RuO₂ nanoparticles supported on MnO₂ nanorods as high efficient bifunctional electrocatalyst of lithium-oxygen battery

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Abstract

RuO₂ nanoparticles supported on MnO₂ nanorods (denoted as np-RuO₂/nr-MnO₂) were synthesized via a two-step hydrothermal reaction. SEM and TEM images both illustrated that RuO₂ nanoparticles are well dispersed on the surface of MnO₂ nanorods in the as-prepared np-RuO₂/nr-MnO₂ material. Electrochemical results demonstrated that the np-RuO₂/nr-MnO₂ as oxygen cathode of Li-O₂ batteries could maintain a reversible capacity of 500 mAh g⁻¹ within 75 cycles at a rate of 50 mA g⁻¹, and a higher capacity of 4000 mAh g⁻¹ within 20 cycles at a rate as high as 200 mA g⁻¹. Moreover, the cell with the np-RuO₂/nr-MnO₂ catalyst presented much lower voltage polarization (about 0.58 V at a rate of 50 mA g⁻¹) than that measured with only MnO₂ nanorods during charge/discharge processes. The catalytic property of the

np-RuO₂/nr-MnO₂ and MnO₂ nanorods were further compared by conducting studies of using rotating disk electrode (RDE), chronoamperometry and linear sweep voltammetry. The results illustrated that the np-RuO₂/nr-MnO₂ exhibited excellent bifunctional electrocatalytic activities towards both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Furthermore, in-situ high-energy X-ray diffraction was employed to trace evolution of species on the np-RuO₂/nr-MnO₂ cathode during the discharge processes. In-situ XRD patterns demonstrated the formation process of the discharge products that consisted of mainly Li₂O₂. Ex-situ SEM images were recorded to investigate the morphology and decomposition of the sphere-like Li₂O₂, which could be observed clearly after discharge process, while are decomposed *almost* after charge process. The excellent electrochemical performances of the np-RuO₂/nr-MnO₂ as cathode of Li-O₂ battery could be contributed to the excellent bifunctional electrocatalytic activities for both the ORR and OER, and to the one-dimensional structure which would benefit the diffusion of oxygen and the storage of Li₂O₂ in the discharge process of Li-O₂ battery.

Introduction

Lithium ion batteries (LiBs) as the prevailing power source have been widely used in portable electronic devices[1]. Nevertheless, owing to the limitation of their theoretical energy density, exploring the battery systems that have higher energy density to meet the growing demands by fast development of electric vehicles and large scale energy storage has become a significant assignment[2]. Since the discovery that lithium peroxide could reversibly form and decompose in non-aqueous electrolytes reported by Bruce et al. in 2006[3], non-aqueous lithium-oxygen (Li-O₂) batteries have attracted extensive interests, because of their extremely high theoretical energy density about 11400 kW kg⁻¹ which is much higher than that of commercial LiBs[2, 4-6]. However, non-aqueous Li-O₂ batteries are still facing tremendous challenges on improving cycle performance, increasing power density and reducing voltage hysteresis[2, 5]. The performances of a Li-O₂ batter, i.e. the cycleability, power density and voltage hysteresis depend mostly on the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) involved in the discharge/charge processes. The active intermediates (O²⁻, LiO₂ and so on) in discharge step can cause unwanted side reactions with non-aqueous electrolyte or carbon materials at oxygen cathode to decay the electrochemical performance of the non-aqueous Li-O₂ batteries[5, 7-11]. The main discharge product of Li₂O₂ which forms on oxygen cathode but cannot dissolve in non-aqueous electrolytes also influence oxygen diffusion and reduce the electrical conductivity of oxygen cathode[5, 7, 8, 11-13]. As a consequence, the reversible formation and decomposition of Li₂O₂ will become more difficult, leading to the increasing electrochemical polarization of ORR and OER in discharge/charge processes.

To solve those above mentioned problems, great efforts have been made on different components of non-aqueous Li-O₂ batteries. It is well known that non-aqueous Li-O₂ batteries are typically composed of non-aqueous electrolyte, porous catalysts as oxygen cathode and lithium metal as anode. First of all, different non-aqueous electrolytes were compared in order to find the best electrolyte with high

oxygen solubility and high stability against discharge product, for instance, carbonate-based solvents[14], ether-based solvents[15], DMSO-based electrolyte[7, 16], TEGDME-LiCF₃SO₃ electrolyte[17] and so on, were investigated in detail. Recently, it has reported that soluble redox mediators such as tetrathiafulvalene (TTF)[18] and LiI[19-21] in electrolytes can reduce voltage hysteresis of OER in charge process. More importantly, the porous cathode catalyst is always regarded as the key element to be improved in its electrocatalytic activity.

Many porous catalysts have been explored with high efficiency in Li-O₂ batteries, mainly comprising carbon materials[19, 22-29], transitional metal oxides[30-36], noble metal[6, 37-41], Perovskite-type oxides[42-44]. They can present high catalytic activity in ORR to assist in oxygen reduction or in OER to facilitate decomposition of Li₂O₂. To further increase the stabilities of porous catalysts, some wise strategies like free-standing electrodes[29], pure metal oxide electrodes[45] and carbon electrodes[19, 22] with large surface area have been tested in Li-O₂ batteries and achieved good results. Recently, to further reduce the overpotential in discharge/charge processes, the optimal designs of catalysts are considered for constructing bifunctional materials [37, 46] and increasing pore volume of catalysts[22, 47]. Platinum-gold nanoparticle as a highly active bifunctional electrocatalyst has been successfully synthesized by Yang et al. to accelerate ORR and OER kinetics in Li-O₂ batteries[37]. Zhou et al. have prepared Ru nanoparticles supported on binder-free multi-walled carbon nanotube paper as cathode[47]. This cathode can provide the void space to store discharge products (mainly Li₂O₂) and the Ru nanoparticles can efficiently catalyze Li₂O₂ decomposition.

It is frequently reported that MnO₂ materials are good catalysts toward the ORR, and RuO₂ nanoparticles show strong catalytic activity toward both the ORR and OER[48-50]. The RuO₂/MnO₂ hybrid materials have been prepared through different methods, and they can effectively deliver good electrocatalytic activity[51-54]. However, the catalytic activity of the RuO₂/MnO₂ hybrid materials needs to be still improved, and the unclear formation mechanism of the discharge products in Li-O₂ batteries on these catalysts should be investigated by in situ technique.

In this study, RuO₂ nanoparticles supported on MnO₂ nanorods (denoted as np-RuO₂/nr-MnO₂) were synthesized via a two-step hydrothermal reaction. The Li-O₂ battery with the np-RuO₂/nr-MnO₂ as cathode catalyst presented much lower voltage polarization (about 0.58 V at a rate of 50 mA g⁻¹) in charge/discharge processes than that with only MnO₂ nanorods as cathode. The excellent electrochemical performance of the np-RuO₂/nr-MnO₂ in Li-O₂ battery could be contributed to their excellent bifunctional electrocatalytic activities toward both the ORR and OER, and also to the one-dimensional structure that promotes the diffusion of oxygen and the storage of Li₂O₂ in the discharge process. Furthermore, in-situ high-energy X-ray diffractions and ex-situ SEM images obtained in this study illustrated clearly the formation and decomposition of the discharge products.

Experimental Section

Materials synthesis

In the first step, MnO₂ nanorods were prepared via a facile hydrothermal reaction. 0.4 g KMnO₄ was firstly dissolved in 40 ml deionized water, and then 0.9 g MnSO₄·H₂O was added into the KMnO₄ solution. After stirring for 30 minutes at room temperature, the mixed solution was transferred into a Teflon-lined stain-less steel autoclave (50 ml) and heated at 180 °C for 10 h. The precursor was separated by centrifugation, washed with deionized water and dried at 80 °C under vacuum for 10 h. Then, 0.1 g MnO₂ nanorods were dispersed into a solution of 30 mg RuCl₃ in 40 ml deionized water by sonication for 30 min. The pH value was adjusted to 11 by adding appropriate amounts of sodium hydroxide. After stirring for 30 minutes at room temperature, the mixture was transferred into a Teflon-lined stain-less steel autoclave (50 ml) and heated at 180 °C for 12 h. np-RuO₂/nr-MnO₂ were separated by centrifugation, washed with deionized water and dried at 80 °C under vacuum for 10 h.

Materials characterization

Crystallographic information of the as-synthesized products was collected by powder X-ray diffraction (XRD; Philips X' Pert Pro Super diffractometer equipped with graphite monochromatized Cu K α radiation). Morphologies and structures of the as-synthesized products were characterized by field emission scanning electron microscopy (HITACHI S-4800) and transmission electron microscopy (FEI Tecnai-F30 FEG). The weight ratio of RuO $_2$ was determined by inductively coupled plasma optical emission spectrometer (ICP-OES: Thermo Electron IRIS Intrepid II XSP). The specific surface area of MnO $_2$ nanorods and np-RuO $_2$ /nr-MnO $_2$ were measured by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption and desorption isotherms on a Tristar3000 system.

The in-situ synchrotron HEXRD measurements were carried out at Beamline 11-ID-C of the Advanced Photon Sources (Argonne National Lab). The X-ray wavelength was 0.11725 Å. In-situ synchrotron HEXRD patterns were collected with custom-designed coin cells with a hole cycled with a MACCOR cycler at a rate of 100 mA g $^{-1}$ for 20 h. The in-situ coin cells were placed inside an oxygen chamber to provide the electrochemical reaction atmosphere. During the discharge process, the XRD patterns were collected for 1 min, with 10 min intervals, using a Perkin-Elmer 2D X-ray detector. 2D images were converted into a 1D plot of 2 θ versus intensity by using the FIT2D program calibrated against a CeO $_2$ standard.

Electrochemical measurement

Electrochemical properties of non-aqueous Li–O $_2$ batteries were measured by assembling them into CR2025-type coin cells. The electrode slurries were made by mixing the active material, acetylene black and LA132 binder in a weight ratio of 8:1:1 by stirring for 12 h. The working electrodes were made by spreading the slurry onto carbon cloth with a loading of 1.0 ± 0.2 mg and dried at 80 °C in vacuum oven for 10 h. Non-aqueous Li–O $_2$ batteries were assembled in an argon-filled glove box with water and oxygen contents less than 0.5 ppm. Li foil was used as the counter electrode and polypropylene (PP) film (Celgard 2400) as the separator. The electrolyte was made from 1 M LiCF $_3$ SO $_3$ in tetraethylene glycol dimethyl ether (TEGDME).

After completing the assembly, the cells were placed in a sealed container filled with 1 atm high-purity oxygen. The cells were galvanostatically charged and discharged after 5 h rest on a battery test system (LAND-V34, Land Electronic Co., Ltd., Wuhan) at room temperature.

A rotating disk electrode (RDE, disk area of 0.196 cm^2) was used as working electrodes to characterize the catalytic activity toward the ORR and OER of the catalysts in different electrolytes. Prior to the electrochemical test, the RDE was polished with $1.0\text{ }\mu\text{m}$ alumina slurry and $0.3\text{ }\mu\text{m}$ alumina slurry to afford a mirror finish. The catalyst ink was prepared by ultrasonically mixing 3 mg of np-RuO₂/nr-MnO₂ with 475 μL of ethanol, 475 μL of deionized water, and 50 μL of 5 wt % Nafion for 1 h. Then, 20 μL suspension of np-RuO₂/nr-MnO₂ was loaded onto the glassy-carbon disk surface of RDE, resulting in a catalyst loading of 0.3 mg cm^{-2} . For comparison, a 3 mg mL^{-1} suspension of MnO₂ nanorods was obtained according to the same procedure described above, and the catalyst loading was 0.3 mg cm^{-2} . The RDE tests in 0.1 M KOH aqueous solution were executed with the graphite as counter electrode and the SCE as reference electrode. The scan rate was 10 mV/s and the O₂ gas flow was about 60 mL/min. The RDE tests in the O₂-saturated 1 M LiCF₃SO₃/TEGDME electrolyte were performed with the lithium foil as both counter electrode and reference electrode. These RDE tests in non-aqueous electrolyte were carried out in a glove box filling with oxygen, with the same scan rate and O₂ gas flow.

Chronoamperometry and linear sweep voltammetry (LSV) were employed to further investigate the catalytic activity toward the ORR and OER of the catalysts in non-aqueous electrolyte[55, 56]. The working electrode was prepared through the procedure described above. Chronoamperometry in non-aqueous O₂-saturated 0.1 M LiCF₃SO₃/TEGDME electrolyte with O₂ flow was performed with an hour at 2.25 V. Lithium foils were used as both counter electrode and reference electrode. LSV test from 2.25 V to 4.7 V at a scan rate of 0.5 mV/s was executed following the chronoamperometry.

Results and discussions

X-ray diffraction patterns illustrate the crystallinity and phase information of the products. As shown in **Figure 1**, the XRD patterns of the as-prepared MnO₂ nanorods can be indexed to a pure phase of tetragonal MnO₂ (JCPDF no. 01-081-2261; space group: P42/mnm; $a_0 = 4.4041 \text{ \AA}$, $c_0 = 2.8765 \text{ \AA}$). After the decoration of RuO₂ nanoparticles, no obvious diffraction peak for RuO₂ can be observed in the XRD pattern of np-RuO₂/nr-MnO₂. That could be owing to the small particle size of RuO₂ nanoparticles in np-RuO₂/nr-MnO₂. The weight ratio of RuO₂ in the np-RuO₂/nr-MnO₂ was determined to be 7.2 wt.% by using inductively coupled plasma optical emission spectrometer (ICP-OES). As shown in **Figure S1**, the N₂ adsorption/desorption measurement indicates that MnO₂ nanorods have a Brunauer–Emmett–Teller (BET) surface area of $12.4 \text{ m}^2 \text{ g}^{-1}$ and the BET surface area of the np-RuO₂/nr-MnO₂ is $31.9 \text{ m}^2 \text{ g}^{-1}$.

Figure 2a and **Figure 2b** display scanning electron microscopy (SEM) images with different magnification of the as-prepared MnO₂ nanorods. The SEM image in lower magnification clearly presents that the products are mainly composed of nanorods. It can be measured that the width of MnO₂ nanorods is about 100 nm to 200 nm in **Figure 2b**. **Figure 2c** and **Figure 2d** display SEM images with different magnification of np-RuO₂/nr-MnO₂. SEM image in **Figure 2c** illustrates that the morphology of MnO₂ nanorods have been well preserved in succeeding hydrothermal reaction after decoration of RuO₂. It is clearly observed from **Figure 2d** that there are not obvious agglomerations of RuO₂ nanoparticles. So it can infer that the RuO₂ nanoparticles should disperse uniformly on MnO₂ nanorods. In addition, there is plenty of void space in the np-RuO₂/nr-MnO₂ thanks to the one-dimensional structure of the MnO₂ nanorods, which could benefit the diffusion of oxygen and the storage of Li₂O₂ in discharge process of the Li-O₂ batteries.

To further observe the dispersion of RuO₂ nanoparticles on MnO₂ nanorods, transmission electron microscopy (TEM) images of MnO₂ nanorods and np-RuO₂/nr-MnO₂ are compared in **Figure 3**. As shown in **Figure 3a**, MnO₂ nanorods

have smooth surface without obvious nanoparticles on them. After the decoration of RuO₂ nanoparticles, it appears lots of nanoparticles dispersed on the MnO₂ nanorods in **Figure 3b**. There are no large agglomerates on the MnO₂ nanorods. TEM image of high magnification of the np-RuO₂/nr-MnO₂ is shown in **Figure 3c**. It illustrates that the RuO₂ nanoparticles which can be measured to be about 3-5 nm are dispersed uniformly on MnO₂ nanorods. In the HR-TEM image of np-RuO₂/nr-MnO₂ shown in **Figure 3d**, the measured d-spacing of the lattice planes inside the nanorod is ca. 0.211 nm, which can be indexed to the d-spacing of (111) planes of MnO₂. Moreover, the d-spacing of lattice planes at the edge of the nanorod is different to that inside the nanorod. The measured d-spacings of lattice planes on three places at the edge are ca. 0.201 nm, 0.225 nm and 0.221 nm, which are consistent with (210), (200) and (111) planes of RuO₂, respectively.

The charge/discharge curves at different rates of MnO₂ nanorods and np-RuO₂/nr-MnO₂ electrodes tested in Li-O₂ batteries are compared in **Figure 4a** and **Figure 4b**, respectively. The overpotential of np-RuO₂/nr-MnO₂ electrode is measured about 0.58 V at a rate of 50 mA g⁻¹. MnO₂ nanorods electrode shows an overpotential of 1.18 V in charge voltage platform that is 0.60 V higher than that of the np-RuO₂/nr-MnO₂. At a relatively higher rate of 200 mA g⁻¹, the overpotential of np-RuO₂/nr-MnO₂ electrode is increased to 0.98 V, and MnO₂ nanorods electrode also displays a higher overpotential of 1.24 V. In addition, the np-RuO₂/nr-MnO₂ electrode presents little higher discharge voltages than MnO₂ nanorods electrode, 10 mV at a rate of 50 mA g⁻¹ and 40 mV at a rate of 200 mA g⁻¹, respectively. As a consequence, these improvements in electrochemical polarization would enhance the round-trip efficiency of the Li-O₂ battery. These results demonstrate that np-RuO₂/nr-MnO₂ have a relatively higher catalytic activity than MnO₂ nanorods toward both the ORR and OER. Furthermore, the electrocatalytic activities of MnO₂ nanorods and np-RuO₂/nr-MnO₂ toward both the ORR and OER in 0.1 M KOH aqueous solution measured by using a rotating disk electrode (RDE) are compared through a rotating disk electrode (RDE). The RDE test results of two samples and empty glassy carbon electrode for the ORR at 1600 rpm are shown in **Figure 4c**. The ORR limiting

diffusion current densities of MnO₂ nanorods and np-RuO₂/nr-MnO₂ are 4.54 and 6.01 mA cm⁻², and the ORR half-wave potentials ($E_{1/2}$) of them are -0.345 and -0.158 V (vs. SCE), respectively. These values illustrate that the np-RuO₂/nr-MnO₂ can deliver higher catalytic activity towards the ORR than MnO₂ nanorods. **Figure 4d** compares the RDE test results of two samples and glassy carbon electrode for the OER at 1600 rpm. The OER limiting diffusion current densities of MnO₂ nanorods and np-RuO₂/nr-MnO₂ are 7.00 and 88.13 mA cm⁻², respectively. It can be clearly seen that the np-RuO₂/nr-MnO₂ exhibits much higher catalytic activity than MnO₂ nanorods towards the OER. Furthermore, the RDE results in the O₂-saturated 1 M LiCF₃SO₃/TEGDME electrolyte are compared in **Figure S2**[57]. The ORR apparent activity and the OER current density of np-RuO₂/nr-MnO₂ are relatively higher than that of MnO₂ nanorods in non-aqueous electrolyte. The catalytic activity of these two catalysts in non-aqueous electrolyte are further investigated by chronoamperometry and linear sweep voltammetry (LSV) [55, 56]. **Figure 4e** displays the current response of the catalysts by holding a constant potential of 2.25 V for 1 h to deposit Li₂O₂. It demonstrates that the catalytic activity of np-RuO₂/nr-MnO₂ for ORR is much higher than MnO₂ nanorods in non-aqueous electrolyte, attributing to the synergistic effect between RuO₂ nanoparticles and MnO₂ nanorods. Linear sweep voltammetry from 2.25 V to 4.7 V after the chronoamperometry was preformed to compare the OER performance of the catalysts (**Figure 4f**). The results demonstrate a much higher current response of np-RuO₂/nr-MnO₂, corresponding to that more Li₂O₂ has been oxidized. On the linear sweep voltammogram of the np-RuO₂/nr-MnO₂ two current peaks can be observed clearly; the first current peak at 3.5 V and the second one at 4 V. The first current peak at 3.5 V could be assigned to the OER catalyzed by RuO₂ nanoparticles as demonstrated by Zhou et al.[49], and the second one is quite consistent with the only peak appeared in the voltammogram of MnO₂ nanorods. These results demonstrated that np-RuO₂/nr-MnO₂ exhibits excellent bifunctional electrocatalytic activity for both the ORR and OER.

To evaluate the cycleability of np-RuO₂/nr-MnO₂ electrodes in Li-O₂ batteries, the tests were carried out by limiting the discharge capacity at different rates[31]. The

selected charge/discharge curves of the Li-O₂ battery using np-RuO₂/nr-MnO₂ as cathode at a current density of 50 mA g⁻¹ with a cut-off capacity of 500 mAh g⁻¹ is shown in **Figure 5a**. As illustrated in **Figure 5b**, the corresponding discharge capacity of the battery can be maintained till 70th cycle, and the discharge voltage decreases very slowly from 2.82 V to 2.60 V during the 75 cycles. The results indicate that the np-RuO₂/nr-MnO₂ electrode holds an excellent cycling stability with lower overpotential at a lower rate, attributing to its strong bifunctional ability to efficiently promote the formation and decomposition of Li₂O₂. As indicated in **Figure S3**, the fully discharge capacity of the np-RuO₂/nr-MnO₂ is 6787.5 mAh g⁻¹ at a rate of 200 mA g⁻¹ with the cut-off voltage range of 2.4-4.2 V. Moreover, the space between the one-dimensional structures of MnO₂ nanorods can store the discharge product (Li₂O₂). When the rate is increased to 200 mA g⁻¹ with a cut-off capacity of 4000 mAh g⁻¹, the np-RuO₂/nr-MnO₂ electrode can maintain this capacity within 20 cycles. The selected charge/discharge curves of the battery are presented in **Figure 5c** and the corresponding discharge capacity and discharge voltage are shown in **Figure 5d**. In the initial 20 cycles, there is no loss of discharge capacity of the battery and the discharge voltage decreases very slowly. After 20 cycles, the overpotential of the battery increases very fast and the battery has failed. We consider that some undecomposed discharge products with higher limiting capacity is accumulated on the electrode, which harms the electrode.

To further investigate the formation and component of the discharge products, in-situ high-energy X-ray diffraction (HEXRD) was employed to monitor the evolution of product species on electrode in discharge processes. This Li-O₂ battery was tested for 20 h at a rate of 100 mA g⁻¹. It can be clearly seen in **Figure 6** that the intensity of the peak at 2.425 to 2.45 degree is gradually increasing in discharge process, which is consistent with the d-spacing of (200) planes of Li₂O₂. It is interesting that the intensity of the peak does not increase in initial 5 h which is corresponding to the specific capacity of 500 mAh g⁻¹. It can infer that Li₂O₂ as the formative products has not developed with high crystallinity which could be easily decomposed in charge process. As a result, the battery with np-RuO₂/nr-MnO₂

electrode exhibits an excellent cycleability with a limiting capacity of 500 mAh g⁻¹. With the limiting capacity increasing, the formative Li₂O₂ can develop with higher crystallinity which is decomposed more difficultly in charge process. Hence, the battery with np-RuO₂/nr-MnO₂ electrode failed quickly after 20 cycles with a higher limiting capacity of 4000 mAh g⁻¹.

Ex-situ SEM characterization was also used to illustrate the formation and decomposition of Li₂O₂ at a high capacity. The charge/discharge curves of the first cycle of the battery using np-RuO₂/nr-MnO₂ electrode at a rate of 200 mA g⁻¹ with a limiting capacity of 4000 mAh g⁻¹ is shown in **Figure 7a**. Three parallel batteries were assembled to compare the change of the morphologies of the electrodes before discharge (b), after discharge (c) and after charge (d), respectively. SEM image of the pristine electrode in **Figure 7b** indicates that the np-RuO₂/nr-MnO₂ catalysts are dispersed uniformly on the electrode with plenty of void space between them. In **Figure 7c**, after a deep discharge process with a capacity of 4000 mAh g⁻¹, this electrode was covered by a lot of sphere species size of 2 to 3 μm on the catalysts, which may be the discharge products (Li₂O₂) as reported[7]. After the charge process, the sphere species of Li₂O₂ disappeared on the electrode as shown in **Figure 7d**, which indicates that the Li₂O₂ has been almost decomposed in initial charge process. Comparison of the XRD pattern of the pristine electrode and that of the electrode after subjected to 1 cycle test in **Figure S4** can further confirm that Li₂O₂ is decomposed almost completely after the first charge process. These results demonstrate clearly that the np-RuO₂/nr-MnO₂ can facilitate efficiently both the formation and decomposition of Li₂O₂ in charge/discharge process.

Conclusions

In summary, RuO₂ nanoparticles supported on MnO₂ nanorods were synthesized via a two-step hydrothermal reaction. Electrochemical results demonstrated that the np-RuO₂/nr-MnO₂ served as a catalyst on oxygen cathode of Li-O₂ batteries could deliver enhanced electrochemical performances than MnO₂ nanorods. Moreover,

electrochemical characterization results illustrate that np-RuO₂/nr-MnO₂ exhibits excellent bifunctional electrocatalytic activities than MnO₂ nanorods for both the ORR and OER. The results of in-situ HEXRD illustrated the formation process of Li₂O₂ at the cathode. Ex-situ SEM images demonstrated that the np-RuO₂/nr-MnO₂ could promote efficiently the formation and decomposition process of Li₂O₂ in charge/discharge process. The current study demonstrates that the rational design in nanostructure is the effective strategy for preparation of efficient bifunctional electrocatalysts as cathode of advanced Li–O₂ batteries.

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Figure 1 Comparison of XRD patterns of MnO₂ nanorods and np-RuO₂/nr-MnO₂.

Figure 2 a) b) SEM Images in different magnification of MnO₂ nanorods. c) d) SEM Images in different magnification of np-RuO₂/nr-MnO₂.

Figure 3 a) TEM image of MnO_2 nanorods. b) TEM image of $\text{np-RuO}_2/\text{nr-MnO}_2$. c) TEM image in high magnification of $\text{np-RuO}_2/\text{nr-MnO}_2$. d) HR-TEM image of $\text{np-RuO}_2/\text{nr-MnO}_2$.

Figure 4 a) Charge/discharge curves of MnO₂ nanorods and np-RuO₂/nr-MnO₂ at a rate of 50 mA g⁻¹. b) Charge/discharge curves of MnO₂ nanorods and np-RuO₂/nr-MnO₂ at a rate of 200 mA g⁻¹. c) The ORR curves of MnO₂ nanorods, np-RuO₂/nr-MnO₂ and empty glassy carbon electrode in 0.1 M KOH aq. d) The OER curves of MnO₂ nanorods, np-RuO₂/nr-MnO₂ and glassy carbon electrode in 0.1 M KOH aq. e) Chronoamperometry showing normalized current evolution with time at 2.25 V in non-aqueous O₂-saturated 0.1 M LiCF₃SO₃/TEGDME electrolyte with O₂ flow. f) Linear sweep voltammetry from 2.25 V to 4.7 V at a scan rate of 0.5 mV/s following a hold at 2.25 V for 1 h.

Figure 5 a) Charge/discharge curves of np-RuO₂/nr-MnO₂ at a rate of 50 mA g⁻¹. b) The cycle performance and terminal voltages of np-RuO₂/nr-MnO₂ in initial 75 cycles at a rate of 50 mA g⁻¹. c) Charge/discharge curves of np-RuO₂/nr-MnO₂ at a rate of 200 mA g⁻¹. d) The cycle performance and terminal voltages of np-RuO₂/nr-MnO₂ in initial 25 cycles at a rate of 200 mA g⁻¹.

Figure 6 (a) In-situ HEXRD patterns and (b) the corresponding contour plot of the electrode collected during the 1st discharge process for 20 h at 100 mA g⁻¹ together with their discharge curve.

Figure 7 a) 1st Charge/discharge curve of np-RuO₂/nr-MnO₂ with a limiting capacity of 4000 mAh g⁻¹ at a rate of 200 mA g⁻¹. b) SEM image of the pristine electrode. c) SEM image of the electrode after discharge process with a limiting capacity of 4000 mAh g⁻¹. d) SEM image of the electrode after charge process with a limiting capacity of 4000 mAh g⁻¹.

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Graphical Abstract