium-oxygen batteries

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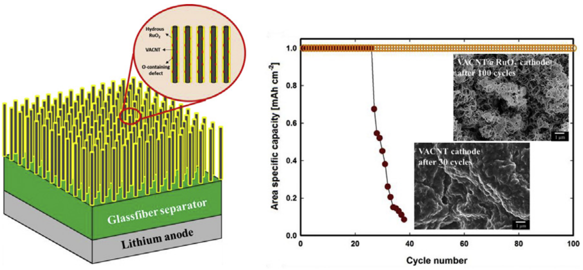
HIGHLIGHTS

- VACNT-RuO_2 core-shell cathode is fabricated for non-aqueous Li-O_2 batteries.
- The cathode showed binder-free and hierarchical structure.
- Hydrous RuO_2 shell eliminated the contact between VACNT and the electrolyte.
- Battery's cycling stability is remarkably improved with the novel cathode.

GRAPHICAL ABSTRACT



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ABSTRACT

Exploitation of hierarchical porous carbons is increasingly attractive for high-capacity lithium (Li)-oxygen (O_2) battery cathodes. However, their practical applications in non-aqueous electrolytes are limited by poor rechargeability, primarily due to the decomposition of carbon electrode and electrolyte. In this work, we report a vertically aligned carbon nanotube (VACNT)-ruthenium dioxide (RuO_2) core-shell (VACNT@RuO_2) cathode for non-aqueous Li-O_2 batteries. The cathode is fabricated with VACNT as the core material and hydrous RuO_2 as the shell material, which eliminates the direct contact between the carbon and nucleophilic reactive intermediate species in the electrolyte. In comparison with the VACNT cathode, the VACNT@RuO_2 cathode presents a superior rate capability (3.3-fold less reduction in capacity) and cycling stability (sustainable for 100 cycles), with a maximum capacity as large as 13.2 mAh cm^{-2} (6600 mAh $g^{-1}_{electrode}$) at 1.0 mA cm^{-2}. The proposed cathode exhibiting a binder-free and hierarchical core-shell structure is a promising candidate for rechargeable non-aqueous Li-O_2 batteries.

1. Introduction

Non-aqueous lithium (Li)-oxygen (O_2) batteries have gained increasing attention as one of the most promising electrochemical energy storage technologies during the past few decades [1,2]. With the ability to deliver a theoretical specific energy of 3600 Wh kg^{-1}, far exceeding that of the state-of-the-art Li-ion batteries at ~400 Wh kg^{-1}, non-aqueous Li-O_2 batteries possess an exciting potential for matching the ever-growing energy demand for electric vehicles and portable devices [3–7]. Several technical limitations, however, must first be overcome to build a rechargeable system before they can be used for practical applications.

Major challenges associated with the discharge products, mainly lithium peroxide (Li_2O_2), arise from their poor solubility in non-aqueous electrolytes [8]. As an electrical insulator, Li_2O_2 not only physically blocks electrolyte pathways but also electrically

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passivates cathode surfaces, thereby reducing the battery's capacity and rate capability [9,10]. An ideal cathode must have a large pore volume and high surface area to enable more efficient transportation of Li ions, O_2 and electrons; indeed, the well-connected pore structure with short diffusion pathways are favorable [11]. Hence, the binder-free and hierarchical porous carbon electrodes have been extensively investigated over a wide range of carbons [12–19]. Mitchell et al. first applied a vertically aligned carbon nanofiber (VACNF) directly grown onto the porous current collector as the cathode, doubling the capacity of the carbon black electrode around 3240 mAh $g_{electrode}^{-1}$ [12]. Subsequently, Shui et al. presented the VACNF cathode in a coral-like shape to have more appropriate distribution of solid discharge products, and, as a result, reported an unprecedentedly large capacity of up to 40,000 mAh $g_{electrode}^{-1}$ [13]. The hierarchical porous cathodes composed of different carbon materials with enlarged surface area, e.g., carbon hollow sphere and graphene, are explored in succession [14–17]. More recently, Lim et al. fabricated a hierarchically-woven carbon nanotube cathode and improved both the capacity and rate capability [18,19]. Yet, despite these efforts, the Li-O_2 batteries with the aforementioned cathodes, without exception, have suffered from a severe capacity fading, caused by the instability of carbon electrode and electrolyte [20].

Carbon electrode decomposition is another challenging issue that needs to be addressed. It was initially presumed that, during discharge, Li_2O_2 chemically reacts with carbon and forms lithium carbonate (Li_2CO_3) by $C + Li_2O_2 + 1/2\ O_2 \rightarrow Li_2CO_3$ [21,22]. Itkis et al. proposed a more realistic mechanism, in which the intermediate superoxide anion (O_2^-) triggers the formation of oxygen-containing groups on the carbon surfaces, and eventually convert them into Li_2CO_3 or other carbonate species by nucleophilic reaction [23]. These byproducts have wider bandgaps compared to that of Li_2O_2 (~4.5 eV) and thus require much higher electrical energy for complete oxidation [24]. Further production of Li_2CO_3 is accompanied by the electrolyte decomposition at charge voltages higher than 4.0 V, owing to the limited electrochemical window in the oxidative environment [25–27]. The formation and decomposition of Li_2CO_3 are, with no doubt, irreversible. Hence, a cathode design that can effectively eliminate the surfaces of carbon electrode in direct contact with electrolyte and Li_2O_2 would greatly benefit the cycling stability of non-aqueous Li-O_2 batteries.

To achieve a binder-free and hierarchically porous carbon electrode with improved cycling stability, we report a vertically aligned carbon nanotube (VACNT)-ruthenium dioxide (RuO_2) core-shell (VACNT@RuO_2) cathode for non-aqueous Li-O_2 batteries. As illustrated in Fig. 1, the VACNT is synthesized via chemical vapor deposition (CVD) method and used as the core material to fabricate a binder-free and hierarchical porous structure. Subsequently, the hydrous RuO_2 is deposited onto the surfaces of VACNT, in the form of a continuous film, to prevent the defect sites on carbon surfaces from oxidizing into Li_2CO_3. RuO_2 has high electrocatalytic activities towards both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [28], and hydrous RuO_2 exhibits even superior electrocatalytic activity towards OER than that of anhydrous rutile RuO_2 due to the improved flexibility on the active sites [29]. The electrochemical performance of a non-aqueous Li-O_2 battery with the VACNT@RuO_2 cathode, including discharge-charge behavior, rate capability and cycling stability, is examined in comparison to those with the CNT and VACNT cathodes.

2. Experimental

2.1. Fabrication of the VACNT@RuO_2 cathode

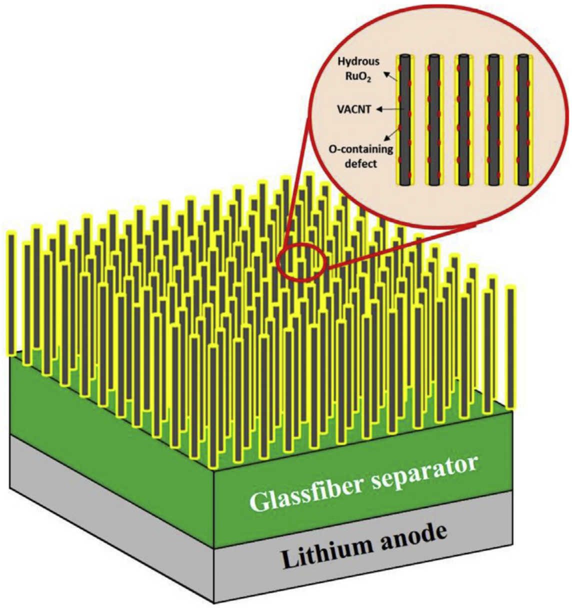

Fig. 1. Schematic illustration of the VACNT@RuO_2 cathode employed in a non-aqueous Li-O_2 battery.

The VACNT was synthesized via a catalytic CVD method [30]. A 10 mM aqueous solution of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99 wt %, Sigma Aldrich) and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 99 wt%, Sigma Aldrich) with a 1:1 M ratio was drop-coated onto aluminum foil and dried at an ambient temperature overnight. The substrate was subsequently placed into a quartz tube reactor, tightly sealed and thoroughly purged with a Ar (95 wt%)-H_2 (5 wt %) mixture gas for 20 min to remove excess O_2. The reactor was then heated at a constant rate of 5 °C min^{-1} until the temperature reached 640 °C. The substrate was annealed for 15 min at a fixed temperature of 640 °C to convert Fe_2O_3 into Fe catalyst, and the carbon source was then introduced into the reactor by bubbling the mixture gas through as-purchased ethylenediamine (99 wt%, Sigma Aldrich) for 20 min. Subsequently, the reactor was left to cool naturally to ambient temperature under high-purity Ar gas flow. The collected sample was immersed into 3 M potassium hydroxide (85 wt%, VWR Scientific) aqueous solution at 80 °C to detach a VACNT layer from the substrate, followed by a sequential treatment with 8 M hydrochloric acid (37 wt%, VWR Scientific) and distilled water for the removal of residual metal impurities [31]. The resultant VACNT was freeze-dried for 24 h to prevent a wetting (or capillary) induced collapse of the hierarchical structure [32].

The hydrous RuO_2 was deposited onto the surfaces of pre-synthesized VACNT via a sol-gel method reported elsewhere [33]. The VACNT was firstly immersed into 30 wt% nitric acid (68 wt%, VWR Scientific) at 110 °C for 4 h. The acid-treated VACNT was dipped into a 0.1 M ruthenium chloride hydrate ($RuCl_3 \cdot 3H_2O$, 99.98 wt%, Sigma Aldrich) aqueous solution and sonicated for 10 min. The 0.3 M sodium bicarbonate (99.5 wt%, Sigma Aldrich) was then added drop-wise to the mixture until the pH value reached 7 [33]. After vigorous stirring for 20 h, the VACNT coated with $RuO_x \cdot (OH)_y$ was collected and rinsed several times with distilled water. The sample was slowly dried at 30 °C for 24 h and then annealed at 150 °C for 20 h in air. Finally, the VACNT and VACNT@RuO_2 cathode samples are cut into circular discs using a 10 mm diameter punch and additionally dried at 120 °C over 48 h prior to characterization. For all cathodes, the carbon loading was measured to be 0.62 ± 0.01 mg cm^{-2}.