3D web freestanding RuO$_2$–Co$_3$O$_4$ nanowires on Ni foam as highly efficient cathode catalysts for Li–O$_2$ batteries†

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The mechanism of Li–O$_2$ batteries is based on the reactions of lithium ions and oxygen, which hold a theoretical higher energy density of approximately 3500 W h kg$^{-1}$. In order to improve the practical specific capacity and cycling performance of Li–O$_2$ batteries, a catalytically active mechanically robust air cathode is required. In this work, we synthesized a freestanding catalytic cathode with RuO$_2$ decorated 3D web Co$_3$O$_4$ nanowires on nickel foam. When the specific capacity was limited at 500 mA h g$^{-1}$, the RuO$_2$–Co$_3$O$_4$/NiF had a stable cycling life of up to 122 times. The outstanding performance can be primarily attributed to the robust freestanding Co$_3$O$_4$ nanowires with RuO$_2$ loading. The unique 3D web nanowire structure provides a large surface for Li$_2$O$_2$ growth and RuO$_2$ nanoparticle loading, and the RuO$_2$ nanoparticles help to promote the round trip deposition and decomposition of Li$_2$O$_2$, therefore enhancing the cycling behavior. This result indicates the superiority of RuO$_2$–Co$_3$O$_4$/NiF as a freestanding highly efficient catalytic cathode for Li–O$_2$ batteries.

Introduction

As a favorable solution to the energy shortage and environment-mental crisis, electric vehicles (EVs) are gaining more and more attention. Almost all EVs are Li-ion battery-driven and achieve unsatisfactory mileage due to the limited energy density of Li-ion batteries.$^1$ With a high theoretical energy density of approximately 3500 W h kg$^{-1}$, Li–O$_2$ batteries (LOBs) could be the leader for use in EVs.$^{2,4}$ The mechanism of LOBs is based on a simple series of reactions between lithium ions and oxygen, namely, oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs).$^5-7$ In the discharge process the ORR happens, where oxygen is reduced to form Li$_2$O$_2$ with the lithium ions from the electrolyte,$^8$ while the OER happens in the charge process, when the Li$_2$O$_2$ electrochemically decomposes to oxygen and lithium ions. Despite their high performance, they still have many disadvantages, such as poor cycling ability, high charging voltages, low energy efficiency and poor electrolyte stability, as well as cathode stability in the cell environment.$^9-11$

In traditional LOBs, carbonaceous materials and organic binders have been used to compose a typical oxygen cathode.$^{12,13}$ However, the use of carbon materials and a binder to cover the surface of cathodes results in tough challenges, such as the resulting high polarization and poor cycle life and limited conductivity.$^{14-16}$ In addition, because of the low solubility of the discharge product Li$_2$O$_2$ in organic electrolyte, any undecomposed Li$_2$O$_2$ can block the path of oxygen diffusion, leading to electrode degradation.$^{17}$ Accordingly, the ideal electrode should contain a porous structure and bifunctional catalysts with excellent ORR and OER performance.$^{18-20}$ Among the many investigated binder-free oxygen cathodes, the use of commercial nickel foam (NiF), which is widely used as a substrate due to its good electron conductivity and 3D porous structure, is beneficial for Li$_2$O$_2$ deposition and electron transferability.$^{21-24}$

Catalysts when used as important cathode materials can effectively lower the overpotential and enhance the cycling stability of Li–O$_2$ batteries. Transition metal oxide catalysts and noble metal oxide catalysts are widely used. Cobalt oxide-based catalysts, for example, such as the widely studied compound Co$_3$O$_4$, can serve as good bifunctional catalysts for Li–O$_2$ batteries due to their low cost, high redox activity and favorable catalytic activity for both ORR and OER.$^{25-28}$ Cui et al. first reported free-standing Co$_3$O$_4$ arrays growing on the surface of NiF that showed a low polarization and a relative high capacity of 1880 mA h g$^{-1}.^{29}$ However, the cycling stability of the material was limited to only 5 cycles due to the use of propylene carbonate electrolyte, which is known to be unsuitable for the long-term operation of Li–O$_2$ cells.$^{30}$ Lee et al. synthesized Co$_3$O$_4$ nanowire (NW) arrays vertically grown on NiF and...
demonstrated that this type of morphology is restrained by the decomposition of Li$_2$O$_2$\textsuperscript{31} He et al. synthesized Co$_3$O$_4$ rectangular nanosheets that led to a higher specific capacity of 1380 mA h g$^{-1}$ and better cycling stability over 54 cycles at a fixed current density of 100 mA g$^{-1}$\textsuperscript{32}.

Normally, freestanding oxide arrays grown on substrates are usually well structured but have poor catalytic activity. Many studies have found that the catalytic performance of pristine freestanding arrays could be markedly improved after the loading of noble metals/oxides. Many precious metals/oxides such as Pt,$^{33}$ Pd,$^{34}$ Au,$^{35}$ and Ru/RuO$_2$,$^{37-39}$ have been used in LOBs. Among these noble metals, Ru and RuO$_2$ have attracted great interest due to their excellent catalytic activity, which dramatically reduces the charging overpotential and improves the round-trip efficiency.\textsuperscript{40} Liao et al. successfully grew nanoporous Ru on NiF via a galvanic replacement reaction and showed that this material has a voltage window of 2.75–3.75 V with a limited capacity of 1000 mA h g$^{-1}$.\textsuperscript{41} Liu et al. reported a Ru nanoparticle decorated carbon-free O$_2$ cathode using 3D ultralight porous nickel which demonstrated a relatively high specific capacity of 2410 mA h g$^{-1}$ at a limited current density of 150 mA g$^{-1}$.\textsuperscript{42} However, if too much of the noble metal is used, the cost of the material will be too high for commercial use in EVs. To produce a low-cost cathode catalyst, it is necessary to reduce the noble metal content in the battery whilst maintaining a high catalytic performance.

In this work, we synthesized Co$_3$O$_4$ nanowires directly on nickel foam using a two-step hydrothermal and heat treatment process. Then, RuO$_2$ nanoparticles were decorated on the Co$_3$O$_4$/NiF using immersion methods to produce a cathode for Li–O$_2$ batteries, resulting in enhanced catalytic activity due to the freestanding structure and RuO$_2$ loading. Therefore, compared with LOBs with a Co$_3$O$_4$ cathode, the ones with a RuO$_2$–Co$_3$O$_4$ cathode exhibited a much more improved electrochemical performance with a durable cycling stability of 122 cycles at a limited capacity of 500 mA h g$^{-1}$.

**Experimental section**

**Electrode preparation**

Analytical grade chemicals were purchased and used without any further purification. Nickel foam was cut into 2 cm $\times$ 5 cm pieces and then cleaned in acetone and ethanol for half an hour. After tailoring, the pretreated pieces were dried in an oven overnight and weighed before use, and the weight was recorded as $m_1$. In a typical synthesis of the Co$_3$O$_4$ nanowires, 2 mmol of Co(NO$_3$)$_2$ and 3 mmol of (NH$_4$)$_2$SO$_4$ were weighed and mixed in 80 ml of deionized (DI) water under magnetic stirring for 10 min. Then 10 mmol of urea was dissolved in another 20 ml of DI water and stirred for 10 min. After that, the latter solution was slowly dropped into the former pink solution followed by a further 20 min of stirring. Then, pretreated nickel foam combined with the precursor solution was transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and put into an electric oven and heated at 120 °C for 8 h. In order to remove the redundant particles, the products were removed from the autoclave and rinsed more than 3 times with ultrapure water and anhydrous alcohol. Ni-supported Co$_3$O$_4$ nanowires were finally obtained after heating at 300 °C for 2 h in air, after which the Co$_3$O$_4$/NiF was weighed again, and the weight was recorded as $m_2$. To prepare RuO$_2$–Co$_3$O$_4$ nanowires, the previously synthesized materials were steeped in a RuCl$_3$ aqueous solution (3 mg l$^{-1}$) for 1 h, followed by drying at 60 °C for 6 h and annealing at 300 °C for 2 h in air. RuO$_2$–Co$_3$O$_4$/NiF was weighed, and the weight was recorded as $m_3$. The loading masses of RuO$_2$–Co$_3$O$_4$ and Co$_3$O$_4$ are based on the difference between $m_3$ and $m_1$ as well as the difference between $m_2$ and $m_1$, respectively. The loading mass of RuO$_2$–Co$_3$O$_4$ on Ni foam was found to be approximately 0.8 mg cm$^{-2}$. According to the energy dispersive X-ray spectroscopic (EDS) results, the weight percentage of RuO$_2$ in RuO$_2$–Co$_3$O$_4$ is around 2.5% (Fig. S1†). The Ru–Co$_3$O$_4$/NiF cathode was synthesized by following a literature procedure.\textsuperscript{48}

**Electrode characterization**

The nanowires grown on the NiF were scraped off and examined using powder X-ray diffraction (PXRD) on a Bruker D8 advance powder diffractometer with Cu Kz radiation operating at 40 keV. X-ray photoelectron spectroscopic (XPS) studies were conducted with an ESCALAB MARK II spherical analyser using a magnesium anode (Mg 1253.6 eV) X-ray source. The morphologies of the air electrodes (or nanowires grown on NiF) were observed using a scanning electron microscope (SEM, Quanta 200F) fitted with an energy dispersive X-ray spectrometer (EDS) operating at 15 kV. Transmission electron microscopy (TEM) was carried out using a JEM 2100 LaB6 microscope. RuO$_2$–Co$_3$O$_4$/NiF was immersed in absolute ethanol and sonicated for 30 min, after which the solution was dropped onto holey carbon-coated Cu grids. The discharge products were characterized by Raman spectroscopy (JOBIN YVON Technology, Horiba LabRAM HR Evolution) at a 532 nm excitation wavelength in the range of 100–1000 cm$^{-1}$.

**Electrochemical measurements**

The electrochemical properties of the non-aqueous Li–O$_2$ batteries were measured on top-holed CR2032-type coin cells. The non-aqueous Li–O$_2$ batteries were assembled in an argon-filled glove box with less than 0.5 ppm water and oxygen content. The as-prepared RuO$_2$–Co$_3$O$_4$/NiF was tailored (0.7 cm $\times$ 0.7 cm) and used as the cathode. Li metal foil was used as the anode and a glass fiber membrane (Whatman GF/D) was chosen as the separator. The electrolyte used was 1 M LiTFSI (Aladdin) in tetrathyleneglycol dimethyl ether (TEGDME, Aladdin). The catalytic cathodes were dried in an oven at 80 °C for more than 6 h before use to eliminate the influence of water. After assembly, the cells were sealed in a vessel filled with high-purity oxygen. The cells were galvanostatically charged and discharged after 5 h of rest on a battery test system (LAND-V34, Land Electronic Co. Ltd, Wuhan) at room temperature. The cell performance evaluations (current density and specific capacity) of the RuO$_2$–Co$_3$O$_4$ electrodes were calculated based on the total weight of Co$_3$O$_4$ and RuO$_2$, and those of the bare Co$_3$O$_4$ electrodes were based on the weight of Co$_3$O$_4$. Cyclic voltammetry
(CV) measurements were conducted on an electrochemical workstation (AMETEK Solartron 1260/1287) within a potential range of 2.0–4.3 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopic (EIS) measurements were taken at the initial state, 1ˢᵗ-discharged state and 1ˢᵗ-charged state at a fixed specific capacity of 500 mA h g⁻¹. The AC voltage was 10 mV in amplitude and the frequency range used was between 10 mHz and 100 kHz.

Results and discussion

3D web Co₃O₄ nanowires grown on Ni foam (Co₃O₄/NiF) were synthesized through a mild hydrothermal route followed by annealing of the material in an air atmosphere. RuO₂–Co₃O₄ nanowires were prepared by simply steeping Co₃O₄/NiF in a RuCl₃ aqueous solution, followed by annealing in an air atmosphere. The crystal structure of the as-prepared RuO₂–Co₃O₄/NiF was characterized by powder X-ray diffraction (PXRD), as shown in Fig. 1a, using RuO₂–Co₃O₄ exfoliated from RuO₂–Co₃O₄/NiF. All of the diffraction peaks correspond to crystalline Co₃O₄ (PDF # 42-1467). There is no obvious peak for RuO₂ due to the small loading amount. X-ray photoelectron spectroscopy (XPS) was used to study the oxidation state of RuO₂–Co₃O₄ (Fig. 1b and c). The XPS spectrum of Co 2p, as shown in Fig. 1b, consists of two primary peaks with binding energies of 779.8 and 795.0 eV, which were assigned to Co 2p₃/2 and 2p₁/2, respectively. The 15.2 eV spin-energy separation of the two binding energies is a feature of Co₃O₄. The small peaks observed at 788.20 and 805.20 eV close to the main peaks are common satellite peaks. The binding energies of Ru 3p₃/2 and 3p₁/2 in RuO₂–Co₃O₄ can be observed at 462.2 eV and 486.9 eV, respectively (Fig. 1c), and were assigned as Ru(IV) species. The PXRD and XPS results confirmed the formation of RuO₂–Co₃O₄ on the Ni foam.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to further study the morphology and structure of the as-prepared RuO₂–Co₃O₄/NiF cathode. The SEM images of RuO₂–Co₃O₄/NiF (Fig. 2a) show the nanowires growing on the surface of the Ni foam, presenting a 3D web-like morphology. Fig. 2b shows a magnified SEM image where the nanowires are evenly distributed and randomly leaning on the Ni foam with a porous structure. It is noted that this morphology is the same as that without RuO₂ nanoparticle loading (the morphology of Co₃O₄/NiF is shown in Fig. S2†). The distance between each nanowire is measured as ca. 1 μm and could allow for the transportation of O₂ or electrolyte. The architecture of the catalyst-cathode is of paramount importance for Li–O₂ cells, since the cathode should provide enough channels for the transportation of Li⁺ ions or oxygen and guarantee enough space for the deposition of discharge products from the electrochemical reactions. Fig. 2c–e show the elemental mapping of Fig. 2a (the as-prepared RuO₂–Co₃O₄/NiF cathode). It is easy to observe that Co and Ru are uniformly distributed on the surface of NiF, which might be beneficial for both the ORR and OER processes in Li–O₂ cells. The energy dispersive spectrometer (EDS) results of RuO₂–Co₃O₄ reveal that only a small amount of RuO₂ is loaded on the Co₃O₄ nanowires and that the weight percentage of RuO₂ in RuO₂–Co₃O₄ is 2.4% (Fig. S1†).
From the TEM images of RuO$_2$–Co$_3$O$_4$/NiF (Fig. 2f), it can be seen that the width of the Co$_3$O$_4$ nanowires measures about 40 nm. The particles (measuring less than 10 nm) were uniformly distributed on the surface of the Co$_3$O$_4$ nanowires and could be confirmed as RuO$_2$ from a lattice spacing measurement of 0.256 nm that corresponds to the (101) planes of RuO$_2$ in the HRTEM image (Fig. 2g). It is noteworthy that a lattice spacing of 0.467 nm corresponding to that of Co$_3$O$_4$ (111) planes can also be observed in the HRTEM image. According to previous literature, Co$_3$O$_4$ (111) planes have an excellent electrocatalytic performance, and can increase the cycling performance of Li–O$_2$ batteries by reducing the charge and discharge overpotential. The related selected area electron diffraction (SAED) pattern of RuO$_2$–Co$_3$O$_4$/NiF is shown in Fig. 2f. The diffraction rings can be indexed to the (220), (400), (422), (440) and (533) planes of Co$_3$O$_4$ as well as the (101) plane of RuO$_2$, indicating well-defined crystallinity.

We decorated the Co$_3$O$_4$ nanowires with RuO$_2$, which has been demonstrated to be effective for producing a cathode for ORR and OER to enhance the cycling properties of Li–O$_2$ batteries. The electrochemical performance of the Co$_3$O$_4$/NiF and RuO$_2$–Co$_3$O$_4$/NiF catalysts was then tested in assembled Li–O$_2$ cells. Fig. 3a and b show the first discharge/charge curves for these Li–O$_2$ batteries at different current densities of 100 mA g$^{-1}$, 150 mA g$^{-1}$ and 200 mA g$^{-1}$ in a voltage window of 2.0–4.2 V. In these rate studies, the overpotential of both catalysts was almost the same, while there was a huge difference observed in their specific capacities. The discharge capacity of the Co$_3$O$_4$/NiF electrode was found to be 2406.6 mA h g$^{-1}$ at 100 mA g$^{-1}$, which was much lower than that of the RuO$_2$–Co$_3$O$_4$/NiF electrode (9620 mA h g$^{-1}$ under the same conditions), indicating the better ORR catalytic performance of RuO$_2$–Co$_3$O$_4$ than that of Co$_3$O$_4$. The rate performances of the RuO$_2$–Co$_3$O$_4$/NiF and Co$_3$O$_4$/NiF electrodes were further studied at higher discharge/charge current densities of 150 mA g$^{-1}$ and 200 mA g$^{-1}$. The discharge capacity of the RuO$_2$–Co$_3$O$_4$/NiF based battery reached 9186.5 mA h g$^{-1}$ and 5882.3 mA h g$^{-1}$ at current densities of 150 mA g$^{-1}$ and 200 mA g$^{-1}$, respectively, while the Co$_3$O$_4$/NiF based battery only reached 1657.3 mA h g$^{-1}$ and 1010.7 mA h g$^{-1}$ under the same conditions. The high specific capacity indicated that the passivation of the electrode could be slowed due to the controllable 3D web structure and uniformly distributed RuO$_2$.

Cyclic voltammograms (CVs) were recorded to study the ORR and OER properties of the RuO$_2$–Co$_3$O$_4$/NiF and Co$_3$O$_4$/NiF electrodes. As shown in Fig. 3c and d, the CV curves of RuO$_2$–Co$_3$O$_4$ and Co$_3$O$_4$ were measured in a voltage window of 2.0–4.3 V. Both the RuO$_2$–Co$_3$O$_4$/NiF and Co$_3$O$_4$/NiF electrodes displayed a reduction peak during the cathodic scan and the ORR onset potentials of both electrodes were measured to be about 2.90 V, indicating the excellent catalytic performance for ORR. It is worth noting that the reduction peak current density of the RuO$_2$–Co$_3$O$_4$ electrode was a bit higher than that of the Co$_3$O$_4$ electrode, which is related to the higher electrochemical activity and conductivity of the RuO$_2$-doped catalyst. During the succeeding anodic scan process, a relatively strong oxidation peak could be observed at 3.60 V for RuO$_2$–Co$_3$O$_4$ and the intensity of the following peaks was reduced. For the Co$_3$O$_4$/NiF electrode, the OER peak appeared until the second cycle. This phenomenon indicated that the RuO$_2$–Co$_3$O$_4$/NiF electrode might have a better OER performance, and in general, the overall CV results demonstrated the much better catalytic activity of RuO$_2$–Co$_3$O$_4$/NiF electrode.

Fig. 4a shows the voltage profiles of the Co$_3$O$_4$-catalyzed Li–O$_2$ battery with a fixed specific capacity of 500 mA h g$^{-1}$ under a current density of 100 mA g$^{-1}$ in the voltage range of 2.0–4.3 V. Although the discharge plateau of the battery was higher at 2.75 V and the charge plateau remained lower at 3.60 V in the first cycle, indicating an overpotential of 0.85 V, the cycling performance could only be maintained by up to 18 cycles, with a rapid voltage decrease below 2 V being observed at the 19$^{th}$ cycle, as shown in Fig. 4c. The cyclic performance of the battery
could be greatly increased by using the RuO$_2$–Co$_3$O$_4$/NiF catalyst. In Fig. 4b it can be seen that the RuO$_2$–Co$_3$O$_4$/NiF based Li–O$_2$ battery exhibits a lower overpotential of 0.7 V in the first cycle, which is much better than the performance of Co$_3$O$_4$/NiF. When the specific capacity is limited to 500 mA h g$^{-1}$ at the same current density, the battery incorporating RuO$_2$–Co$_3$O$_4$/NiF achieved a durable cycling performance of 122 cycles before the cut-off voltage at below 2 V (Fig. 4d). This result proves that the RuO$_2$–Co$_3$O$_4$/NiF electrode could significantly increase the cycle life of a Li–O$_2$ battery. A comparison of reported works and this work is shown in Table S1† proving the superiority of the electrode synthesized in this work. We also studied the effects of Ru loading. Ru–Co$_3$O$_4$/NiF-catalyzed batteries were also used under these conditions, and the charge/discharge curves of the 40$^{th}$ cycles are shown in Fig. S3.† The Ru–Co$_3$O$_4$/NiF based Li–O$_2$ battery exhibits an overpotential of 0.73 V in the 1$^{st}$ cycle, indicating the good catalytic performance brought about by the Ru loading. However, the overpotential increases to 1.24 V in the 40$^{th}$ cycle, which is much larger than that of RuO$_2$–Co$_3$O$_4$/NiF (0.95 V, Fig. S4†). These results indicate that even though Ru–Co$_3$O$_4$/NiF has an electrocatalytic activity as high as that of RuO$_2$–Co$_3$O$_4$/NiF, its cyclability is unsatisfactory. Therefore, RuO$_2$ modified Co$_3$O$_4$/NiF was considered to be the best choice for improving the performance of the Li–O$_2$ battery in this system.

To investigate the growth mechanism of the discharge products of these two batteries equipped with different cathodes, ex-SEM characterization of the catalytic cathodes was implemented in both the discharged and charged states. Fig. 5 shows a schematic illustration of the formation of the discharge products on the surfaces of the Co$_3$O$_4$ nanowires and RuO$_2$–Co$_3$O$_4$ nanowires, which exhibit different growth mechanisms of Li$_2$O$_2$ and briefly describe the following ex-SEM observations. Fig. 6 shows the SEM images of the Co$_3$O$_4$-catalyzed and RuO$_2$–Co$_3$O$_4$-catalyzed cells in their initial states, and after discharging and charging, respectively. Fig. 6b shows an SEM image of the discharged Co$_3$O$_4$ electrode. It can be seen that Li$_2$O$_2$ grows on the surface of the Co$_3$O$_4$ nanowires, as well as between the nanowires. The knitted 3D web structure of the nanowires is fully covered by Li$_2$O$_2$. After charging, most of the intermediates remained undecomposed. Only a few decompose as the size of the ball-like intermediates decreased from ~8 μm to ~3 μm (Fig. 6c). For RuO$_2$–Co$_3$O$_4$, its knitted 3D web structure was maintained after Li$_2$O$_2$ deposition (Fig. 6e), which was indicated by the Raman results shown in Fig. S5.† Four characteristic peaks from Co$_3$O$_4$ located at 189, 471, 514 and 678 cm$^{-1}$ correspond to the 2F$_{2g}$, 1E$_{g}$, and 1A$_{1g}$ Raman active modes of the Co$_3$O$_4$ nanocrystals, respectively. 29 The other two peaks correspond to the stretching mode of O$_2$ in Li$_2$O$_2$ at 798 cm$^{-1}$ and the lattice modes at 267 cm$^{-1}$, 51,52 An enlarged SEM image can be found in Fig. S6,† showing that the Ru-doped Co$_3$O$_4$ nanowires were evidently covered with Li$_2$O$_2$ sheets. According to Lee’s work, during discharge, Li$_2$O$_2$ grows on the surface of the nanowires little by little until the whole surface of the nanowires is covered with Li$_2$O$_2$.33 Our results are similar to theirs. In contrast to the pristine Co$_3$O$_4$ nanowires, the knitted 3D web nanowires remained unbroken after charging (Fig. 6f), suggesting enhanced mechanical strength and a better performance.

In order to further investigate the variation of the intermediates (Li$_2$O$_2$) formed in Li–O$_2$ batteries at different discharge/charge stages, the electrochemical impedance spectra (EIS) of Li–O$_2$ batteries with Co$_3$O$_4$/NiF and RuO$_2$–Co$_3$O$_4$/NiF catalysts were measured. The Nyquist plots containing a semicircle and a sloping line were fitted by employing the equivalent circuit, as shown in the insets in Fig. 7, and the fitting results are summarized in Table 1. It is obvious that the impedance of both Li–O$_2$ batteries increased for the poor electronic conductive discharge products (Li$_2$O$_2$) formed during discharging. After the charging process, the impedance of the Li–O$_2$ batteries with the

![Fig. 5](image5.png)  
**Fig. 5** Schematic illustrations of the formation of discharge products on the surfaces of Co$_3$O$_4$ nanowires and RuO$_2$–Co$_3$O$_4$ nanowires.

![Fig. 6](image6.png)  
**Fig. 6** SEM images of Co$_3$O$_4$ (a) at the initial state, (b) after the 10$^{th}$ discharge and (c) after the 10$^{th}$ charge. SEM images of RuO$_2$–Co$_3$O$_4$ (d) at the initial state, (e) after the 10$^{th}$ discharge and (f) after the 10$^{th}$ charge.

![Fig. 7](image7.png)  
**Fig. 7** Nyquist plots of the (a) Co$_3$O$_4$-catalyzed and (b) RuO$_2$–Co$_3$O$_4$-catalyzed Li–O$_2$ batteries at the initial, 1$^{st}$ discharge and 1$^{st}$ charge states. For both tests, the charge and discharge capacities were 500 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$.
Table 1  Fitting results of the Nyquist plots using the equivalent circuit

| Co$_3$O$_4$-catalyzed Li–O$_2$ batteries | C$_{dl}$ | $R_0$ (Ω) | $R_d$ (Ω) | Y      | n    |
|---------------------------------|--------|---------|---------|-------|------|
| Initial                         | 18.60  | 131.6   | 2.16 x 10$^{-5}$ | 0.79  |
| After discharge                 | 19.74  | 224.1   | 8.34 x 10$^{-5}$ | 0.81  |
| After charge                    | 18.86  | 152.7   | 7.48 x 10$^{-5}$ | 0.77  |

| Ru$_2$O$_2$-Co$_3$O$_4$-catalyzed Li–O$_2$ batteries | C$_{dl}$ | $R_0$ (Ω) | $R_d$ (Ω) | Y      | n    |
|--------------------------------------------------|--------|---------|---------|-------|------|
| Initial                                          | 17.14  | 102.8  | 3.38 x 10$^{-5}$ | 0.71  |
| After discharge                                  | 17.80  | 130.1  | 2.85 x 10$^{-4}$ | 0.74  |
| After charge                                     | 19.04  | 107.5  | 2.19 x 10$^{-4}$ | 0.80  |

Co$_3$O$_4$/NiF cathode increased (Fig. 7a), indicating that the discharge products were not fully decomposed upon charging. On the contrary, the Li–O$_2$ batteries with the Ru$_2$O$_2$–Co$_3$O$_4$/NiF cathode almost recovered the initial impedance after the charge process (Fig. 7b). This indicated that the generated discharge products were almost completely decomposed after charging, which is consistent with the SEM results. Hence, the EIS results confirmed the microstructure observation and electrochemical experiments and further confirmed the unique properties of the Li–O$_2$ batteries with a Ru$_2$O$_2$–Co$_3$O$_4$/NiF catalyst.

Conclusions

In summary, Ru$_2$O$_2$–Co$_3$O$_4$ with a 3D web microstructure was prepared via a simple hydrothermal method followed by impregnation and an annealing treatment. The 3D web freestanding Co$_3$O$_4$ nanowires growing on the surface of NiF offer a porous structure for O$_2$ diffusion, and provide a large surface space for the loading of RuO$_2$ nanoparticles, as well as Li$_2$O$_2$ formation and decomposition. The uniformly distributed RuO$_2$ particles boost the catalytic activity of the Li–O$_2$ batteries. Hence, the 3D porous structure of the freestanding Co$_3$O$_4$ nanowires loaded with RuO$_2$ was maintained after Li$_2$O$_2$ deposition and the discharge products were fully decomposed after charging. Therefore, Li–O$_2$ batteries with the freestanding Ru$_2$O$_2$–Co$_3$O$_4$/NiF cathode achieved a higher specific capacity and advanced cycling performance. When measurements were conducted at a limited specific capacity of 500 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$, the Ru$_2$O$_2$–Co$_3$O$_4$/NiF based Li–O$_2$ battery achieved 122 stable cycles. In other words, this excellent catholyte material is worthy of further investigation in the field of Li–O$_2$ batteries.

Conflicts of interest

The authors declare no conflict of interest.

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