Realizing Formation and Decomposition of Li$_2$O$_2$ on Its Own Surface with a Highly Dispersed Catalyst for High Round-Trip Efficiency Li-O$_2$ Batteries

The decomposition of Li$_2$O$_2$ on its own surface

Decomposition sites

Li$_2$O$_2$

Electrolyte

O$_2^-$

Surface of CNT cathode with RuNCs@RCC3

HIGHLIGHTS

A novel highly dispersed electrocatalyst RuNCs@RCC3 for Li-O$_2$ batteries was designed.

Rapid formation and decomposition of large Li$_2$O$_2$ on its own surface.

Excellent electrochemical performance of RuNCs@RCC3 in Li-O$_2$ batteries.

Superior stability and durability of RuNCs@RCC3 in Li-O$_2$ batteries.

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Realizing Formation and Decomposition of Li$_2$O$_2$ on Its Own Surface with a Highly Dispersed Catalyst for High Round-Trip Efficiency Li-O$_2$ Batteries

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SUMMARY

The rapid and effective formation and decomposition of Li$_2$O$_2$ during cycling is crucial to solve the problems associated with the practical limitation of lithium-oxygen (Li-O$_2$) batteries. In this work, a highly dispersed electrocatalyst with Ru nanoclusters inside the special organic molecular cage (RuNCs@RCC3) through a reverse double-solvent method for Li-O$_2$ batteries has been proposed for the first time. This RuNCs@RCC3 shows an effective catalyst enabling reversible formation and decomposition of the Li$_2$O$_2$ at the interface between the Li$_2$O$_2$ and the liquid electrolyte, rather than the sluggish solid-solid interface reactions on commonly used solid catalysts. As a result, the Li-O$_2$ cells with RuNCs@RCC3 show enhanced electrochemical performance, including low overpotential (310 mV at a current density of 100 mA g$^{-1}$), high specific capacity (15,068 mAh g$^{-1}$), good rate capability (1,800 mAh g$^{-1}$ at a current density of 2.8 A g$^{-1}$), and especially superior cycle stability up to 470 cycles.

INTRODUCTION

Rechargeable lithium-oxygen (Li-O$_2$) batteries can provide a theoretical energy density of 3,600 Wh kg$^{-1}$, delivering five times the energy density of the state-of-the-art Li-ion batteries, which are promising for electric vehicle applications (Asadi et al., 2018; Gallant et al., 2013; Xu et al., 2017). However, there are still several serious challenges for further promoting, including the slow kinetics, large overpotential, low specific capacity, poor rate capability, and cycle stability (McCloskey et al., 2013; Yu et al., 2018; Oh et al., 2012; Yao et al., 2015). The difficulty in formation and decomposition of the discharge product (Li$_2$O$_2$) during cycling for the Li-O$_2$ system is at the heart of the problem. The specific capacity, the rate capability, the overpotential, and the cycle life are determined by the amount, the morphology, the accumulation behavior, and the formation and decomposition pathway of Li$_2$O$_2$, respectively. Previous studies have reported that these can be partially overcome by tailoring the nature of Li$_2$O$_2$. For example, Johnson et al. (2014) have proposed that high-donor-number solvents (electrolytes) can induce Li$_2$O$_2$ particle growth in solution, leading to sustained discharge and higher capacities. Aetukuri et al. (2015), Adams et al. (2013), and Mitchell et al. (2013) have elucidated that trace amounts of electrolyte additives (such as H$_2$O and CH$_3$OH), or the low current density, could facilitate the formation of Li$_2$O$_2$ toroids. Our previous studies (Xu et al., 2013, 2016) have demonstrated that use of sophisticated cathode possessing targeted properties could tailor the deposition and the morphology of Li$_2$O$_2$ and thus improve the electrochemical performance of Li-O$_2$ batteries. Although the discharge capacity and the rate capability have been effectively improved, the slow kinetics of the large insoluble Li$_2$O$_2$ decomposition during charge is still a daunting challenge, and more effort is needed. Therefore various catalysts including metal oxides (Geng and Ohno, 2015; Liu et al., 2014a, 2014b; Yilmaz et al., 2013), metal nitrides (Shui et al., 2012; Kundu et al., 2015), metal nanoparticles (Yang et al., 2014; Lin et al., 2018a, 2018b), and organometallic compounds (Ren et al., 2011; Freunberger et al., 2011) have been used for the Li$_2$O$_2$ decomposition during charge. Even if significant progress in the overpotential of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) has been achieved, there are still some serious issues concerning the usage of those solid catalysts, which need to be resolved. The insoluble Li$_2$O$_2$ particles covering the solid catalysts’ surface during discharging could lead to the degradation of the cathode due to the toxic effect on the catalyst. Especially, it would also cause voltage polarization and slow the electrochemical kinetics at the solid (Li$_2$O$_2$)-solid catalyst interface with rare reaction sites during discharge/charge (Chang et al., 2017). Studies have shown that soluble redox mediators (RMs) would be promising candidates for lowering the overpotential of ORR and OER (Sun et al., 2014; Gao et al., 2016). By tuning the formation and decomposition...
pathway of Li$_2$O$_2$ from the limited surface to the solution, the RMs significantly improve the specific capacity and reduce the overpotential of the Li-O$_2$ batteries, which can be a promising strategy to realize rapid reversible cycling of Li$_2$O$_2$ (Chen et al., 2013). However, the RMs in Li-O$_2$ batteries may have some toxic side effects, such as shuttle reactions and detrimental interactions with the Li-metal anodes of these cells. Worse still, the organic materials that are suited to serve as RMs due to C-H bonds next to O or N atoms are likely to react with the O$_2$ or O$_2^-$ formed in ORR (Park et al., 2018). Therefore, the development of highly stable soluble catalysts to efficiently catalyze Li-O$_2$ reactions, which simultaneously possess good inert nature toward Li anode and reduced oxygen species (Li$_2$O$_2$, LiO$_2$), is highly desirable but still challenging. Recently, several researches are exploring to solve these questions such as using ruthenium-based catalyst (Cai et al., 2018; Lin et al., 2016) and soluble electrocatalyst (Lin et al., 2018a, 2018b), which exhibit excellent electrochemical performance.

With these factors in mind, a highly dispersed electrocatalyst with superior catalytically active Ru nanoclusters inside the special organic molecular cage (RuNCs@RCC3) through a reverse double-solvent method for Li-O$_2$ batteries has been proposed. Also, the RuNCs@RCC3 can achieve rapid formation and decomposition (Li$_2$O$_2$) at the interface between Li$_2$O$_2$ and electrolyte. Furthermore, the as-prepared catalysts possess excellent catalytic activities, stability, and durability owing to the good confinement of Ru nanoclusters to the discrete RCC3 matrix. Consequently, the catalysts endow the batteries with outstanding performance, including relatively low charge voltage, ultrahigh specific capacity, and long cycle life.

RESULTS AND DISCUSSION

Synthesis and Characterization of the RuNCs@RCC3 Catalyst

The synthetic process and mechanism of encapsulating Ru nanoclusters (RuNCs) inside RCC3 catalysts (RuNCs@RCC3) are illustrated in Figure 1. To design a highly dispersed catalyst, the amine cage RCC3 was selected as the support because of its excellent solubility in electrolyte solvents (Hasell and Cooper, 2016; Yang et al., 2018). As shown in Figure 1A, the chiral imine cage CC3R was formed by cycloimination of 1,3,5-triformylbenzene and (1R,2R)-1,2-diaminocyclohexane and exhibited an apparent Brunauer-Emmett-Teller
surface area of ~500 m² g⁻¹ in highly crystalline form (Figure S1). Then RCC3 can be easily synthesized by reducing CC3R to the corresponding dodecaamine cage RCC3 using NaBH₄ with an yield close to 100% (Briggs and Cooper, 2017), which is further confirmed by Fourier transform infrared spectroscopy (FTIR, Figures S2 and S3), and ¹³C nuclear magnetic resonance (NMR) spectroscopy (Figures 2I, S3, and S4), mass spectrum (Figure S5), and elemental analysis (Table S1) (Liu et al., 2014a, 2014b). Figure 1B shows the synthesis and working mechanism of the RuNCs@RCC3 for Li-O₂ batteries. CH₂Cl₂ molecules were encapsulated in RCC3 cages by the reverse double-solvent approach to disperse the RuNCs@RCC3 in the electrolyte. A small amount of Ru(C₅H₇O₂)₃/CH₂Cl₂ as hydrophobic solution was slowly added into the organic cage/water dispersion; subsequently, the as-prepared NaBH₄ aqueous solution was employed to rapidly reduce the metal precursors; and the RuNCs@RCC3 was successfully prepared. The corresponding powder X-ray diffraction (PXRD) measurement is displayed in Figure S6.

The morphology of the RuNCs@RCC3 was investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). As shown in Figures 2A and S7, the stable RCC3 presents octahedron crystals with the size of ~2 µm. Similar to the RCC3, no changes in structure and composition were observed in the FESEM (Figure 2B) and TEM (Figure 2C) images and the FTIR spectra (Figure 2D) of the as-prepared RuNCs@RCC3, suggesting that the RCC3 is intact after the encapsulation of RuNCs. The PXRD pattern of RuNCs@RCC3 shows a broad peak in the range of 10°–30°, further
suggesting that the RCC3 cage is well maintained (Figure 2E). Meanwhile, no diffraction peaks of RuNCs are observed, indicating the successful formation of ultra-small well-dispersed RuNCs. As described in the N₂ adsorption-desorption isotherms (Figure 2F), desolvated RCC3 shows no porosity to N₂ owing to its collapsed structure, and as revealed in the Figure S10, the Ru nanoparticles (RuNPs)/RCC3 shows a rare nonporous characteristic, which should be ascribed to the aggregation of RuNPs on the surface of RCC3. On the contrary, the obtained RuNCs@RCC3 achieves an increased porosity to N₂, illustrating that the incorporation of RuNCs inside the pores of RCC3 contributes to the increased porosity of RCC3. In addition, X-ray photoelectron spectroscopy (XPS) was further adopted to identify the nature of the RuNCs@RCC3 surface. As shown in Figure 2G, the binding energies at 280.2 and 284.3 eV are attributed to Ru 3d₅/₂ and Ru 3d₇/₂, respectively (Chakroune and Viau, 2005; Hrbek, 1986). The binding energies at 280.9 and 281.5 eV are ascribed to the trace amounts of RuO₂, which originated from the surface oxidation of Ru in air. In addition, the peak at 284.6 eV belongs to the main C-C bond (Figure 2G). The N1s XPS spectrum shows the major existence of pyrrodic N at 398.8 eV in Figure 2H. However, the RuNCs can hardly be observed through the TEM of RuNCs@RCC3 (Figure S8) due to their ultrafine size, which is consistent with the result of energy-dispersive X-ray spectroscopy elemental mapping (Figure S9), indicating that the RuNCs were successfully embedded in the cage cavities. NMR measurement was used to study the structure of RuNCs@RCC3, particularly the spatial relationship between RCC3 and the encapsulated RuNCs (Victoria et al., 2009). The ¹³C NMR spectrum of RuNCs@RCC3 is identical to that of RCC3 (Figure S4), demonstrating the stable configuration of the RCC3 cages. On the contrary, all the peaks in the ¹H NMR spectrum of RuNCs@RCC3 (Figure 2I) are broadened compared with those of RCC3 due to the encapsulation of RuNCs. The mass spectrum of the RuNCs is not obtained because of the low intensities of the expected large number of isotope peaks, owing to the broad and continuous small particle size distribution (Figure S5). These results further prove the successful entering of RuNCs into the cage cavities.

**Electrochemical Properties and Discharging Mechanism of the RuNCs@RCC3 in Li-O₂ Cells**

Li-O₂ batteries with a carbon nanotube (CNT) (Figure S11) cathode, a lithium anode, and tetraethylene glycol dimethyl ether (TEGDME) and CH₂Cl₂ [VTEGDME:VCH₂Cl₂ = 2:1]/LiTFSI electrolyte were assembled to further study the formation and decomposition of Li₂O₂ during cycling. All results for the specific capacities and current densities are calculated based on the total carbon mass on the cathode (0.45 mg cm⁻²). The electrochemical behavior of Li-O₂ cell is shown in Figure 3. For comparison, the cells without catalyst and with RuNPs were assembled respectively. Figure 3A displays the first discharge-charge voltage profiles of the Li-O₂ cells with RuNCs@RCC3, RuNPs, and without catalyst at a current density of 100 mA g⁻¹. The discharge and charge voltages of the Li-O₂ cells can be improved with the RuNCs@RCC3 catalysts, leading to the enhancement the round-trip efficiency, which is vital for energy storage devices. The discharge voltage of the cell with RuNCs@RCC3 is obviously higher than that of RuNPs by ~123 mV and without catalyst by ~178 mV. However, the charge voltage with RuNCs@RCC3 is much lower than that with RuNPs by ~383 mV and without catalyst by ~920 mV, which is further supported by the excellent solubility of RuNCs@RCC3 in the electrolyte. The solubility tests of TEGDME, RuNCs@RCC3, and RuNPs/RCC3 in CH₂Cl₂/TEGDME at different stages are displayed in Figure 3B. Interestingly, RuNCs@RCC3 can be highly dispersed to form a transparent solution and remains unchanged even after a week. However, the as-prepared RuNPs/RCC3 catalyst is insoluble as a dark dispersion. Presumably, the RCC3 cage shell serves as an effective protector for Ru nanoclusters, preventing them from aggregations, as well as endowing them with a high dispersibility and more active sites. The excellent solubility of RuNCs@RCC3 in the electrolyte offered more exposed reaction sites for the electrochemical reactions on the cathode and Li₂O₂ surface (Figure 3C). On the contrary, only a small number of reaction sites existed on the cathode surface with RuNPs or without catalyst, showing poor electrochemical performance toward both formation and decomposition of Li₂O₂ (Figure 3C). Furthermore, benefiting from the RuNCs@RCC3, the cells exhibit high rate capacity. The discharge voltage plateau of the cells with RuNCs@RCC3 was higher than that with RuNPs or without catalyst at different current densities (Figure 3D), which is consistent with the discharge-charge voltage profiles in Figure 3A. The electrochemical impedance spectra of these three types of Li-O₂ cells were displayed in Figure S12. The interfacial resistance of the cell with RuNCs@RCC3 is lower than that with RuNPs or without catalyst, demonstrating the better rapid electron, ionic, and mass transport, as well as the improved rate capability. Furthermore, Figure 3E shows that RuNCs@RCC3 delivers a much higher discharge capacity of 15,068 mAh g⁻¹ than the cells with RuNPs and without catalyst (11,536 and 6,066 mAh g⁻¹, respectively). Meanwhile, the charge capacity for Li-O₂ cell with RuNCs@RCC3 below 4.2 V is close to the discharge...
capacity, whereas the coulombic efficiency of the cell without catalyst is only ca. 35.2%, demonstrating a significantly enhanced charging efficiency. What’s more, even at a very high current density of 1,000 mA g\(^{-1}\), the discharge capacity can still reach 2,893 mAh g\(^{-1}\) (Figure S13). The difference in the specific capacities of the cell with RuNCs@RCC3 or without catalyst might be ascribed to the different deposition behaviors and morphologies of the discharge product. And for this, the morphologies of the discharge product on the two cathodes were studied. The related FESEM images of the two discharged cathodes at different capacities of 500 and 2,000 mAh g\(^{-1}\) are displayed in Figures S14, 3F, and 3G. The discharged CNT cathode without RuNCs@RCC3 shows small disks/toroid (100–200 nm in size) morphology of the Li\(_2\)O\(_2\) at a specific capacity of 500 mAh g\(^{-1}\) (Figure S14A). With the increasing discharge capacity, the cathode surface is almost fully covered by the small disk-like Li\(_2\)O\(_2\) particles (≈200nm in size) (Figure 3F), which would execrably impede Li\(^+\), O\(_2\), and charge transfer on the cathode during subsequent discharge, resulting in severe polarization and premature finish of the discharge (Gallant et al., 2013). By contrast, on the surface of the cathode with RuNCs@RCC3, the aggregated micrometer-sized flower-like products could be clearly observed (Figure S14B, 2 μm in size, and Figure 3G, 10–20 μm in size). This obvious difference can be ascribed to the growth pathway of Li\(_2\)O\(_2\) with RuNCs@RCC3 possessing more reaction sites, which can induce more LiO\(_2\)* nucleation to generate...
large Li$_2$O$_2$, which is beneficial to maintain the active sites for ORR, and enable a high discharge specific capacity of the Li-O$_2$ cell. To definitively demonstrate the effect of the catalyst, rather than other influences such as the excess water in the electrolyte, Karl Fischer titration on the neat electrolyte, the electrolytes after the addition of RuNCS@RCC3, and the electrolyte after cell cycling was carried out (Figure S15). The results demonstrate that the water content in the electrolyte shows slight increment with the addition of RuNCS@RCC3. Even after the 20th cycle, the water content in the electrolyte with RuNCS@RCC3 is still lower than 50 ppm. Therefore, the formation of large Li$_2$O$_2$ is due to the RuNCS@RCC3 and not because of excess water in the electrolytes. Figure 3C shows the electrochemical growth mechanism of the disk-like and flower-like Li$_2$O$_2$. The ORR reaction only occurred on the surface of the cathode without RuNCS@RCC3 limited by the distribution of the active sites. As the cathode surface would gradually be covered by the insoluble Li$_2$O$_2$ particles with the continuous discharge, it is difficult to obtain the larger Li$_2$O$_2$, resulting in premature finish of the discharge process. In sharp contrast, on the cathode with RuNCS@RCC3, the ORR reaction can occur on the surface of the discharge product Li$_2$O$_2$, resulting in the continuous growth of Li$_2$O$_2$ and the eventual formation of micrometer-sized flower-like assemblies. In detail, high solubility and accessibility of the open “skeleton” create a fast pathway for highly active RuNCS “blood” to reach the surface of Li$_2$O$_2$ (Viswanathan et al., 2011): the enhanced conductivity of the outer non-stoichiometric Li$_2$O$_2$ by deposited RuNCS enables electrons to be transferred to the surface of Li$_2$O$_2$, which ensures all of the conditions for ORR reaction. As shown in Figure S16, the XRD patterns of the discharge cathodes prove that Li$_2$O$_2$ is the only crystalline product in the two cases, despite the different morphologies of the discharged product. In addition, the peak of the LiOH can hardly be observed around 2-theta angles of 20° (Figure S17), also indicating that Li$_2$O$_2$ is the only crystalline product. According to the titration experiment (Figure S18), the yield of Li$_2$O$_2$ on the surface of CNT cathodes with RuNCS@RCC3 after the first discharge to 1.5 mAh was found to be about 73.5% compared with the theoretical capacity at the current density of 200 mA g$^{-1}$, further confirming that the discharge capacity of the CNT cathode with RuNCS@RCC3 catalysts is mainly due to the formation of Li$_2$O$_2$.

Reversibility and Charging Mechanism of the RuNCS@RCC3 in Li-O$_2$ Cells

The mechanism of the Li$_2$O$_2$ decomposition process was systematically investigated by FESEM during recharging in Figure 4. Large flower-like Li$_2$O$_2$ was formed on the surface of the CNT cathode with RuNCS@RCC3 (Figure 3G) at a capacity of 2,000 mAh g$^{-1}$ and immediately begins to melt when recharging to 500 mAh g$^{-1}$ (Figure 4A); the partial flower-like Li$_2$O$_2$ crystals remain visible through the FESEM micrograph. The Li$_2$O$_2$ crystals gradually decrease in size and disappear at the end of the recharging, which is described by the FESEM images at capacities of 1,000 mAh g$^{-1}$ (Figure 4B) and 2,000 mAh g$^{-1}$ (Figure 4C). Figure 4E shows the Li$_2$O$_2$ decomposition process affected by the RuNCS@RCC3 catalyst. For the cathode with the RuNCS@RCC3, the decomposition sites were exposed both on the surface of the cathode and the flower-like Li$_2$O$_2$. Owing to the existence of plenty of decomposition sites with RuNCS@RCC3, the flower-like Li$_2$O$_2$ could be easily decomposed on the interface between the solid Li$_2$O$_2$ and the liquid electrolyte, which is completely different from the solid-solid interface reaction catalyzed by solid catalysts (Feng et al., 2013). In contrast, we found that the electron transfer merely happens at the interface of the discoid Li$_2$O$_2$ and the CNT surface (Figures 4D and 4F). This traditional catalytic mechanism shows poor electrochemical kinetics on charging, leading to higher charging voltage due to the small contact area between the insoluble Li$_2$O$_2$ particles and the solid catalyst (consistent with Figure 3A). Based on the above results, the RuNCS@RCC3 catalyst exhibits excellent superiority in terms of the improved kinetics and thermodynamics of Li$_2$O$_2$ formation and decomposition, stimulating us to investigate the cycling stability of the Li-O$_2$ batteries with RuNCS@RCC3. The battery tests were carried out according to the widely used capacity-limited cycle method. Surprisingly, the voltage obtained at the discharge terminal of the Li-O$_2$ cells with RuNCS@RCC3 is >2 V for 470 cycles; in contrast, the discharge voltages of the RuNPs and pristine CNT are down to <2 V after 315 and 288 cycles (Figure 4G). Even with a specific capacity of 5,000 mAh g$^{-1}$ at a current density 500 mA g$^{-1}$, the Li$_2$O$_2$ cells with RuNCS@RCC3 remain more than 14 cycles (Figure S19). These results demonstrate the excellent reversibility and cycle stability of the CNT cathode with the RuNCS@RCC3.

Stability of the RuNCS@RCC3 in Li-O$_2$ Cells

The stability of the catalyst upon cycling was further studied. The evolution of the morphology of the recharged cathode after the fifth and 20th cycles was examined (Figure 5). As shown in Figures 5E and 5F, the flower-like discharge products disappear after recharging and the clean surface of the whole cathode is almost fully recovered after the 20th recharge, indicating good reversibility and stability of the Li-O$_2$ cell.
with RuNCs@RCC3, whereas the thin layers with muddy parasitic products appear on the cathode surface without RuNCs@RCC3 after the fifth recharging and the thickness increases with the cycling going on (Figures 5A–5D). 1H NMR spectra show that parasitic products are lithium formate (HCO$_2$Li) and lithium acetate (CH$_3$CO$_2$Li) from the side reactions between the electrolyte and Li$_2$O$_2$ or intermediates during cycling (Figures 5G and S20). This continuous accumulation of by-products poisons the cathode surface and hinders the transmission of the intermediate, electrons, O$_2$, and Li$^+$ within the cathode, consequently leading to the death of the Li-O$_2$ cell without RuNCs@RCC3. Also, the cathode with RuNCs@RCC3 shows much less parasitic discharged products than the other two cathodes without RuNCs@RCC3 after 5 and 20 cycles. In addition, FTIR spectra (Figure S21) demonstrate that the amount of the irreversibly decomposed product deposited on the cathode with RuNCs@RCC3 is less than that on the cathode without RuNCs@RCC3 after the 20th recharging, which is consistent with the above NMR results. These results clearly illustrate the superior electrochemical stability of the RuNCs@RCC3, which may be ascribed to its inertness toward the Li metal anode and reduced oxygen species (O$_2^-$ or O$_2$) (McCloskey et al., 2013). To support this hypothesis, the RuNCs@RCC3 was physically mixed with Li metal, Li$_2$O$_2$, and KO$_2$ in the DMSO/dicyclohexyl-18-crown-6 (crown ether) for more than 30 days, forming the metastable solvated LiO$_2$ (Black et al., 2012). As shown in Figure S22, no significant change is observed in FTIR spectra after processing, indicating excellent durability and chemical stability of the RuNCs@RCC3.
Considering the superior electrochemical stability of the RuNCs@RCC3, the evolution of the morphology and crystallinity of the discharge products after the fifth and 20th cycles was also examined. Although the discharged products are mainly the disk-like Li$_2$O$_2$ on the cathode without RuNCs@RCC3 after the first discharge (Figures S14A and 3F), crystalline Li$_2$O$_2$ becomes rarely visible at the fifth cycle and disappears after the 20th cycle (Figures 6A and 6B). The degradation of the crystallinity of Li$_2$O$_2$ can be ascribed to the increasing accumulation of the by-products on the cathode surface and the presence of CO$_2$ in the electrolyte, which hinder the nucleation and recrystallization of Li$_2$O$_2$, leading to the formation of amorphous Li$_2$O$_2$ (Xu et al., 2016). The micrometer-sized, flower-like products can be clearly observed on the cathode with RuNCs@RCC3 even after 20 cycles (Figures 6C and 6D). The differences in the stability of Li$_2$O$_2$ on cycling indicate that the RuNCs@RCC3 could suppress the formation of the parasitic products during cycling, resulting in favorable rechargeability and good stability of Li-O$_2$ batteries.

**Conclusions**

In summary, a highly dispersed RuNCs@RCC3 catalyst realizing the formation and decomposition from the top of the large Li$_2$O$_2$ in Li-O$_2$ cells by a reverse double-solvent approach is fabricated. The Li-O$_2$ batteries with RuNCs@RCC3 are capable of low discharge-charge gap (310 mV at a current density of 100 mA g$^{-1}$), high specific capacity (15,068 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$), high-rate capability (1,800 mA g$^{-1}$ with the upper limit current density of 2.8 A g$^{-1}$), and long-term stability (470 cycles at a...
current density of 200 mA g\(^{-1}\)). The improved performance was attributed to the stability and durability of the catalyst with highly catalytic activity, which is vital for electrochemical catalytic reactions, including a high fraction of exposed active reaction sites, porous structure for the rapid formation and decomposition of large Li\(_2\)O\(_2\), and a soluble, stable, and durable conductive network with good electroconductivity. Furthermore, the role of the RuNCs@RCC3 as an electrocatalyst for electron transfer in the electrolyte (which differs from an RM) must also be considered. The aforementioned experimental study has opened the way to further research in such highly dispersed catalysts for Li-O\(_2\) batteries to realize practical devices.

**Limitations of the Study**

The parasitic reactions with RuNCs@RCC3 catalysts, RuNPs, and without catalyst are analyzed in detail, but the differential electrochemical mass spectroscopy (DEMS) is not available for quantitative analysis of the by-products because of the limited laboratory conditions.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.03.013.
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AUTHOR CONTRIBUTIONS
J.-J.X. and L.-N.S. developed the concept, designed the experiments, and co-wrote the manuscript. J.J.X. and L.-N.S. prepared the materials and performed the experimental measurements and experimental data analysis. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Realizing Formation and Decomposition of Li$_2$O$_2$ on Its Own Surface with a Highly Dispersed Catalyst for High Round-Trip Efficiency Li-O$_2$ Batteries

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Supplemental Figures

**Figure S1.** N\textsubscript{2} adsorption/desorption isotherms of CC3R. Porous organic cages are a unique class of microporous material composed of discrete molecules with intrinsic, guest accessible cavities (Briggs et al., 2017; Hasell et al., 2016; Liu et al., 2014). Supplemental Figure 1 shows the chiral imine cage with an apparent Brunauer–Emmett–Teller (BET) surface area of \(~500\) m\textsuperscript{2}/g, as the reduced derivative parent of RCC3 and CC3R, is formed by [4+6] cycloimination. Related to Figure 1.
Figure S2. FTIR spectra of RCC3 (without purification). FTIR measurement shows the main peaks of -CH$_2$-, -C=N-, -C=C-, -C-N- in the RCC3. The double peaks near the 3400 cm$^{-1}$ may be contributed to –NH$_2$- originating from the reactant of (1R,2R)-1,2-diaminocyclohexane. Related to Figure 1.
Figure S3. $^1$H NMR spectrum of RCC3 (without purification). $^1$H NMR (300 MHz, Chloroform-d) $\delta$ 7.31 (s, 1H), 7.13 (s,5H), 3.84 (d, $J = 14.0$ Hz, 6H), 3.57 (d, $J = 14.1$ Hz, 6H), 2.02 (d, $J = 12.4$ Hz, 7H), 1.66 (d, $J = 8.8$ Hz, 6H), 1.30 – 1.11 (m, 11H), 1.00 (s, 4H), 0.08 (s, 4H). Related to Figure 1.
Figure S4. $^{13}$C NMR spectra of RCC3, RuNCs@RCC3. The peaks of RuNCs@RCC3 are consistent with the RCC3, indicating that the encapsulation of RuNPs has no effect on the structure of RCC3. $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 141.09, 124.98, 61.18, 50.45, 31.56, 24.87. Related to Figures 1 and 2.
Figure S5. (A) FTMs + c ESI spectra of the dried RCC3 (with purification) and (B) RuNCs@RCC3. The molecular mass of the RCC3 is 1141.8886, the same as the calculated m/z of the protonated dried RCC3 1141.8892. The mass spectra for the RuNCs was not achieved because of the low intensities of the expected large number of isotope peaks due to the broad and continuous small particle size distribution. Related to Figures 1 and 2.
Figure S6. XRD patterns of RCC3 cage with CH$_2$Cl$_2$, H$_2$O, and the desolvated RCC3. As shown in these patterns, the desolvated RCC3 shows a broad band in the range of 10–30° because of the collapse of the cavities upon solvent removal. Surprisingly, the diffraction peaks of the crystalline RCC3 reappear with the addition of CH$_2$Cl$_2$ to desolvated RCC3, while such phenomenon is not observed with the addition of water, indicating that the collapsed cavities of RCC3 have great affinity to hydrophobic molecules returning to the original crystalline state. This feature helps the incorporation of metal precursors into cage cavities by the reverse double-solvents approach. Related to Figure 2.
Figure S7. FESEM image of RCC3 (with purification). Related to Figure 2.
**Figure S8.** (A) TEM of RuNCs@RCC3 with the morphology of octahedron. (B) Enlarged TEM image of RuNCs@RCC3. From the TEM image, the Ru nanoparticles were hardly observed on the surface of RCC3 due to its ultrafine size with Ru nanoclusters inside the cage cavities. Related to Figure 2.
Figure S9. FESEM image for EDS mapping of RuNCs@RCC3. According to Supplemental Figure 9, the C and N elements are the typical distribution while the Ru element is rare on the surface of RCC3, which is consistent with the TEM image. Also, countless catalytic sites are beneficial to promote the formation/decomposition of Li$_2$O$_2$ in the electrolyte during the cycling of Li-O$_2$ battery, which provides a nice electrochemical performance improvement of Li-O$_2$ battery with RuNCs/CNT cathodes. Related to Figure 2.
Figure S10. $N_2$ adsorption/desorption isotherms. $N_2$ adsorption/desorption isotherms of RuNPs/RCC3. As revealed, the RuNPs/RCC3 shows nonporous characteristics with a low surface area of 2.98 m$^2$ g$^{-1}$, which should be ascribed to the aggregation of RuNPs on the surface of RCC3. Related to Figure 2.
Figure S11. FESEM image of the pristine CNT cathode. To illustrate the role of RuNCs@RCC3 in the morphological evolution of the discharge products during discharge and charge process, CNT is selected as the cathode in the Li-O2 cells. As revealed by the FESEM results, the superior pore structure interconnected through CNT can be a key condition for tailoring the growth and the morphology of Li2O2. Related to Figure 3.
Figure S12. Electrochemical impedance spectra of the Li–O2 cells with the CNT cathodes without catalyst, with RuNPs and with RuNCs@RCC3 at pristine stage. The equivalent-circuit parameters are obtained by curve fitting using the Zview software with the equivalent circuit shown in the inset. The data points are the measured values and the solid line is the calculated impedance curve using the equivalent circuit. $R_{\text{ohm}}$ is the Ohmic resistance of the Li–O2 cell. $R_{\text{int}1}$ is the interfacial resistance between the Li anode and the electrolyte. $R_{\text{int}2}$ is the interfacial resistance between the cathode and the electrolyte. $W_1$ is the Warburg impedance arising from the Li$^+$ concentration gradients. The fitting values of $R_{\text{int}2}$ are 336, 38.56, and 28.57 $\Omega$ cm$^{-2}$ for the CNT cathodes without catalyst, with RuNPs, with RuNCs@RCC3, respectively. Related to Figure 3.
Figure S13. Rate capability measurement. Galvanostatic discharge curves of the Li-O$_2$ cells with the CNT cathodes without catalyst, with RuNPs, and with RuNCs@RCC3 at the current density of 1000 mA g$^{-1}$. Related to Figure 3.
Figure S14. (A) FESEM image of the CNT cathode without catalyst after being discharged at a current density of 200 mA g\(^{-1}\) and a specific capacity of 500 mAh g\(^{-1}\). (B) FESEM image of the CNT cathode with RuNCs@RCC3 after being discharged at a current density of 200 mA g\(^{-1}\) and a specific capacity of 500 mAh g\(^{-1}\).

At the initial stage, the discharged product on the CNT cathode without catalyst shows small discs (100–200 nm in size) morphology, which is consistent with the reported studies (Xu et al., 2016). In sharp contrast, aggregated micrometer-sized flower-like products appear on the CNT cathode with RuNCs@RCC3. This obvious difference can be ascribed to the growth pathway of Li\(_2\)O\(_2\) with RuNCs@RCC3 possessing more reaction sites which can induce more LiO\(_2^*\) nucleation to generate large Li\(_2\)O\(_2\). Related to Figure 3.
Figure S15. The related data about Karl Fischer (KF) titration of the pristine electrolyte, the pristine electrolyte with RuNCs@RCC3 and after 20th cycle of the electrolyte with the RuNCs@RCC3 catalyst, the red line represents the error relative to the average value. The corresponding resulting pictures by the instrument are also displayed. The results demonstrate that the water content in the electrolyte shows slight increment with the addition of RuNCs@RCC3. Even after the 20th cycle, the water content in electrolyte with RuNCs@RCC3 is still lower than 50 ppm. Related to Figure 3.
Figure S16. The XRD patterns of the discharged pristine CNT cathode without catalyst and the CNT cathode with RuNCs@RCC3. The spectra for standard Li$_2$O$_2$ are also shown for reference. The XRD peaks of the discharged cathodes can be assigned to Li$_2$O$_2$, although the morphologies of the discharge products are different. Related to Figure 3.
Figure S17. The XRD patterns of the pristine, discharged and recharged CNT cathode with RuNCs@RCC3 which is performed down to 2-Theta angles of 10 degrees. Related to Figure 3.
**Figure S18.** Color changes during both acid-base titration and iodometric titration. Related to Figure 3.
**Figure S19.** Electrochemical performance. Variation of voltage on the terminal of discharge of the Li-O\textsubscript{2} cells at a current density of 500 mA g\textsuperscript{-1} and a specific capacity limit of 5000 mAh g\textsuperscript{-1} with RuNCs@RCC3 catalyst. The inset represents the galvanostatic discharge curve of the Li-O\textsubscript{2} cells with RuNCs@RCC3. Related to Figure 4.
Figure S20. $^1$H NMR spectra of the pristine CNT cathodes without catalyst, with RuNPs and RuNCs@RCC3 after the first discharged. The spectra of TEGDME (tetraethylene glycol dimethyl ether), HCO$_2$Li, and CH$_3$CO$_2$Li are also shown for reference. NMR measurement further demonstrates that there are no byproducts observed for the discharged products of the CNT cathode with RuNCs@RCC3, while irreversible discharge products accumulated on the other two cathodes during cycling. Related to Figure 5.
Figure S21. FTIR spectra of the CNT cathode after different discharge–charge cycles with RuNCs@RCC3, RuNPs and without catalyst. The spectra for Li$_2$O$_2$, Li$_2$CO$_3$, HCO$_2$Li and CH$_3$CO$_2$Li are also shown for reference. Related to Figure 5.
Figure S22. FTIR spectra of RuNCs@RCC3 and RuNCs@RCC3 with KO₂. We generated metastable superoxide from the well-known reaction of KO₂ with dicyclohexyl-18-crown-6 (crown ether) and DMSO mixed solutions, which complexes the K⁺ to metathesis with a lithium salt, forming metastable solvated LiO₂ (Black et al., 2012). These results clearly demonstrate that the RuNCs@RCC3 with KO₂ has nearly the same structure as the pristine RuNCs@RCC3, showing the superior stability of RuNCs@RCC3 towards the LiO₂. Related to Figure 5.
**Supplemental Tables**

**Table S1.** Atomic mass ratios of C, H and N in RCC3. Related to Figure 2.

| Run   | Weight (mg) | C (wt.%) | H (wt.%) | N (wt.%) |
|-------|-------------|----------|----------|----------|
| 1     | 2.8040      | 72.04    | 9.310    | 13.75    |
| 2     | 2.8620      | 73.58    | 9.351    | 14.07    |
| 3     | 2.3270      | 71.78    | 9.310    | 13.62    |
| Theoretical value | | 75.72 | 9.47 | 14.72 |
Table S2. Results of acid-base titration and iodometric titration. The titration is conducted on cathodes (with separator) to quantitatively analyze the amount of both deposited products and soluble products during discharge. Related to Figure 3.

| cathode         | Specimen | 5mM Na₂S₂O₃ dosage (mL) | nLi₂O₂,t (μmol) | nLi₂O₂,e (μmol, 1.5mAh) | Y_{Li₂O₂} (%) Mean value |
|-----------------|----------|--------------------------|-----------------|-------------------------|--------------------------|
| Without catalyst| 1        | 7.92                     | 19.80           | 27.99                   | 71.4±1.4                 |
|                 | 2        | 8.10                     | 20.25           | 27.99                   |                          |
|                 | 3        | 7.98                     | 19.95           | 27.99                   |                          |
| With RuNPs      | 1        | 7.28                     | 18.20           | 27.99                   | 64.0±1.6                 |
|                 | 2        | 7.16                     | 17.90           | 27.99                   |                          |
|                 | 3        | 6.98                     | 17.65           | 27.99                   |                          |
| With RuNCs@RCC3 | 1        | 8.32                     | 20.80           | 27.99                   | 73.5±1.3                 |
|                 | 2        | 8.20                     | 20.50           | 27.99                   |                          |
|                 | 3        | 8.16                     | 20.40           | 27.99                   |                          |

Where nLi₂O₂,t is the titrated amount of Li₂O₂, and nLi₂O₂,e is the expected amount of Li₂O₂ given a 2.000 e⁻/Li₂O₂ process during discharge (18.66 μmol s⁻¹ Li₂O₂ per mAh would be expected to give a 2 e⁻/Li₂O₂ process). The obtained values are calculated with standard deviation of three replicate trials. Li₂O₂ yields (Y_{Li₂O₂}) are calculated using the following equation:

\[
Y_{Li₂O₂} = \frac{nLi₂O₂,t}{nLi₂O₂,e} \times 100\%
\]
Transparent Methods

Chemicals and Materials: All chemicals were directly used without further purification. Methanol, dichloromethane, (R,R)-1,2-diaminocyclohexane, trifluoroacetic acid, sodium borohydride, Ruthenium (III) acetylacetonate, Ruthenium chloride hydrate, Starch soluble, Sodium Thiosulfate pentahydrate, Potassium iodide, anolyte for coulometric Karl Fischer titration and Ammonium Nitrate were purchased from Aladdin Reagent, 1,3,5-triformylbenzene was purchased from Zhengzhou alpha chemical co. LTD, Ammonium Molybdate was purchased from 9 Ding Chemistry, Phenolphthalein was purchased from BeiJing Chemistry, Li$_2$CO$_3$, CH$_3$CO$_2$Li and HCO$_2$Li were purchased from Sigma-Aldrich. Li$_2$O$_2$ was purchased from Acros. CNT was purchased from Cnano Technology Limited Company. Lithiated Nafion was purchased from the DuPont Company. CP (carbon paper) was purchased from Torray. Diethylamine, ethanol, N-methyl-2-pyrrolidinone, TEGDME, LiTFSI and deuterium oxide, and deuterochloroform were purchased from Aladdin Reagent.

Synthesis of RuNCs@RCC3 by a reverse double-solvents approach: The synthesis method for the RuNCs@RCC3 was described by Yang et al. (2018) with a slight modification. In a typical synthesis, 85 mg of dried RCC3 powder was dispersed in 20 mL water and sonicated for 20 min. Then 0.02 mL Ru(C$_5$H$_7$O$_2$)$_3$/CH$_2$Cl$_2$ containing 0.01 mmol Ru$^{3+}$ solution as the hydrophobic solution was slowly added into the cage/water dispersion, and the resulting mixture was continuously stirred for 3 h. Finally, 0.5 mL of the newly prepared NaBH$_4$ (50 mg) aqueous solution was quickly added into the above mixture and kept stirring for 3 h. The obtained samples were centrifuged and washed with water and DMF, then resolved in CH$_2$Cl$_2$ subsequent with removing the solvents. The obtained solid samples were dried in air at 70 °C for 2.5 h and further used for the catalytic reactions.
Synthesis of CC3R: 10 mL CH₂Cl₂ was slowly added to 0.5 g 1,3,5-triformylbenzene labeled as A, and the (R,R)-1,2-diaminocyclohexane (0.5 g, 4.464 mmol) in the same solvent labeled as B. Then the B solution was slowly added into the A solution. Finally, 10 μL trifluoroacetic acid was directly added into the above solution for imine bond formation. The mixture solution was capped and kept for one week for successful crystallization on the edges of the vessel. Subsequently, the crystalline product was centrifuged and washed with CH₂Cl₂/CH₃OH mixture (v/v, 5/95), dried at 100 °C under vacuum overnight.

Synthesis of RCC3: The as-prepared CC3R was completely dissolved in a 25 mL CH₂Cl₂/CH₃OH mixture (v/v, 1/1), and 0.5 g NaBH₄ was added into the mixture and stirred for 15 h at room temperature followed by the addition of 1 mL distilled water, stirred for 9 h. Then the solvent was removed via rotary evaluation, washed with water and centrifuged, the final product was dried at 70 °C under vacuum overnight.

Purification of RCC3 cages: 100 mg RCC3 was dissolved in 10 mL acetone for 24 h followed by the centrifugation. The obtained product could be completely dissolved in 10 mL CH₂Cl₂/CH₃OH mixture (v/v, 1/1) by constant stirring. 0.1 mL distilled water was added and stirred for 48 h. The solvent was removed and the pure RCC3 was obtained.

Synthesis of the RuNPs-Free catalyst: The RuNPs-Free catalyst was prepared by a similar process to the Ru-NPs-Free catalyst, except for unused RCC3.

Synthesis of the RuNPs/RCC3 catalyst: The RuNPs/RCC3 catalyst was synthesized by the conventional impregnation method. 85 mg of RCC3 powder was ultrasonically dissolved in 30 mL H₂O, stirred for 20 min. Then RuCl₃.xH₂O (0.01 mmol) in 0.02 mL CH₃OH was subsequently added and stirred for 20 min
followed by the addition of 50 mg NaBH₄, stirred for 3 h, resulting in the generation of RuNPs/RCC3 catalyst.

**Electrolytes:** Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) was the preferred lithium salt for all experiments reported in this manuscript. 1 M LiTFSI in tetraethylene glycol dimethylether (TEGDME) was prepared. The water content in electrolyte is measured by KarlFischer titration.

**Preparation of RuNCs@RCC3 electrolyte:** 20 mg RuNCs@RCC3 catalyst was directly immersed into 1 mL CH₂Cl₂ with 2 mL TEGDME (1 M LiTFSI) and stirred for 2 days.

**Preparation of RuNPs/CNT cathode:** The synthesis method of RuNPs was similar to the RuNCs@RCC3 without using RCC3. Then the solid powder was mixed with 3 mL CH₂Cl₂/TEGDME (1 M LiTFSI) for comparison.

**Li-O₂ cell preparation and electrochemical measurements:** The electrochemical performance of Li-O₂ cell was tested in a 2025-type coin cell. All of the cells were assembled in a glove box under an Ar atmosphere with a lithium metal foil anode, a glass fiber separator, an oxygen cathode and an electrolyte containing 1 M LiTFSI in TEGDME. The pristine CNT cathode was prepared by coating homogenous ink composed of a mixture of 80 wt% CNT powder and 20 wt% Poly(vinylidene fluoride) onto the CP current collector. And 30 wt% RuNPs, 50 wt% CNT powder and 20 wt% Poly(vinylidene fluoride) deposited on CNT cathode was prepared in the same manner. The active material loading was 0.45 mg cm⁻². The electrochemical performances of the CNT cathodes with RuNCs@RCC3, with RuNPs, and without catalyst were tested in a specific capacity-controlled mode under various current densities. The electrochemical impedance spectroscopy of the cell was evaluated using a CHI660E electrochemical workstation within a frequency range of 10⁵ to 10⁻² Hz.
**Characterization:** The morphology and structures of the materials were characterized using various physiochemical techniques, including X-ray diffraction (XRD), $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectra (FTIR), mass spectrometry, field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The discharge and recharge products were characterized using XRD, SEM, NMR technology.

**Sample preparation procedure for NMR measurements:** The side reactions of the recharged cathode were analyzed using NMR measurements. 2025-type coin cells were disassembled in the Ar-filled glove box (H$_2$O level < 0.1 ppm, O$_2$ level < 0.1 ppm). The cathode was rinsed with pure anhydrous acetonitrile for several times to remove residual salts and/or ionic liquids, followed by a rinse with Deuterated D$_2$O (99.8%) and immediately transferred into the Nuclear magnetic tube for testing.

**Chemical Titrations:** The chemical titration processes performed in this study according to the previous study (McCloskey, et al., 2013; Qiao, et al., 2017). Here, a brief description of the procedures has been displayed. To collect the full information of soluble products, the obtained cathodes and glass fiber separators of cells without catalyst and with RuNPs were directly used without washing and evaporating procedures. Yet the cathode and glass fiber separator of the cell with RuNCs@RCC3 was immersed into CH$_2$Cl$_2$ for 5 min so as to getting rid of Ru, because Ru would catalyze the decomposition reaction of hydrogen peroxide and then caused low Li$_2$O$_2$ yields. Then the sample was taken out of the glove box, and put into a conical flask with 5.0 mL ultrapure DI-water immediately. The flask was vigorously shaken for 20 s to promote the complete reaction of Li$_2$O$_2$ with H$_2$O. The involved reaction is as follows:

$$\text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} = 2\text{LiOH} + \text{H}_2\text{O}_2$$
The whole titration process can be divided into two steps: (1) Acid-Base Titration (towards OH\(^-\)) and (2) Iodometric Titration (towards H\(_2\)O\(_2\)). For the acid-base titration, the base was titrated using a standardized 5 mM HCl solution, with the end point indicated by a drop of phenolphthalein in isopropanol. The involved reaction is as follows:

\[
\text{LiOH} + \text{HCl} = \text{LiCl} + \text{H}_2\text{O}
\]

The iodometric titration was straightly followed with the addition of three reagents into the existed solution in sequence: 1 mL 2wt% KI aqueous solution, 1 mL 3.5 M H\(_2\)SO\(_4\) solution and 50 \(\mu\)L Mo-based catalyst solution. The Mo-based catalyst solution was prepared by dissolving 0.5 g ammonium molybdate ((NH\(_4\))\(_2\)MoO\(_4\)) and 1.5 g ammonium nitrate (NH\(_4\)NO\(_3\)) into 5 mL 30 wt\% ammonia aqueous solution, then diluting to 25 mL using ultrapure DI-water. The resultant solution turned to an orange color due to the formation of I\(_2\). Then, the I\(_2\) was titrated to a faint pale yellow color by employing 5 mM Na\(_2\)S\(_2\)O\(_3\) aqueous solution. 0.5 mL 1\% starch solution was added for the precise end-point detection. The solution rapidly turned to a dark blue color and the titration was resumed till the color was completely disappeared. The involved reaction is as follows:

\[
\text{H}_2\text{O}_2 + 2\text{KI} + \text{H}_2\text{SO}_4 = \text{I}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}
\]

\[
\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}
\]

The details of analysis on original data and images of color-changes are shown in the corresponding Supplementary Information Section above (Figure S18 and Table S2).
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