A RuO₂ nanoparticle-decorated buckypaper cathode for non-aqueous lithium–oxygen batteries†

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We report a non-aqueous lithium–oxygen battery with its cathode made of a RuO₂ nanoparticle-decorated buckypaper (weaved with carbon nanotubes). Compared with conventional slurry-formed cathodes, the present cathode has two striking features: (i) no binder is required, avoiding the problems of surface-loss and instability due to the introduction of a polymeric binder, and (ii) no additional current collector is needed, increasing the practical specific capacity. The present battery demonstrates a discharge plateau of 2.56 V and a charge plateau of 4.10 V at a current density of 0.4 mA cm⁻², with a discharge capacity of 4.72 mA h cm⁻² (1150 mA h gᵣ₋₋⁻₋₋¹). It is also shown that at a fixed capacity of 2.0 mA h cm⁻², the energy efficiency of the battery reaches 71.2%, 65.4%, and 58.0% at a current density of 0.2, 0.4, and 0.8 mA cm⁻², respectively. Furthermore, the battery is able to operate for 50 cycles at a fixed capacity of 1.0 mA h cm⁻², showing its good cycling stability. The results suggest that the RuO₂ nanoparticle-decorated buckypaper cathode offers promise for a high-practical specific capacity, high-energy efficiency, and stable electrode for non-aqueous lithium–oxygen batteries.

Introduction

Non-aqueous lithium–oxygen batteries are regarded as one of the most promising power sources for electric vehicles and portable devices, mainly due to their high energy density output as a result of two factors. First, lithium is the lightest metal and has the highest specific capacity of 3.86 × 10⁹ mA h g⁻¹, corresponding to a specific energy density of 1.14 × 10⁴ W h kg⁻¹ for a theoretical potential of 2.96 V. Second, the cathode active material, oxygen, can be retrieved from ambient air without occupying the battery volume. To make this technology commercially viable, however, a number of technical barriers must be overcome, including low practical discharge capacity, low energy efficiency, and short cycle life. A typical non-aqueous lithium–oxygen battery consists of a lithium metal anode, a lithium ion conducting electrolyte, and a porous cathode. During discharge, oxygen is taken from ambient air and reduced at the porous cathode to form the discharge product lithium peroxide (Li₂O₂). Due to its insolubility in non-aqueous electrolytes, Li₂O₂ grows in the pores of the porous cathode when the capacity is increased, and can eventually block the transport pathways of oxygen, lithium ions, and electrons, terminating the discharge process. During charge, the solid Li₂O₂ discharge product deposited on the cathode must be electrochemically decomposed to lithium and oxygen. A high charge overpotential poses another major challenge, which causes a decrease in the energy efficiency and aggravates side reactions, shortening cycle life. Hence, to obtain an optimum battery performance, the cathode must be designed in such a way which can enhance the transport processes as well as the reaction kinetics, while allowing high catalytic activities in charge and discharge processes to lower overpotential.

Tremendous efforts have been made to the development of a suitable cathode for non-aqueous lithium–oxygen batteries. Various kinds of carbon materials with unique morphology and porous structure have been tested, such as carbon powder, nanotubes, and graphene. In addition to the morphology and structure, the surface modifications (e.g. N-doped) of carbon materials have shown great effects on the battery performance. Besides, different kinds of catalyst materials, especially transition metal oxides and their composites, have been widely investigated. Conventionally, the cathode is fabricated by loading the catalyst onto a porous current collector (e.g. carbon paper and nickel-based composites) through casting of a slurry mixture comprising the catalyst, conductive matrix (e.g. Ketjen black, Vulcan XC-72 carbon, and Super P) and polymeric binder (e.g. polytetrafluoroethylene and polyvinylidene fluoride). However, these additives not only complicate fabrication procedures, but also increase the cathode weight. The practical specific capacity is lowered as a result, especially when taking the heavy weight of the current collector into consideration. In our previous...
studies, carbon powder and nanotubes with a polymeric binder were used to fabricate the cathode; although no current collectors are required in this type of cathode, the involvement of insulating polymeric binders increases the contact resistance, reducing the effective surface area of the cathode. In addition, the stability of polymeric binders is a critical issue and they pose the problem of decomposing into irreversible side products during battery operation, resulting in poor reversibility. Thus, a cathode that is free of additional current collectors and binders would be ideal for addressing the previously mentioned issues.

Various types of cathodes which are free of additional current collectors and binders have been reported. Zhang et al. designed a free-standing MnO2@carbon paper cathode, with birnessite-type MnO2 nanosheets grown vertically on the surface of carbon paper and interconnected to form a three-dimensional porous architecture. A battery with this cathode was reported to deliver a capacity of around 140 mA h g\textsubscript{MnO2}\textsuperscript{−1}, and exhibited over 90 cycles with a capacity of more than 1000 mA h g\textsubscript{MnO2}\textsuperscript{−1} and a high coulombic efficiency of around 100% in the voltage range of 2.2–4.4 V. Wei et al. fabricated a non-carbon cathode by electrodeposition of an amorphous MnO2 layer on the surfaces of stainless steel fibers. A battery with this cathode delivered a capacity of 1780 mA h g\textsubscript{MnO2}\textsuperscript{−1} at 100 mA g\textsubscript{MnO2}\textsuperscript{−1} and was able to operate for more than 10 cycles with a fixed capacity of 500 mA h g\textsubscript{MnO2}\textsuperscript{−1}, demonstrating its good stability. Kim et al. developed a cathode with Au nanoparticles coated on a nickel nanowire substrate. This cathode showed a high capacity of 921 mA h g\textsubscript{Au}\textsuperscript{−1} at a current density of 300 mA g\textsubscript{Au}\textsuperscript{−1}, and exhibited excellent cycle stability with a capacity retention of 98.1% after 100 cycles at 500 mA g\textsubscript{Au}\textsuperscript{−1}.

In this work, we present a cathode made of a RuO2 nanoparticle-decorated buckypaper (weaved with carbon nanotubes). Our previous study showed that cathodes formed from interconnected carbon nanotubes had larger pore space than carbon powder-based cathodes, facilitating the transport of species. Buckypaper is a porous structure composed of interpenetrating carbon nanotubes and does not require the employment of binders, preventing surface-loss and instability that would otherwise be introduced with the use of polymeric binder additives. Unlike previously reported buckypaper cathodes which were supported by a metal substrate/current collector, no additional current collector is used, increasing the practical specific capacity. RuO2 has been proven to be an effective catalyst for non-aqueous lithium–air batteries, and the cathodes with RuO2 or RuO2 decorated supporting materials reported in previous papers were formed through casting of a slurry mixture comprising the catalysts and binders onto a supporter/current collector. Here, the cathode was formed by directly decorating RuO2 nanoparticles onto the surfaces of buckypaper to enhance the catalytic activities. A non-aqueous lithium–oxygen battery was constructed to test the discharge and charge performance of this RuO2 nanoparticle-decorated buckypaper cathode, and compared to that of a blank buckypaper cathode. The formation and decomposition of the discharge product were detected, and the morphologies of the cathodes after discharge and charge were examined. Moreover, the energy efficiencies of the battery with this RuO2 nanoparticle-decorated buckypaper cathode at various current densities were studied, as well as the cycling stability.

**Experimental**

**Fabrication of the RuO2/buckypaper cathode**

The buckypaper used in this experiment was composed of multi-walled carbon nanotubes and made via a filtration method (Suzhou Creative Nano-Carbon Co. Ltd., purity: 95.5%, porosity: 75%, specific surface area: 53.8 m\textsuperscript{2} g\textsuperscript{−1}, and carbon nanotube loading: 4.0 mg cm\textsuperscript{−2}, Fig. S1†). A previous study indicated that the practical specific capacity increases with a decrease in the cathode thickness. However, a thin cathode may require a substrate to ensure sufficient mechanical strength. The inclusion of the substrate will decrease the practical capacity. In this work, we chose a 60 μm-thick buckypaper as the cathode. As this buckypaper has sufficient mechanical strength (10 MPa), neither substrate nor current collector is required. To remove the possible residual metal catalysts used in the carbon nanotube fabrication process, the as-received buckypaper was soaked in 10% HCl solution at 40 °C for 6 h and then rinsed with distilled water. After that, the sample was dried under vacuum at 120 °C for 12 h and denoted as buckypaper.

To fabricate the RuO2 nanoparticle-decorated buckypaper, the as-treated buckypaper was immersed in a 0.01 M RuCl\textsubscript{3} solution. A 0.05 M K\textsubscript{2}CO\textsubscript{3} aqueous solution was added slowly to the above solution while being stirred until the pH value reached 7, which was monitored by using a digital pH meter. Then, the buckypaper was rinsed with distilled water, dried at 80 °C for 8 h and heat treated at 120 °C. The as-prepared sample was denoted as RuO2/buckypaper. Finally, both the buckypaper and RuO2/buckypaper cathodes for the battery test were cut into discs with a diameter of 8 mm.

**Material characterization**

The cross-section and the surface morphologies of the buckypaper and RuO2/buckypaper cathodes were observed by using a scanning electron microscope (SEM, JEOL-6700F) at an acceleration voltage of 5.0 kV. Transmission electron microscopy (TEM) images were obtained by operating a high-resolution JEOL 2010F TEM system with a LaB\textsubscript{6} filament at 200 kV. The samples were dispersed in ethanol, sonicated and dripped onto the holey carbon-coated Cu grids. The BET surface area of the RuO2/buckypaper cathode was examined via nitrogen adsorption–desorption. The compositions of the buckypaper and RuO2/buckypaper cathodes were analyzed by using a Philips high resolution X-ray diffraction system (XRD, model PW 1825) using a Cu-K\textalpha source operating at 40 kV. X-ray photoelectron spectroscopy (XPS) characterization was performed by using a Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W. The peak position correction was corrected by referencing the C 1s peak position of carbon (284.8 eV, PHI Handbook of Photoelectron Spectroscopy), and shifting all other peaks in the spectrum accordingly. A Fourier-transform infrared (FTIR) test was carried out on a
spectrum in the frequency range of 400–1000 cm\(^{-1}\). To test the content of RuO\(_2\) in the RuO\(_2\)/buckypaper cathode, thermogravimetric analysis (TGA) was performed on a TGA Q5000 (TA instruments) under air atmosphere from 25 °C to 800 °C, heated at a rate of 10 °C per minute.

**Electrochemical measurements**

The lithium–oxygen battery consists of a lithium metal foil as the anode, a glass-fiber separator (Whatman GF/C), and the as-prepared cathode. The electrolyte was composed of 150 μL 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma-Aldrich, 99.95%) in tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich, 99%) with the water concentration at less than 5 ppm. To eliminate the influence of moisture on the battery, the cathode electrode and glass-fiber separator were dried in a vacuum, and the electrolyte was dried with molecular sieves before use. The battery was assembled in an argon-dried glovebox (Etelux, Lab 2000) at water and oxygen contents below 1 ppm. After assembly, the inlet of the battery was tightly connected to high purity oxygen (≥99.997%, H\(_2\)O ≤ 1 ppm, CO\(_2\) ≤ 1 ppm) with a constant flow to exhaust the remaining argon. Then, the outlet of the battery was sealed and the battery was exposed to oxygen at a constant pressure of about 1 atm. The galvanostatic discharge and charge tests were conducted on a battery cycling system (Neware, CT-3008W) at a current density of 0.1 mA cm\(^{-2}\) (100 mA g\(^{-1}\)). To test the energy efficiencies of both buckypaper and RuO\(_2\)/buckypaper cathodes at different current densities, the battery was discharged and charged at a fixed capacity of 2.0 mA h cm\(^{-2}\) with current densities of 0.2, 0.4, and 0.8 mA cm\(^{-2}\), respectively. The cycling stability was tested at a current density of 0.4 mA cm\(^{-2}\) with a fixed capacity of 1.0 mA h cm\(^{-2}\), and a cut-off voltage of 2.0 V for discharge and 4.8 V for charge. All tests were performed at room temperature (25 °C).

The cathode compositions after discharge and charge were analyzed by XRD, FTIR, and XPS. The cathode morphologies after discharge and charge were observed by using a SEM. To obtain the cathode after the test, the battery was disassembled in the argon glovebox, and the cathode was rinsed with pure TEGDME and then dried at room temperature in a vacuum chamber. For all measurements, a home-made gas container filled with argon was used to transfer the cathodes.

**Results and discussion**

**Characterization of the RuO\(_2\)/buckypaper cathode**

The XRD patterns of the buckypaper and RuO\(_2\)/buckypaper cathodes in the range of 2θ from 10° to 90° are shown in Fig. 1a. For both cathodes, three diffraction peaks are identified as the (002), (100), and (101) peaks of carbon; the peak at 30° may have been caused by residual metal catalysts after acid treatment (~0.36%, Fig. S2a†). For the RuO\(_2\)/buckypaper cathode, three additional diffraction peaks are identified to be the (110), (101), and (002) peaks of RuO\(_2\) (JCPDS # 88-0823), suggesting that RuO\(_2\) is formed. The formation of RuO\(_2\) is further demonstrated by XPS spectra in the range of 279 to 288 eV, as shown in Fig. 1b. The weight content of RuO\(_2\) in the RuO\(_2\)/buckypaper cathode is determined to be ~2.80% through TGA (Fig. S2b†), which is about 0.115 mg cm\(^{-2}\).

The SEM image of the cross-section of the RuO\(_2\)/buckypaper cathode is shown in Fig. 1c. After the decoration of RuO\(_2\) nanoparticles, the RuO\(_2\)/buckypaper cathode maintains a thickness of ~60 μm. The surface morphology of the RuO\(_2\)/buckypaper cathode is shown in Fig. 1d. Carbon nanotubes with diameters of 20 to 60 nm are weaved to form a porous structure, similar to the surface morphology of the buckypaper cathode (Fig. S3†). In addition, RuO\(_2\) nanoparticles are decorated on the surfaces of carbon nanotubes, as shown in the inset of the high-resolution SEM image. From the TEM image in Fig. 1e, RuO\(_2\) nanoparticles are distributed over the carbon nanotube surface, with an average particle size of 2.60 ± 0.04 nm. The high-resolution TEM image in Fig. 1f shows a multi-walled carbon nanotube decorated with RuO\(_2\) nanoparticles, and clear lattice fringes of RuO\(_2\) are observed in the Fig. 1f inset, indicating the crystalline nature of the particles. The regular interplanar spacing of 2.013 Å is ascribed to the (210) plane of RuO\(_2\) (JCPDS #88-0823). The results demonstrate that RuO\(_2\) nanoparticles are
introduced into the buckypaper cathode and decorated on the surface of multi-walled carbon nanotubes.

Discharge and charge performance

The discharge and charge curves of the buckypaper and RuO2/buckypaper cathodes at a current density of 0.4 mA cm−2 are presented in Fig. 2a. For the buckypaper cathode, the discharge voltage first decreases to a plateau of 2.53 V, and then gradually decreases with an increase in the discharge capacity. It then drops rapidly to 2.0 V, with a capacity of 4.53 mA h cm−2. On charge, after a short region of about 3.70 V, the voltage increases to a high plateau of 4.50 V, and reaches 4.80 V toward the end of charge. For the RuO2/buckypaper cathode, the discharge voltage almost maintains a plateau of about 2.56 V. This higher voltage arises from the high electrocatalytic activity of the RuO2 nanoparticles for the oxygen reduction reaction.48 When the voltage drops to 2.0 V, the RuO2/buckypaper cathode delivers a capacity of 4.72 mA h cm−2, which is about 4.2% higher than that of the buckypaper cathode. Even while taking the additional mass caused by the introduction of RuO2 nanoparticles (~2.80%) into account, its specific capacity is still slightly larger (1.36%) than that of the buckypaper cathode. Additionally, considering the total mass, the specific capacity based on the RuO2/buckypaper cathode is 1150 mA h gcathode−1, a value much higher than that of our previous carbon nanotube-based cathode with the polymeric binder (~730 mA h gcathode−1)9 and the reported MnO2@carbon paper cathode (~140 mA h gcathode−1).42 On charge, the voltage of the RuO2/buckypaper cathode increases to a plateau of about 4.10 V, a reading that is 400 mV lower than that of the buckypaper cathode, and reaches 4.45 V at the end of charge. Thus, an improved charge performance is obtained using this RuO2/buckypaper cathode. To study the effect of RuO2 loading on the electrochemical performance, we prepared another RuO2/buckypaper cathode with a RuO2 loading of ~7.62% (Fig. S2e,† 0.330 mg cm−2). It is seen that the discharge voltage plateau has a little increase of ~10 mV, and the charge voltage plateau remarkably decreases to 3.94 V (Fig. S4f). However, the discharge capacity decreases to 3.91 mA h cm−2 (900 mA h gcathode−1), which is smaller than that of the buckypaper cathode. Similar results have been reported by Yilmaz et al., in which the RuO2/CNT cathode with 32 wt% RuO2 has a lower charge voltage but a decreased capacity than that of a CNT cathode.48 The decreased discharge capacity may be attributed to the decrease in the specific surface area49 (Fig. S5f) and the changes in the discharge product morphology.52 To avoid the sacrifice of the capacity, in our following study, we focused on the RuO2/buckypaper cathode with a RuO2 loading of ~2.80%.

To study the compositions of the buckypaper and RuO2/buckypaper cathodes after discharge and charge, XRD, FTIR, and XPS were employed, and the results are presented in Fig. 2b–d, respectively. Fig. 2b shows the XRD patterns of both cathodes. For the buckypaper cathode, after discharge the peaks are identified as the (100), (101), (102), and (110) peaks of Li2O2 (JCPDS 209-0355), suggesting that the main discharge product is Li2O2. After charge, these peaks disappear, indicating the decomposition of Li2O2. For the RuO2/buckypaper cathode, after discharge the (100), (101), and (110) peaks of Li2O2 are detected, and the (002) peak related to RuO2 disappears, suggesting that Li2O2 covers the surface of RuO2 nanoparticles (Fig. S6†). After charge, the peaks correspond to Li2O2 disappear, while the peaks correspond to carbon and RuO2 re-appear, demonstrating that the discharge product is removed from the surfaces of carbon nanotubes and RuO2 nanoparticles. FTIR spectra of the discharged and charged buckypaper and RuO2/buckypaper cathodes are presented in Fig. 2c. The absorbance peak at around 430 cm−1 (marked as the shaded area) is derived from Li2O2 in the discharged buckypaper and RuO2/buckypaper cathodes, and its disappearance in the charged cathodes indicates the decomposition of Li2O2 in the following charge process. Fig. 2d compares the Li 1s XPS spectra of the discharged and charged cathodes. The Li 1s region for the buckypaper and RuO2/buckypaper cathodes after discharge includes contribution from the underlying Li2O2 (Li 1s: 54.5 eV)53 and surface lithium carbonate species (Li 1s: 55.3 eV)53 formed by the reaction between electrolyte and Li2O2. Upon charge, for both buckypaper and RuO2/buckypaper cathodes, the Li 1s peak corresponding to Li2O2 disappears, suggesting the decomposition of Li2O2.58 On the basis of the above XRD, FTIR, and XPS results, it is demonstrated that for both buckypaper and RuO2/buckypaper cathodes, Li2O2, as the major discharge product, is reversibly formed in the discharge process and is decomposed in the following charge process.

To provide insight into how a RuO2/buckypaper cathode leads to a lower charge voltage than the buckypaper cathode, we examined the morphologies of both cathodes after discharge. For the buckypaper cathode, at the side facing oxygen the surface is fully covered by the Li2O2 particles with a disc-like morphology (Fig. 3a1), congruent with previous reports;56–58 at the side facing the separator (Fig. 3a2), however, the carbon...
nanotube surfaces are covered with a film-like discharge product with remaining open pores. We explain that the oxygen concentration in the cathode decreases from the oxygen side to the separator side during discharge, and a higher oxygen concentration results in a higher reaction rate. Hence, the fraction of the solid product is larger at the oxygen side, which decreases toward the separator side (Fig. S7a†). The large-sized particles at the oxygen side eventually occupy the pores, which act as further blockages to the oxygen transport pathway and lead to low utilization of the inner region near the separator. In the charge process, the decomposition of the film-like discharge product may occur initially due to enlarged contact areas within the electrolyte and carbon nanotube surfaces, resulting in a lower charge voltage region,13 followed by the decomposition of large-sized particles with a higher charge voltage plateau,15 which is consistent with the charge curve in Fig. 2a. For the RuO2/buckypaper cathode, as shown in Fig. 3b1 and b2, both sides facing the oxygen and separator present a similar morphology, with a film-like discharge product covering the surface. The first-principle calculations showed that Li2O2 is likely to wet the RuO2 surfaces and grow into thin films rather than particles,51 and previous experiments demonstrated that RuO2 nanoparticles contribute to the formation of poorly crystalline Li2O2 that is coated over the carbon nanotubes with a large contact area.48 Therefore, the change in the morphology of the discharge product is caused by the introduction of RuO2 nanoparticles onto the carbon nanotube surface. During discharge, the film-like Li2O2 morphology facilitates the oxygen transport, which helps to utilize the whole cathode (Fig. S7b†). In the charge process, the increased contact area of the discharge product associated with possible increased electrical conductivity due to the poorly crystalline Li2O2 (ref. 48) results in a lower charge voltage, as shown in Fig. 2a. It is also worth noting that although the charge performance improved with the addition of RuO2 nanoparticles, the film-like product morphology may lead to a lower discharge capacity than large-sized product particles,39–41 which may be used to explain the decreased capacity in Yilmaz’s work48 and the decrease in capacity with an increase in the RuO2 loading in our experiment (Fig. S4†). After charge, as shown in Fig. 3a3 and b3, the surfaces of buckypaper and RuO2/buckypaper cathodes recovered to their pristine states, indicating that the discharge product had indeed decomposed, consistent with the results from XRD, FTIR and XPS.

**Energy efficiency**

The energy efficiencies of the battery with the buckypaper and RuO2/buckypaper cathodes at various current densities were studied with a fixed capacity of 2.0 mA h cm−2, and the results are shown in Fig. 4. At a current density of 0.2 mA cm −2, as shown in Fig. 4a, the discharge and charge voltage plateau of the buckypaper cathode is about 2.60 V and 4.36 V, respectively. For the RuO2/buckypaper cathode, the discharge voltage plateau is about 2.65 V, with an increase of 50 mV, while the charge voltage plateau only reaches 3.76 V, with a remarkable decrease of 600 mV. When the current density increases to 0.4 mA cm−2, as shown in Fig. 4b, the discharge and charge voltage plateau of the buckypaper cathode is about 2.53 V and 4.50 V, respectively. For the RuO2/buckypaper cathode, the discharge and charge voltage plateau is about 2.57 V and 3.95 V, respectively. With an increase in the current density to 0.8 mA cm−2, as shown in Fig. 4c, the discharge voltage plateau of the buckypaper and RuO2/buckypaper cathodes is about 2.33 V and 2.36 V, respectively; and the charge voltage plateau is about 4.68 V and 4.20 V, respectively. Hence, the RuO2/buckypaper cathode leads to an increase in the discharge voltage and a large decrease in the charge voltage at various current densities.
current densities, resulting in a higher energy efficiency than that of the buckypaper cathode. As shown in Fig. 4d, when the current density increases from 0.2 to 0.4 mA cm\textsuperscript{–2}, the energy efficiency of the RuO\textsubscript{2}/buckypaper cathode decreases from 71.2\% to 65.4\%, higher than that of the buckypaper cathode which decreases from 61.0\% to 57.0\%. Even at a high current density of 0.8 mA cm\textsuperscript{–2}, the energy efficiency of the RuO\textsubscript{2}/buckypaper cathode is still as high as 58.0\%, showing a remarkable improvement compared to that of the buckypaper cathode.

**Cycling stability**

The cycling stability of the battery with the RuO\textsubscript{2}/buckypaper cathode was tested at a current density of 0.4 mA cm\textsuperscript{–2} with a fixed capacity of 1.0 mA h cm\textsuperscript{–2}, and compared with that of the battery with the buckypaper cathode. As shown in Fig. 5a, the discharge voltage plateau of the buckypaper cathode is about 2.53 V, and continues to decrease with cycling. In contrast, the charge voltage plateau is about 4.40 V, and increases with cycling. The high charge voltage would cause the decomposition of the electrolyte and the carbon cathode to form irreversible side products\textsuperscript{18}. The charge voltage reaches 4.80 V at the 21\textsuperscript{st} cycle before being fully charged, remaining some undecomposed discharge product Li\textsubscript{2}O\textsubscript{2}. The accumulation of side products and undecomposed Li\textsubscript{2}O\textsubscript{2} in the buckypaper cathode decreases the reaction sites and increases the transport resistances, and eventually leads to the capacity decay at the 30\textsuperscript{th} cycle. For the battery with the RuO\textsubscript{2}/buckypaper cathode, as shown in Fig. 5b, the discharge voltage plateau for the first cycle is about 2.56 V, while the charge voltage plateau is about 3.94 V, which is remarkably 460 mV lower than that of the buckypaper cathode. With an increase of the cycle number, the discharge voltage gradually decreases, and the charge voltage increases, which may be attributed to the accumulation of side products caused by the decomposition of the electrolyte\textsuperscript{62} (as shown in XPS results in Fig. 2d) and the passivation of the lithium anode due to oxygen crossover\textsuperscript{63,64}. Even at the 50\textsuperscript{th} cycle, the discharge voltage plateau remains at 2.31 V, and the terminal charge voltage at 4.75 V. Thus, the battery with the RuO\textsubscript{2}/buckypaper cathode can maintain its discharge capacity and coulombic efficiency for 50 cycles without signs of degradation, as shown in Fig. 5c and d, respectively, demonstrating its good cycling stability.

**Conclusions**

In this work, we have created a non-aqueous lithium–oxygen battery with its cathode made of a RuO\textsubscript{2} nanoparticle-decorated buckypaper (weaved with carbon nanotubes). Compared with conventional slurry-formed cathodes, the present cathode is free of binders, avoiding surface-loss and instability problems introduced by polymeric binders. In addition, the cathode does not need an additional current collector, leading to an increase in its practical specific capacity. The present battery demonstrates a discharge plateau of 2.56 V and a charge plateau of 4.10 V at a current density of 0.4 mA cm\textsuperscript{–2}, with a discharge capacity of 4.72 mA h cm\textsuperscript{–2} (1150 mA h g\textsubscript{cathode}\textsuperscript{–1}). The reversible formation and decomposition of Li\textsubscript{2}O\textsubscript{2} as the major product in the discharge and charge processes were demonstrated by XRD, FTIR, and XPS. The SEM images showed that for the blank buckypaper cathode, the discharge product on the oxygen and separator sides presented different morphologies, with a large disc-like morphology at the oxygen-side and a film-like morphology at the separator-side. However, for the RuO\textsubscript{2} nanoparticle-decorated buckypaper cathode, the product on both sides showed similar film-like morphologies. Hence, the decreased charge voltage may be derived from a change in the product morphology and a possible poor crystalline discharge product due to the contribution of RuO\textsubscript{2} nanoparticles. It is also

**Fig. 4** Discharge and charge curves of the buckypaper and RuO\textsubscript{2}/buckypaper cathodes at a current density of (a) 0.2 mA cm\textsuperscript{–2}, (b) 0.4 mA cm\textsuperscript{–2}, and (c) 0.8 mA cm\textsuperscript{–2} with a fixed capacity of 2.0 mA h cm\textsuperscript{–2}, respectively; (d) comparison of the energy efficiency at various current densities.

**Fig. 5** Cycling stability of the buckypaper and RuO\textsubscript{2}/buckypaper cathodes: discharge/charge curves of a lithium–oxygen battery using (a) buckypaper and (b) RuO\textsubscript{2}/buckypaper cathodes at 0.4 mA cm\textsuperscript{–2} with a fixed capacity of 1.0 mA h cm\textsuperscript{–2}; (c) discharge capacity and (d) coulombic efficiency as a function of cycle number.
shown that at a fixed capacity of 2.0 mA h cm$^{-2}$, the energy efficiency of the battery reaches 71.2%, 65.4%, and 58.0% at a current density of 0.2, 0.4, and 0.8 mA cm$^{-2}$, respectively. Furthermore, the present battery is able to operate for 50 cycles at a fixed capacity of 1.0 mA h cm$^{-2}$, showing its good cycling stability. The results demonstrate that the RuO$_2$ nanoparticle-decorated buckypaper cathode does not require additional current collectors and polymeric binders, and hence offers promise for a high-practical specific capacity, high-energy efficiency, and stable electrode for non-aqueous lithium-oxygen batteries.

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Notes and references


