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

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Abstract

Exploitation of hierarchical porous carbons is increasingly attractive for high-capacity lithium (Li)-oxygen (O2) 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 (RuO2) core-shell (VACNT@RuO2) cathode for non-aqueous Li-O2 batteries. The cathode is fabricated with VACNT as the core material and hydrous RuO2 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@RuO2 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-O2 batteries.

1. Introduction

Non-aqueous lithium (Li)-oxygen (O2) 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-O2 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 (Li2O2), arise from their poor solubility in non-aqueous electrolytes [8]. As an electrical insulator, Li2O2 not only physically blocks electrolyte pathways but also electrically
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, O₂ 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⁻¹ electrode [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⁻¹ electrode [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-O₂ 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, Li₂O₂ chemically reacts with carbon and forms lithium carbonate (Li₂CO₃) by C + Li₂O₂ + 1/2 O₂ → Li₂CO₃ [21,22]. Itkis et al. proposed a more realistic mechanism, in which the intermediate superoxide anion (O₂⁻) triggers the formation of oxygen-containing groups on the carbon surfaces, and eventually convert them into Li₂CO₃ or other carbonate species by nucleophilic reaction [23]. These byproducts have wider bandgaps compared to that of Li₂O₂ (~4.5 eV) and thus require much higher electrical energy for complete oxidation [24]. Further production of Li₂CO₃ 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 Li₂CO₃ are, with no doubt, irreversible. Hence, a cathode design that can effectively eliminate the surfaces of carbon electrode in direct contact with electrolyte and Li₂O₂ would greatly benefit the cycling stability of non-aqueous Li-O₂ batteries.

To achieve a binder-free and hierarchical porous carbon electrode with improved cycling stability, we report a vertically aligned carbon nanotube (VACNT)-ruthenium dioxide (RuO₂) core-shell (VACNT@RuO₂) cathode for non-aqueous Li-O₂ 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 RuO₂ 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 Li₂CO₃. RuO₂ has high electrocatalytic activities towards both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [28], and hydrous RuO₂ exhibits even superior electrocatalytic activity towards OER than that of anhydrous rutile RuO₂ due to the improved flexibility on the active sites [29]. The electrochemical performance of a non-aqueous Li-O₂ battery with the VACNT@RuO₂ 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@RuO₂ cathode

The VACNT was synthesized via a catalytic CVD method [30].
2.2. Characterization

The morphology of the pristine cathodes was observed by transmission electron microscopy (TEM, JEOL, 2010F) and scanning electron microscopy (SEM, JEOL, JSM-6700F). A small section of the pristine cathode was removed to be dispersed in N-methyl-2-pyrrolidinone (99.5 wt%, Sigma Aldrich), sonicated, and drop-coated onto the holey carbon-coated Cu grids for TEM. After battery cycling, the discharged cathodes were disassembled and cleansed with pure tetraethylene glycol dimethyl ether (TEGDME, 99 wt%, Sigma Aldrich) to observe the morphology of the discharge products by SEM. The X-ray diffraction (XRD, Panalytical, PW1825) patterns of the cathodes were collected using Cu Kα radiation (λ = 0.154 nm) at 40 kV, with 2θ value ranging from 20° to 80°. Thermogravimetric analysis (TGA, TA Instruments, Q5000) was conducted by heating the samples in air at a constant rate of 10 °C min⁻¹ to 800 °C. The surface composition of the cathodes was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos, Axis Ultra DLD) with Mg Kα radiation (1253.6 eV). The Raman spectra (Renishaw, Invia Plus) was recorded using Ar laser with 522 nm excitation wavelength. Attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR, Bruker, Vertex 70 Hyperion 1000) was carried out to identify Li₂O₂ and Li₂CO₃ in the cycled cathodes.

2.3. Battery test

The non-aqueous Li-O₂ battery was constructed with a Li foil, a glass microfiber separator (GF/C, Whatman), and either a VACNT or VACNT@RuO₂ cathode, where 100 μL of 1 M lithium Bis[Trifluoromethanesulphonylimide (LiTFSI) (99.95 wt%, Sigma Aldrich) dissolved in TEGDME was employed as an electrolyte.
electrolyte was stored with molecular sieves for several days to maintain water content of less than 10 ppm [34]. In addition, the battery was assembled with a polytetrafluoroethylene (PTFE) fixture (T-810-6, Swagelok) and disassembled in an Ar-filled glove box (Lab 2000, Etelux) with water content below 0.1 ppm. At an ambient temperature, the cell was fed with high purity O2 gas and stabilized for 2 h under open circuit condition. The discharge-charge curves were then examined on a battery cycler (Neware, CT-3008W), at different current densities of 0.2, 0.5 and 1.0 mA cm$^{-2}$, which correspond to applied currents of 0.157, 0.393 and 0.785 mA, respectively. For the cycling stability of the proposed cathode, the battery with a stable reference anode, namely, the lithium iron phosphate (Li$_{1-x}$FePO$_4$, 0.2 < x < 0.3) mixed with carbon black (EC-600 JD, Akzo Nobel) was prepared and tested at a current density of 0.5 mA cm$^{-2}$ with a fixed capacity of 1.0 mAh cm$^{-2}$ [35]. After the use of this anode, we may significantly reduce the effect of the anode on the cycling stability of the battery. The recorded voltage was converted to Li/Li$^+$ by adding 3.45 V. The anodic linear sweep voltammetry was also conducted at potentials ranging from open circuit potential to 4.7 V at a sweep rate of 1 mVs$^{-1}$, where the VACNT and VACNT@RuO$_2$ cathode without Li$_2$O$_2$ was used.

3. Results and discussion

3.1. Characterization of the VACNT@RuO$_2$ cathode

The microstructures of the VACNT and VACNT@RuO$_2$ cathodes are shown in Fig. 2a–d, respectively. After CVD growth, the pristine VACNT displays a large number of pores in sizes of several tens to hundreds of nanometers (Fig. 2a), preserving sufficiently large pores after deposition of RuO$_2$ (Fig. 2b), and no significant structural collapse of the vertical alignment is found for all the samples (Fig. 2c,d). However, for VACNT@RuO$_2$, the carbon nanotubes are further intertwined, in comparison to those in VACNT, attributed to $\pi$-$\pi$ stacking interactions [36]. Indistinct grain boundaries seen in VACNT@RuO$_2$ suggest that hydrous RuO$_2$ may have been fabricated at a relatively low annealing temperature of 150 °C [37]. XRD patterns of the two cathodes are shown in Fig. 2e. Two sharp peaks at 26.5$^\circ$ and 44.0$^\circ$ for graphitic carbon (002) and (100) planes (JCPDS # 65-6212) and a broad peak at 35.1$^\circ$ for rutile RuO$_2$ (101) plane (JCPDS # 43-1027) reveal that RuO$_2$ crystallizes poorly and is composites with graphitized carbons. Fig. 2f presents a high resolution TEM image of VACNT@RuO$_2$ with the selected area electron diffraction (SAED) analysis. It is apparent that an amorphous layer with an average thickness of 3 nm is coated onto the surfaces of multi-walled carbon nanotubes, composed of around 10 graphitic walls with external tube diameters ranging from 10 to 15 nm. Two ambiguous ring patterns shown in the SAED, representing the (110) and (101) planes of RuO$_2$, confirm the amorphous nature of RuO$_2$, which is consistent with the XRD patterns and TEM images [38,39].

The Raman spectra of the VACNT and VACNT@RuO$_2$ cathodes are presented in Fig. 3a. VACNT exhibits strong peaks for the D band at 1337 cm$^{-1}$ and G band at 1596 cm$^{-1}$, which are corresponding to the disordered and ordered carbons, respectively [40]. However, the intensities of these peaks significantly decrease after deposition of RuO$_2$, indicating that the surfaces of VACNT are vastly covered with RuO$_2$. An additional peak observed at 510 cm$^{-1}$ is attributed to

![Fig. 3.](image-url)
the $E_g$ mode of RuO$_2$ [41]. Due to the poorly crystalline structure, the peaks of the $A_{1g}$ mode at 630 cm$^{-1}$ and $B_{2g}$ mode at 690 cm$^{-1}$ are hardly distinguishable from noise [42]. We also perform the thermogravimetric (TG) analysis for VACNT and VACNT@RuO$_2$ to measure the mass of hydrated water and RuO$_2$ (Fig. 3b). The mass of hydrated water is particularly an important factor controlling the electronic properties of hydrous RuO$_2$ [43]. The weight loss of VACNT@RuO$_2$ at temperatures lower than 400°C is mainly attributed to the dehydration of hydrous RuO$_2$, by which the hydration number, $n$, in RuO$_2$$\cdot$nH$_2$O is obtained as 0.91 [44]. Hydrous RuO$_2$ with hydration numbers ranging from 0.5 to 1.0 ensures both amorphous nature and high electronic conductivity of ~300 S cm$^{-1}$ [33,37,39,41,43]. Based on the TG data at 800°C, the RuO$_2$ mass loading for VACNT@RuO$_2$ is determined to be 69.0 wt%. Furthermore, the oxidation state of Ru is investigated by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3c, the O 1s spectra can be separated into four peaks, deconvoluted at binding energies of 534.2 eV, 532.4 eV, 530.9 eV and 529.0 eV, which represent COOH, H$_2$O, RuOH and RuO$_2$, respectively [45]. Similarly, the Ru 3p spectra confirm the co-existence of RuOH and RuO$_2$ (Fig. 3d). The results in Figs. 2 and 3 demonstrate that hydrous RuO$_2$ is uniformly deposited onto VACNT via sol-gel method, and thereby, a cathode with hierarchical core-shell structure can be fabricated.

### 3.2. Discharge and charge performance

The discharge-charge curves of non-aqueous Li-O$_2$ batteries with the VACNT and VACNT@RuO$_2$ cathodes are presented in Fig. 4a. We first compare the discharge-charge characteristics of the VACNT cathode with those of the carbon nanotube (CNT) cathode, which is detached from VACNT and mixed with 10 wt% PTFE binder. The battery with the CNT cathode exhibits a capacity of 1.99 mAh cm$^{-2}$ (2198 mAh g$_{electrode}^{-1}$) at a current density of 0.5 mA cm$^{-2}$, where the discharge and charge voltage plateaus are formed at 2.46 V and 4.31 V, respectively. In contrast, the battery with the VACNT cathode dramatically improves the capacity up to 21.4 mAh cm$^{-2}$ (34,516 mAh g$_{electrode}^{-1}$) and also increases the discharge voltage plateau by 0.13 V. These improvements can be attributed to more efficient utilization of the electrode surfaces and pore volumes in the VACNT cathode, which features a binder-free and hierarchical porous structure (Fig. 2). However, the charge voltage plateau remains higher than 4.2 V for both the CNT and VACNT cathodes, indicating that further attempts should be made to decrease the battery’s charge voltage. VACNT is thus selected to support hydrous RuO$_2$ instead of CNT. As hydrous RuO$_2$ exhibits excellent catalytic activities for both ORR and OER, the discharge and charge voltage plateaus of the VACNT@RuO$_2$ cathode are observed at 2.70 V and 3.88 V, respectively, with a capacity larger than 15.4 mAh cm$^{-2}$ (7700 mAh g$_{electrode}^{-1}$). As compared to the VACNT cathode, the discharge capacity decreased from 21.4 to 15.4 mAh cm$^{-2}$ due to the different crystallinity and morphology of Li$_2$O$_2$. This is supported by Yilmaz et al., who also reported the capacity decrease after the use of MWNT supported RuO$_2$ nanoparticles [46]. Fig. 4b presents the XRD patterns of the discharged cathodes in comparison to those of the pristine cathodes. For the discharged VACNT cathode, the sharp peaks at 32.9°, 35.0°, 40.6° and 58.7° are assigned to (100), (101), (102) and (110) planes of Li$_2$O$_2$ (JCPDS #09-0355). However, the discharged VACNT@RuO$_2$ cathode exhibits three broad peaks at 32.9°, 35.0° and...
58.7°, indicating that poorly crystalline Li₂O₂ is formed. The low crystallinity of Li₂O₂ may be derived from strong oxygen adsorption onto the surfaces of RuO₂ [28,46]. The peak intensity at the (110) plane also significantly decreases by cleavage of the O–O bond [47]. These defective Li₂O₂ surfaces, including Li and O vacancies, are regarded to be beneficial for the transportation of Li ion and electron [28,48–50]. The morphology of the two cathodes is observed by SEM after they are fully discharged, and shown in Fig. 4c,d. The inset displays high resolution images on the cross-sectional surfaces of the discharged cathodes. For the VACNT cathode, the ball-shaped Li₂O₂ as large as 1 μm can be seen, as the LiO₂ intermediates initially dissolve into the electrolyte and then deposit onto the pre-deposited Li₂O₂ during discharge, due to weak oxygen adsorption on the carbon surfaces [50]. Thus, Li₂O₂ only has partial contacts with the VACNT surfaces. However, the film-like Li₂O₂ is formed on the surfaces of the VACNT@RuO₂ cathode, which is in consistence with previous experiments on other metal and metal-oxide electrodes [51–53]. The film-like morphology enlarges the contact between Li₂O₂ deposits and RuO₂ surfaces, hence further improving the electrode surface utilization during charge.

3.3. Rate capability

The rate capability of non-aqueous Li-O₂ batteries with the CNT, VACNT and VACNT@RuO₂ cathodes is tested at current densities of 0.2, 0.5 and 1.0 mA cm⁻², and presented in Fig. 5. As shown in Fig. 5a,b, the batteries with the both CNT and VACNT cathodes show a poor rate capability. For the CNT cathode, the capacity is reduced from 3.64 mAh cm⁻² (5337 mAh g⁻¹ electrode) to 0.54 mAh cm⁻² (792 mAh g⁻¹ electrode) at increasing current densities from 0.2 mA cm⁻² to 1.0 mA cm⁻². The discharge voltage plateau is initially observed to be 2.52 V at 0.2 mA cm⁻² but significantly decrease to 2.24 V at 1.0 mA cm⁻². Similarly, the battery with the VACNT cathode exhibited a severe capacity reduction from 27.9 mAh cm⁻² (45,000 mAh g⁻¹ electrode) to 11.9 mAh cm⁻² (19,194 mAh g⁻¹ electrode), where the discharge voltage plateau was decreased from 2.63 V at 0.2 mA cm⁻² to 2.42 V at 1.0 mA cm⁻². The poor rate performance is due to different kinetic routes in formation of Li₂O₂ at high and low current densities. On cathode surfaces with weak oxygen adsorption, such as VACNT, the dissolution of LiO₂ is dominant at initial stages but become less preferable with increasing current density, due to the solubility limitation, which results in a sharp decrease of the capacity at 1.0 mA cm⁻² [54,55]. However, the VACNT@RuO₂ cathode experiences only 27% decrease in capacity from 18.1 mAh cm⁻² (9050 mAh g⁻¹ electrode⁻¹) at 0.2 mA cm⁻² to 13.2 mAh cm⁻² (6600 mAh g⁻¹ electrode⁻¹) at 1.0 mA cm⁻² (Fig. 5c). At the highest current density of 1.0 mA cm⁻², the discharge voltage plateau remains higher than 2.65 V, and the terminal charge voltage remained lower than 4.09 V. It is suggested that the rate performance of the VACNT@RuO₂ cathode benefits from formation of defective Li₂O₂, which offers additional routes for conduction of the Li ions and electrons during cycling, and therefore shows a remarkable improvement compared to that of the VACNT cathode. In addition, the anodic LSV (Fig. 5d) curve without Li₂O₂ shows no obvious peak for the cathodes at potentials lower than 4.2 V, where electrochemical decomposition of the TEGDME electrolyte occurs, indicating the effect of oxidation of the VACNT and RuO₂ on the charge performance is negligible.

Fig. 5. Discharge and charge curves at various current densities of 0.2, 0.5 and 1.0 mA cm⁻²: (A) CNT cathode, (B) VACNT cathode, (C) VACNT@RuO₂ cathode and (D) LSV curves of the VACNT and VACNT@RuO₂ without Li₂O₂.
Fig. 6. Comparison of the cycling stability at 0.5 mA cm\(^{-2}\) with a fixed capacity of 1.0 mAh cm\(^{-2}\). (A) CNT cathode, (B) VACNT cathode, (C) VACNT@RuO\(_2\) cathode and (D) the capacity of the three cathodes as a function of cycle number.

Fig. 7. ATR-FTIR spectra of (A) the VACNT cathode and (B) the VACNT@RuO\(_2\) cathode with increasing cycle numbers. Reference Li\(_2\)O\(_2\) and Li\(_2\)CO\(_3\) are used for comparison [57]. (C) SEM image of the VACNT cathode after 30 cycles and (D) SEM image of the VACNT@RuO\(_2\) cathode after 100 cycles.
3.4. Cycling stability

Finally, the cycling stability of the CNT, VACNT and VACNT@RuO2 cathodes is evaluated. As presented in Fig. 6a,b, the batteries with the both CNT and VACNT cathodes start to decrease the discharge voltage plateau and increase the charge voltage plateau at the 10th cycle, and in turn, rapidly decay their capacities from 1.0 mAh cm\(^{-2}\) to below 0.2 mAh cm\(^{-2}\) at around 30th cycle. The severe capacity fading may be caused by the decomposition of carbon electrode and electrolyte at charge voltages higher than 4.0 V [21–24,56]. In contrast, the battery with the VACNT@RuO2 cathode delivered more stable cycling profiles with improved energy efficiency (i.e. energy output/input energy per cycle) around 76.4% (Fig. 6c). The discharge and charge voltage plateaus are formed at 2.85 V and 3.73 V, respectively, and the terminal charge voltage remained lower than 3.89 V for 100 cycles. Fig. 6d also showed that the VACNT@RuO2 cathode is operated at 1.0 mAh cm\(^{-2}\) for 100 cycles, without any signs of the capacity decay, while the CNT and VACNT cathodes remained operable for 21 and 26 cycles, respectively, mainly due to the irreversibility rising from the formation of Li2O2 [22]. This implies that eliminating the direct contact between the carbon surfaces and electrolyte may be a critical factor for the battery’s cycle life.

Fig. 7a,b shows the ATR FTIR spectra of the cycled VACNT and VACNT@RuO2 cathodes collected after discharge and charge at desired cycles, respectively. From the reference data, the broad absorption peaks between 450 cm\(^{-1}\) and 600 cm\(^{-1}\) are associated with both Li2O2 and Li2CO3, while the peaks at around 840 cm\(^{-1}\) and between 1400 cm\(^{-1}\) and 1550 cm\(^{-1}\) are solely dependent on the formation of Li2CO3. As presented in Fig. 7a, Li2CO3 accumulates on the surfaces of the VACNT cathode with increasing cycle number, and mostly remains unoxidized after charge. However, for the VACNT@RuO2 cathode, the peaks ascribed to Li2CO3 exhibit much weaker intensities compared to those of the VACNT cathode (Fig. 7b). More importantly, the peaks at 840 cm\(^{-1}\) and between 450 cm\(^{-1}\) and 600 cm\(^{-1}\) repeatedly appear and fade during cycling, suggesting that formation of Li2CO3 at the carbon/Li2O2 interfaces is suppressed [24,57]. This is further supported by SEM images of the cycled cathodes. Fig. 7c shows a large amount of residual solid products, mainly Li2CO3, accumulated on the surfaces of VACNT after 30 cycles, while only a small amount of Li2O2 and Li2CO3 are observed on the VACNT@RuO2 surfaces after 100 cycles (Fig. 7d), presenting an excellent cycling stability.

4. Conclusions

In this work, we fabricated a VACNT-RuO2 core-shell cathode for non-aqueous Li-O2 batteries, and evaluated it in comparison to a VACNT cathode. The continuous RuO2 layer with an average thickness of 3 nm was deposited onto the surfaces of VACNT via sol-gel method, which exhibited a binder-free and hierarchical core-shell structure with carbon surfaces effectively separated from the electrolyte. The cathode promoted the growth of defective Li2O2 in the form of thin film, enlarging its contact with the RuO2 surfaces, and thereby resulted in lowering the charge voltage. Battery tests showed that a dramatic improvement can be achieved in the rate capability with an increased capacity after the use of the VACNT@RuO2 cathode. Highly stable discharge-charge profiles for 100 cycles are mainly attributed to the suppression of carbon decomposition. These results demonstrated that the Li-O2 batteries with the proposed cathode structure has the potential to create excellent opportunities for the development of practical Li-O2 batteries.

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References
