RuO₂ nanoparticles supported on Ni and N co-doped carbon nanotubes as an efficient bifunctional electrocatalyst of lithium-oxygen battery

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ABSTRACT Li₂O₂, as the discharge product of Li-O₂ batteries on cathode, is difficult to be electrochemically decomposed, which will lead to short cycling lifespan of the batteries. In this study, the cycling lifespan of Li-O₂ battery was prolonged significantly by an efficient bifunctional catalyst. The Ni and N co-doped carbon nanotubes (NiNCs) were synthesized firstly, and then RuO₂ nanoparticles were deposited on NiNCs by a hydrothermal route to synthesize RuO₂/NiNC catalysts. Transmission electron microscopy and X-ray diffraction characterizations demonstrated that part of metallic Ni was converted into NiO and Ni(OH)₂ after loading RuO₂, and the existence of NiO layer can prevent further oxidation of metallic Ni. The Li-O₂ battery with RuO₂/NiNC as the cathode catalyst exhibits an overpotential of 0.43 V, which is much lower than the value of 1.03 V measured with the Li-O₂ battery using NiNC as the cathode catalyst. At a rate of 200 mA g⁻¹, the Li-O₂ battery with the RuO₂/NiNC cathode can maintain a reversible capacity of 500 mA h g⁻¹ for 260 cycles, and 117 cycles with a higher reversible capacity of 1000 mA h g⁻¹. The superior property of the RuO₂/NiNC bifunctional catalyst could be ascribed to the high activity of RuO₂ and the rich carbon nanotube structure of NiNC for deposition and decomposition of Li₂O₂.

Keywords: Li-O₂ battery, bifunctional catalyst, RuO₂, Ni and N co-doping, carbon nanotubes

INTRODUCTION

The consumption of fossil energy is continuously increasing after the second industrial revolution. Owing to the limited reserves of fossil energy and serious global

environmental pollution, the development of alternative, environment-friendly new energy sources is urgent [1–3]. For a long period of time, lithium-ion batteries (LiBs) have been widely used in portable electronic devices due to the advantages of long cycle life, light weight and high relative energy density [4–7]. However, with the rapid development of new energy vehicles and large scale energy storage for the exploration and utilization of renewable energy such as solar and wind, the actual energy density of traditional LiBs is unable to meet the requirements. Therefore, the development of new battery systems with higher energy density is the focus of current research [2,8–10]. Since it was demonstrated that lithium peroxide (Li₂O₂) can be reversibly formed and decomposed in non-aqueous system electrolytes by Bruce *et al.* [11] in 2006, the non-aqueous system of lithium-oxygen (Li-O₂) battery has received extensive attention due to its high theoretical energy density of 3505 W h kg⁻¹ [12,13]. However, there are still many challenges such as short cycle life, low actual capacity, large overpotential and low Coulomb efficiency, to be overcome for practical uses of Li-O₂ batteries [14].

The non-aqueous Li-O₂ battery usually consists of a porous catalyst cathode with high specific surface area, Li⁺ conducting electrolyte and lithium metal as the anode. The discharge process occurs on the cathode in such a way that oxygen freely diffuses into the porous catalyst cathode/electrolyte interface, and then combines with Li⁺ in the electrolyte to generate Li₂O₂ ($2\text{Li}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{Li}_2\text{O}_2$, $E_0 = 2.96 \text{ V vs. Li/Li}^+$) [15,16]. Conversely, during charging, Li₂O₂ is decomposed to release oxygen ($\text{Li}_2\text{O}_2 \rightarrow$

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$2\text{Li}^+ + 2\text{e}^- + \text{O}_2$) [14]. Unfortunately, this process is not completely reversible. The superoxide ions of the discharge intermediate product have strong oxidizability [17,18], and can cause unwanted side reactions with electrolyte and the catalyst cathode [19,20], producing other discharge products (e.g., Li_2CO_3) that are different from Li_2O_2 , leading to blockage of the porous cathode to rise charging voltage. Therefore, the present challenge mainly comes from the cycling-instability of the non-aqueous electrolyte and the carbon cathode, leading to the lower round-trip efficiency. Such a problem could be addressed by reasonable design and construction of air electrode to reduce voltage polarization or improve the corrosion resistance of electrolyte and air electrodes in the presence of Li_2O_2 and O_2^- . Hence, electrochemical performance of Li- O_2 batteries is related to the properties of solvents and cathode. Organic solvents including propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) have been widely used in lithium-ion batteries. However, several research groups have proven that these organic carbonate solvents are unstable and easily decomposed in the presence of discharge intermediate products [21]. Thus, the research of Li- O_2 battery electrolyte has attracted wide attention. Ether-based electrolytes have been widely used in Li- O_2 battery due to their high antioxidant stability, high decomposed potential (up to 4.5 V vs. Li/Li^+), good wettability for electrodes, low volatility, and low cost [22].

Owing to the high electrical conductivity, strong oxygen adsorption capacity, low cost and light weight, carbon-based catalysts were investigated widely as cathode catalysts for Li- O_2 battery [23–25]. However, carbon-based catalysts are easy to be oxidized in the presence of oxygen species. Thus far, many studies are focused on cathode catalysts which could be roughly divided into carbon materials [26–32], noble metals [33–35], transition metal oxides [36–39], and N-doped hybrid electrocatalysts [40–43]. These catalyst materials can accelerate at various degrees the decomposition of Li_2O_2 and improve cycle performance of Li- O_2 battery. The discharge product, Li_2O_2 , is insoluble and dielectric, causing blockage of the passage channels in carbon material and resulting in deterioration of battery performance [44–46]. Hence, to control the microstructure of carbon materials becomes an efficient strategy in enhancing their catalytic property. Zhao *et al.* [43] used polyphenyl dopamine as a template to assemble graphene sheets into a three-dimensional (3D) porous N-doped graphene aerogel for enhancing carbon activity. However, the Li- O_2 battery

still has a slow oxygen evolution reaction (OER) rate. Ruthenium-based catalysts have been reported with high OER catalytic activity. Zhou *et al.* [47,48] constructed a series of high-efficiency Li- O_2 battery catalysts with the introduction of RuO_2 nanoparticles. Meanwhile, the reduced oxygen species generated during the discharge process have high activity toward the organic electrolytes and carbon-based electrodes, thus resulting in the generation of side products, such as Li_2CO_3 , ROCO_2Li , LiCO_2R (R is alkyl group or hydrogen) [49–51]. Lithium carbonate (Li_2CO_3) as representative side products of Li- O_2 batteries is difficult to decompose, and it has demonstrated that nickel oxide has the ability to catalyze the decomposition of Li_2CO_3 [52,53]. Our group has demonstrated that Ru and NiO catalysts show high catalytic activity for the decomposition of Li_2CO_3 [54,55]. Therefore, the Ni-based transition metal oxide is expected to become a better substitute material of catalyst.

In this study, the catalyst (RuO_2/NiNC) was prepared by evenly loading RuO_2 nanoparticles onto nickel and nitrogen co-doped carbon nanotubes (NiNCs) through a one-step hydrothermal method. The property of the RuO_2/NiNC bifunctional catalyst could be ascribed to the high activity of RuO_2 and the rich carbon nanotube structure of NiNC for deposition and decomposition of Li_2O_2 . In this catalyst, N-doped carbon can improve the oxygen reduction reaction (ORR) catalytic activity by introducing defect sites, providing consequently abundant sites for the attachment of metal elements [40,56]. The transition metal/metal oxide composites, Ni/NiO, can catalyze the decomposition of carbonate/carboxylate species [52,57]. RuO_2 owns good corrosion resistance and therefore exhibits better catalytic activity for OER and ORR than Ru, which significantly reduces the charge and discharge polarization voltage [58,59]. Finally, the NiNC possesses a nanostructure that provides abundantly accessible sites for RuO_2 attachment. The Li- O_2 batteries using RuO_2/NiNC or NiNC as the cathode catalyst under different test conditions were investigated. Much higher performances including low polarization voltage and long cycling lifespan were confirmed for the RuO_2/NiNC as the cathode catalyst in Li- O_2 batteries.

EXPERIMENTAL SECTION

Materials

Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AR), urea (H_2NCONH_2 , AR), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, AR), and sodium hydroxide (NaOH, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ruthenium

trichloride (RuCl_3 , AR) was purchased from Shanghai Wokai Reagent Chemical Co. Ltd. All the reagents mentioned above were used without any pretreatment before use. The lithium foil (>99.9%, thickness: 2 mm) was brought from China Energy Lithium Co., Ltd. The electrolyte $1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3$ in tetraethylene glycol dimethyl ether (TEGDME) was brought from Dodochem.

Preparation of NiNCs

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.6 g), urea (10.0 g), and citric acid (1.0 g) were dissolved in 150 mL of ethanol and 50 mL of deionized water through intense agitation, a gel formed after 3 h at 75°C until the liquid was almost vaporized, and the gel was transferred to an oven kept at 100°C for 12 h. Before calcination, the gel was dried in dehumidification cabinet for 6 h and ground into powder. Then the mixture was calcined at 350°C for 4 h and then 650°C for 10 h in Ar atmosphere to obtain NiNCs.

Preparation of $\text{RuO}_2/\text{NiNCs}$

The as-prepared NiNCs (0.1 g) were uniformly dispersed into 40 mL of deionized water containing 30 mg of RuCl_3 *via* sonication treatment for 30 min. The pH of the solution was adjusted to 11.0 by adding a certain proportion of sodium hydroxide (NaOH). The mixture stirred at room temperature for 30 min was transferred into a Teflon-lined stain-less steel autoclave (50 mL) and heated at 180°C for 12 h. Ultimately, the precipitate was separated by centrifugation, washed with deionized water thrice and then dried at 80°C under vacuum for 10 h to acquire $\text{RuO}_2/\text{NiNCs}$.

Preparation of NC and RuO_2/NC

As a reference sample, the NCs were synthesized under the same experiment conditions as for the NiNC mentioned above but without $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. And the synthesis of RuO_2/NC was under the same experiment conditions as for the RuO_2/NiNC mentioned above but using 0.1 g of NC instead of 0.1 g of NiNC.

Materials characterization

The as-synthesized products were investigated by powder X-ray diffraction (XRD; Philips X' Pert Pro Super diffractometer equipped with graphite monochromatized Cu K α radiation), field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM; JEOLJEM-2100 microscope). The weight ratio of RuO_2 was determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Nexion 300, Perkin Elmer). The Brunauer-Emmett-Teller

(BET) method was used to test the specific surface area of materials. Raman spectra were recorded on a Raman spectrometer (DilorRaman, LabRam I) coupled with a microscope in reflectance mode with a 532-nm excitation laser source. The elemental surface composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 VB III) with a focused monochromatic Al K α X-ray source.

Electrochemical experiments

CR2025-type coin cells were used to test the electrochemical performance of non-aqueous Li-O_2 batteries. The cathode electrodes consisted of 80 wt.% active materials, 10 wt.% acetylene black, and 10 wt.% LA132 binder which were stirred for 12 h. The slurry was dispersed on carbon cloth to form a working electrode with a loading of $1.0 \pm 0.2 \text{ mg}$ and vacuum dried for 10 h at 80°C . The pre-synthesized material was used as the working electrode, polypropylene (PP) film (Celgard 2400) was used as the separator, and lithium metal was used as the negative electrode to assemble the lithium oxygen battery in an argon-filled glove box with water and oxygen contents less than 0.5 ppm. The electrolyte was $1 \text{ mol L}^{-1} \text{ LiCF}_3\text{SO}_3/\text{TEGDME}$. The assembled cells were placed in a sealed container filled with 1 atm high-purity oxygen. After resting at room temperature for 5 h, the battery was galvanostatically charged and discharged on the LAND-V34 test system (Wuhan, China).

Electrochemical impedance spectra (EIS) of the Li-O_2 cells with RuO_2 as cathode were carried out at a PAR-STAT 2263 Advanced Electrochemical System with a capacity step of 25 mA h g^{-1} from 0 to 500 mA h g^{-1} . The amplitude of the alternating current (AC) signal was set as 5 mV in a frequency range of 100 kHz to 1 mHz.

RESULTS AND DISCUSSION

Fig. 1a shows the SEM image of NiNC, where some carbon nanotubes grown on the carbon sheets. As a comparison, without the Ni source during the synthetic process, the carbon nanotubes cannot be found on the carbon sheets (Fig. S1), indicating that the Ni element can catalyze the growth of carbon nanotubes [60]. Abundant carbon nanotubes on the carbon sheets can provide extra space for the deposition of discharging products (e.g., Li_2O_2), which plays a crucial role in enhancing the electrochemical performance of Li-O_2 batteries. The TEM images further confirm the growth of carbon nanotubes on the carbon sheets. Especially, on the carbon sheets, some nanoparticles with diameters of 5–10 nm can be observed (Fig. 1b). Further locally amplified image of

Figure 1 The SEM and TEM images of NiNC and RuO₂/NiNC: (a) the SEM and the corresponding enlarged SEM image of NiNC. TEM (b) and high-resolution TEM (HRTEM) (c) images of NiNC. (d) The SEM and the corresponding enlarged SEM image of RuO₂/NiNC. TEM (e) and HRTEM (f) images of RuO₂/NiNC. (g–l) Elemental mapping images of RuO₂/NiNC.

nanoparticles shows the lattice spacing of 0.20 nm, which is associated to the (111) plane for the metallic Ni, illustrating that the Ni element is reduced by the carbon material during the pyrolysis process (Fig. 1c). RuO₂ was widely investigated as a functional catalyst to assist the generation and decomposition of Li-O₂, and thus, the electrochemical performance of Li-O₂ batteries can be significantly improved. Herein, the RuO₂ nanoparticles also were loaded on the NiNC in order to further enhance

the performance of batteries *via* a hydrothermal method. From the SEM image, we can observe that the structure of carbon nanotubes can be well maintained after this hydrothermal process (Fig. 1d), and the tiny RuO₂ nanoparticles are found on the carbon nanotubes (inset in Fig. 1d). The ICP-OES quantitative analysis demonstrates that the mass fraction of RuO₂ in the RuO₂/NiNC composite is 5.8%. The TEM images confirmed that RuO₂ nanoparticles are well dispersed in the NiNC substrate

(Fig. 1e, g–l), and the high-resolution image of RuO_2 nanoparticles exhibits the lattice fringe of (110) plane of RuO_2 with a lattice space of 0.32 nm (inset in Fig. 1f). Furthermore, on the carbon sheets after RuO_2 growth, besides the metallic Ni lattice fringes, it can also be found that, part of metallic Ni has been transferred into NiO phase with a lattice space of 0.24 nm ((111) plane) and $\text{Ni}(\text{OH})_2$ phase with a lattice space of 0.27 nm ((100) plane) (Fig. 1f). Detail structure information will be further confirmed below. For comparison, the RuO_2 nanoparticles were also grown on the Ni-free NC (RuO_2/NC) *via* the same hydrothermal process with the same loading mass of RuO_2/NiNC . As displayed in Fig. S2, the RuO_2 nanoparticles aggregate on the NC, meaning that the abundant carbon nanotubes also provide enough active sites for the growth of RuO_2 .

Several characterization methods, like XRD patterns, N_2 adsorption/desorption isotherms, Raman spectroscopy and XPS were further adopted to characterize the structural properties of different cathodes. Fig. 2a compares the XRD patterns of NiNC and RuO_2/NiNC (Fig. S3). For the bare NC material, the XRD pattern shows a typical feature of amorphous carbon (JCPDS No.75-0444) (Fig. S4). However, with the addition of Ni source, diffraction peaks associated to the metallic Ni (JCPDS No. 04-0850) can be found in the XRD patterns of NiNC. After RuO_2 was grown on NiNC, some new diffraction peaks related to the $\text{Ni}(\text{OH})_2$ (JCPDS No. 73-1520) can be detected, indicating that the metallic Ni can be partly processed into $\text{Ni}(\text{OH})_2$ during the hydrothermal reaction. The diffraction peak located at 35.1° can be ascribed to the RuO_2 in RuO_2/NiNC (JCPDS No. 43-1027). Fur-

Figure 2 (a) The XRD patterns of NiNC and RuO_2/NiNC . (b) The N_2 adsorption/desorption isotherms of NiNC and RuO_2/NiNC , and (c) the corresponding pore distribution curves. (d) The Raman spectra of NiNC and RuO_2/NiNC . The XPS spectra of the NiNC and RuO_2/NiNC : (e) survey, (f) Ni 2p, (g) N 1s and (h) Ru 3p.

thermore, the specific surface area and pore distribution were also confirmed by N_2 adsorption/desorption isotherms. The NC exhibits a specific surface area of $107.2 \text{ m}^2 \text{ g}^{-1}$ and a pore diameter of around 17.6 nm (Fig. S5). But for the NiNC, the specific surface area increases to $200.5 \text{ m}^2 \text{ g}^{-1}$, which is two times that of NC (Fig. 2b), and the pore diameter is shrunk to around 6 nm. This can be ascribed to the fact that the carbon nanotubes growth under the catalysis of metallic Ni can significantly enlarge the surface area. After RuO_2 loading, the specific surface areas of RuO_2/NC ($46.3 \text{ m}^2 \text{ g}^{-1}$) (Fig. S6) and RuO_2/NiNC ($67.3 \text{ m}^2 \text{ g}^{-1}$) (Fig. 2b) are relative lower than before loading, which can be attributed to RuO_2 partially occupying the surface active sites. The Raman spectra were also performed to explore the degree of graphitization. As we can see from Fig. 2d, the two main Raman peaks at approximately 1350 and 1600 cm^{-1} can be separately indexed to the D band and G band of the graphitic carbon. And the intensity ratio of D band and G band (I_D/I_G) can be used to signify the degree of graphitization of the materials. The I_D/I_G ratio of NC is calculated to be 1.12 (Fig. S7), while the ratio of NiNC is 1.05 (black line in Fig. 2d), indicating that the NiNC has a high degree of graphitization than NC, which can also be attributed to that the generation of carbon nanotubes increases the percentage of graphitized carbon. After loading RuO_2 , the I_D/I_G of RuO_2/NiNC decreases to 0.97, which is ascribed to RuO_2 occupying the defects on carbon nanosheets and carbon nanotubes, meaning that the RuO_2/NiNC presents a higher graphitized degree (red line in Fig. 2d). A higher graphitized degree guarantees the better electron transfer during electrochemical charge-discharge processes. The XPS was applied to investigate the chemical states of NiNC and RuO_2/NiNC . The peaks related to C 1s, N 1s, O 1s and Ni 2p all can be found in the survey spectra of NiNC and RuO_2/NiNC (Fig. 2e). Particularly, a pair of peaks located within 450 to 500 eV can be observed in RuO_2/NiNC , which are associated to the Ru $3p_{3/2}$ and Ru $3p_{1/2}$ split peaks, also confirming the successful loading of RuO_2 . Further high-resolution XPS spectra were investigated to examine the detail chemical states of Ni, N and Ru elements. For the NiNC, Ni 2p XPS could be divided into three peaks, which are separately identified as the $2p_{3/2}$ peaks of metallic Ni (853.1 eV), Ni^{2+} (854.4 eV) and Ni^{3+} (856.9 eV). However, the metallic Ni disappears after loading RuO_2 , indicating that metallic Ni was oxidized during the hydrothermal reaction. Considering the XRD diffraction peaks of metallic Ni still can be detected in RuO_2/NiNC , it can be speculated that the oxidation of metallic Ni only occurs on the surface of Ni

particles, while the metallic Ni also exists in the bulk (Fig. 2f). Oxidation state of Ni has been demonstrated to be an outstanding catalyst for Li- O_2 batteries, and thus, partial oxidation of Ni particles can be predicted to be a better species for Li- O_2 batteries. Besides, N 1s is also provided to identify the N species in both NiNC and RuO_2/NiNC (Fig. 2g). The N in NiNC and RuO_2/NiNC all can be divided into pyridine N (398.2 eV) and pyrrole N (400.1 eV). However, after being hydrothermally loaded with RuO_2 , part of the N was transformed into graphite N (400.8 eV), which may increase the electron conductivity of the RuO_2/NiNC material. The N doping in the catalyst systems is beneficial to the uniform distribution of metal nanoparticles [61], and meanwhile also conducive to improving the oxygen adsorption, enhancing the electron transfer rate and reducing the overpotential for the charge-discharge processes. Fig. 2h further confirms the chemical states of Ru in the materials. There are no signal for Ru in NiNC, while a pair of split peaks associated to Ru^{4+} can be found in Ru 3p spectrum, meaning that the chemical state of Ru is RuO_2 .

The as-prepared NC, RuO_2/NC , NiNC and RuO_2/NiNC were loaded on the carbon cloth to fabricate oxygen cathodes. And then the oxygen cathodes were matched with Li foils to assemble Li- O_2 cathodes. The initial charge-discharge curves of the Li- O_2 batteries with several oxygen cathodes at 50 mA g^{-1} , 500 mA h g^{-1} were firstly compared. When NC cathode was served as the oxygen cathode, the initial overpotential for charge process is 0.98 V (Fig. S8a), while it drops to 0.90 V after further loading RuO_2 on NC (Fig. S8b), indicating that the RuO_2 benefits the conversion process of Li_2O_2 during the charge-discharge process. With the assistance of NiNC, the charge overpotential increased to 1.03 V, which is basically close to the charge overpotential of NC, implying that although the addition of Ni can promote the growth of carbon nanotubes, the carbon nanotubes have no obvious catalytic activity for the decomposition of Li_2O_2 . Significantly, after further loading of RuO_2 on NiNC, the charge overpotential dramatically drops to 0.43 V, which is only half that of NiNC (Fig. 3a). Results clearly demonstrate that the addition of nickel source can catalyze the formation of carbon nanotubes and provide more attachment sites for RuO_2 , thereby improving the catalytic activity of the oxygen cathode and promoting the decomposition of Li_2O_2 . Furthermore, the cyclic stability of the Li- O_2 batteries with several oxygen cathodes was estimated. At a current density of 200 mA g^{-1} and limited capacity of 1000 mA h g^{-1} , the cell with NiNC cathode shows an initial charge overpotential of 4.03 V,

Figure 3 (a) The initial charge-discharge curves of the Li-O₂ batteries with NiNC and RuO₂/NiNC cathodes. (b) The charge-discharge curves of the cells with NiNC cathode at 200 mA g⁻¹, 1000 mA h g⁻¹. The charge-discharge curves of the Li-O₂ batteries with RuO₂/NiNC cathode at (c) 200 mA g⁻¹, 500 mA h g⁻¹ and (d) 200 mA g⁻¹, 1000 mA h g⁻¹. (e) Voltage of the terminal discharge potential vs. cycle number with a fixed capacity of 1000 mA h g⁻¹ and 500 mA h g⁻¹ at a current density of 200 mA g⁻¹.

and the following charge potential continually increases, and reaches 4.72 V after 62 cycles. Additionally, for the discharge processes, the terminal potential gradually declines to below 2.0 V after 62 cycles, which indicates that the discharge product, Li₂O₂, accumulates on this oxygen cathode and leads to the passivation of the cathodes

(Fig. 3b, e). Terminal potential valuation of the cells with NiNC also notably displays the poor cyclic stability and limited cycling life. Dramatically, an enhanced cycling performance can be achieved by replacing the cathodes with RuO₂/NiNC. Long lifespan is performed under the condition of 200 mA g⁻¹, 500 mA h g⁻¹. The minimum

charge overpotential is 3.89 V, and only increases to 4.49 V after 260 cycles. After over 250 cycles, the terminal discharge potential reduces to the level of below 2.0 V, indicating that the excellent cycling stability can be realized by RuO₂/NiNC cathodes (Fig. 3c, e). Similarly, at a harsher condition of 200 mA g⁻¹, 1000 mA h g⁻¹, the failure of cells occurs after 117 cycles, which is two times of that with NiNC cathodes (Fig. 3d, e). General comparison of terminal discharge potential of the cells based on RuO₂/NiNC is shown up in Fig. 3e. As a comparison, the Li-O₂ batteries based on NC and RuO₂/NC were also investigated in Fig. S9. The discharge potentials drop to lower than 2.0 V at the 79th and 86th cycles with NC and RuO₂/NC cathodes, respectively, which manifests the cathodes cannot well assist the generation and decomposition of Li₂O₂, leading to the failure of cathodes. In summary, the co-existence of RuO₂ and Ni species in the cathodes can well suppress the accumulation of Li₂O₂ on the cathodes, and have effect on accelerating the conversion of Li₂O₂, which leads to the significant enhancement of Li-O₂ batteries. To highlight the excellent performance of our designed catalyst, the electrochemical performances of Li-O₂ batteries based on various carbon cathodes decorated with RuO₂ catalysts were compared as summarized in Table S1.

To assess the effect of RuO₂/NiNC on the generation and decomposition of Li₂O₂, the Li-O₂ battery was cycled at a capacity of 4000 mA h g⁻¹. Fig. 4a displays the cor-

responding charge-discharge curve and the three stages, pristine (labeled as (C)), after discharge (labeled as (D)) and after charge (labeled as (E)) were compared by *ex-situ* XRD and SEM characterization. As shown in Fig. 4b, after initial full discharge, compared with initial stage, a series of diffraction peaks associated to Li₂O₂ (JCPDS No. 73-1640) can be found in the XRD pattern of RuO₂/NiNC, meaning that the generation and accumulation of Li₂O₂ during the discharge process. And after initial full charge process, the diffraction peaks of Li₂O₂ disappeared, which indicates that the Li₂O₂ product can be fully decomposed under the assistance of the RuO₂/NiNC. SEM images further confirm the generation and decomposition processes of Li₂O₂ during the charge-discharge process. The RuO₂/NiNC is well dispersed on the carbon cloth (Fig. 4c). When discharged to 4000 mA h g⁻¹, toroidal shaped Li₂O₂ products with a diameter of 1–2 μm uniformly cover the surface of the RuO₂/NiNC without aggregation (Fig. 4d). And after full charge process, it can be observed that the toroidal shaped Li₂O₂ particles completely disappear, which also demonstrates that the RuO₂/NiNC can promote the full decomposition of Li₂O₂ (Fig. 4e). XPS measurements were performed to detect the products obtained from the RuO₂/NiNC, RuO₂/NC and NiNC electrodes during charging and discharging. As shown in Fig. S10, the C 1s peaks at 284.5, 286.4 and 292.6 eV can be ascribed to C–C, C–O and C–F, respectively, while the peak at 289.3 eV is due to the pro-

Figure 4 (a) The initial charge-discharge curves of the Li-O₂ batteries with RuO₂/NiNC cathode at 200 mA g⁻¹, 4000 mA h g⁻¹. (b) The XRD patterns of the RuO₂/NiNC at initial stage, after discharge and after charge. The SEM images and locally amplified images of RuO₂/NiNC at (c) initial stage, (d) after discharge and (e) after charge.

duction of Li_2CO_3 (Fig. S10a). After charging, the peak of Li_2CO_3 has a significant drop in the RuO_2/NiNC catalyst, suggesting the decomposition of Li_2CO_3 . However, this is not the case for RuO_2/NC and NiNC , as shown in Fig. S10c, e, where there is a significant rise in the peak of Li_2CO_3 . Correspondingly, the peaks at 54.5 and 55.4 eV can be assigned to Li 1s of the products Li_2O_2 and Li_2CO_3 , respectively (Fig. S10b, d, f). After charging, most of the Li_2O_2 peak disappeared in the RuO_2/NiNC catalyst; however, partial Li_2O_2 was still residual in the Ru/NC and NiNC catalysts.

To estimate the electrochemical reaction dynamics during the charge-discharge process, the EIS was carried out to explore the evolution of charge transfer process during the initial cycle. Fig. 5a displays the Nyquist plots cross the initial charge and discharge processes. During the test, the $\text{Li}-\text{O}_2$ battery was performed at a current density of 50 mA g^{-1} , and a limited capacity of 500 mA h g^{-1} , and the Nyquist plots of the cells were monitored each for 30 min charge or discharge. The electrical equivalent for the fitting of Nyquist plots is shown in Fig. 5b. The R_1 is the resistance of electrolyte, and R_2 is defined as the charge transfer resistance (R_{ct}), and the W_o stands for the Warburg resistance, which relates to the Li^+ transfer in the bulk. In the discharged process, the initial R_{ct} is 225Ω , and it increases significantly when discharged to 125 mA h g^{-1} , which may

be ascribed to poor wetting of electrolyte at initial states, resulting in the relative lower Li^+ diffusion dynamics and the accumulation of discharge products. After that, the R_{ct} gradually decreases with continuous discharge up to 500 mA h g^{-1} , which is ascribed to the increase of electrolyte wettability due to the prolonged discharge time and the accumulation of discharge products that make the positive catalyst layer loose. For the charge process, with the decomposition of Li_2O_2 , the porous structure of oxygen cathodes can be released, and thus, the ion transfer is accelerated, leading to a decrease trend of R_{ct} during the charge process. Especially, after full charge, the R_{ct} of the battery is 161Ω , which is significantly smaller than the initial state (225Ω), resulting from the better wetting of the electrolyte. The EIS analysis well matched with the results that RuO_2/NiNC can promote the generation and decomposition of Li_2O_2 , also meaning that the co-existence of RuO_2 and Ni species can dramatically enhance the cycling performance of $\text{Li}-\text{O}_2$ batteries.

CONCLUSIONS

In summary, the RuO_2/NiNC cathode catalyst was synthesized by loading RuO_2 nanoparticles on nickel and nitrogen co-doped carbon nanotubes (NiNC). The $\text{Li}-\text{O}_2$ battery with RuO_2/NiNC as the cathode catalyst holds a longer cycle life of 117 cycles with a fixed capacity of 1000 mA h g^{-1} at 200 mA g^{-1} and a low overpotential of

Figure 5 (a) EIS spectra of $\text{Li}-\text{O}_2$ battery with RuO_2/NiNC during the initial charge-discharge process with a capacity limit of 500 mA h g^{-1} at a current density of 50 mA g^{-1} . (b) The electrical equivalent for the fitting of Nyquist plots and the corresponding R_{ct} values during the (c) discharging and (d) charging processes.

0.43 V with a fixed capacity of 500 mA h g^{-1} at 50 mA g^{-1} . These properties are superior to those of the Li-O_2 battery with NiNC as the cathode catalyst, which could deliver 62 cycles and present a much larger overpotential of 1.03 V under the same experimental conditions. SEM images clearly illustrate the generation of carbon nanotubes after the addition of Ni source. The presence of carbon nanotubes does not significantly reduce the charging polarization of Li-O_2 batteries, but provides abundant accessible sites for subsequent RuO_2 loading, which significantly enhances the catalytic activity of RuO_2/NiNC . In addition, during the charging and discharging process, *ex-situ* XRD and SEM analyses have clearly demonstrated the formation and decomposition of Li_2O_2 , revealing the efficient electrocatalytic activity of RuO_2/NiNC . The significantly enhanced catalytic activity of RuO_2/NiNC is attributed to the synergy of RuO_2 and nanostructure of NiNC, resulting in high catalytic activity for both oxygen reduction and Li_2O_2 decomposition.

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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镍和氮共掺杂碳纳米管负载 RuO_2 纳米颗粒作为锂氧电池的高效双功能电催化剂

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摘要 氧化锂是锂-氧电池的主要放电产物, 其很难电化学分解, 因而导致电池的循环寿命过短. 本文通过有效的双功能催化剂显著提升了锂-氧电池的循环寿命. 首先, 我们合成了镍和氮掺杂的碳纳米管(NiNC), 然后通过水热法在NiNC上负载二氧化钌(RuO_2)纳米粒子合成 RuO_2/NiNC 催化剂. 透射电子显微镜和X-射线粉末衍射证明在水热负载 RuO_2 之后部分金属镍被转变成氧化镍和氢氧化镍, 且氧化镍的存在缓解了金属镍的进一步氧化. 以 RuO_2/NiNC 为正极催化剂的锂氧电池的过电压仅为0.43 V, 远低于使用NiNC作为正极催化剂的1.03 V. 当限定充放电条件为 200 mA g^{-1} , 500 mA h g^{-1} 时循环寿命可达260次, 在 1000 mA h g^{-1} 高比容量下的循环寿命也达到117次. RuO_2/NiNC 催化剂优异的性能归因于 RuO_2 的高活性和NiNC材料丰富的碳纳米管结构促进了放电产物(Li_2O_2)的生成和分解.