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Aprotic lithium-oxygen (Li-O₂) batteries have attracted extensive attention due to their ultrahigh theoretical energy density. However, such Li-O₂ batteries still have a short cycle life due to non-conductive discharge products and severe side reactions. This work proposes a double-cathode-structured Li-O₂ battery, which can enable stable electron transfer among cathodes, RM catalysts, and Li₂O₂/O₂, solving the accumulation of products/by-products and improving Li₂O₂ reaction kinetics.

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Highlights

A novel structure of a Li-O₂ battery with double cathodes

Decoupling O₂ mass transport and electron transfer for cathodic reactions

Long-term performance at a high capacity

Performance of a Li-air battery with double cathodes employing 25% humidity

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Decoupling mass transport and electron transfer by a double-cathode structure of a Li-O_2 battery with high cyclic stability

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SUMMARY

Aprotic lithium-oxygen (Li-O₂) batteries have attracted extensive attention due to their ultrahigh theoretical energy density. However, slow and undesired electron transfer during cathodic reactions causes low cyclic stability in these batteries. Here, we demonstrate that O₂ mass transport and electron transfer for cathodic reactions in Li-O₂ batteries could be decoupled by a double-cathode structure that efficiently enables stable electron transfer between the cathode and Li₂O₂/O₂. This resolves various side reactions and slow Li₂O₂ reaction kinetics issues in conventional Li-O₂ batteries, leading to stable operation of the cell for nearly 2 months at a capacity of 0.2 and 5 mAh cm^{-2} , with more than 4- and 10-fold increases in cycle life when compared with single-cathode batteries. These remarkable improvements in the cyclic stability of Li-O₂ batteries with double cathodes provide an interesting concept for improving the operational stability of other metal-rechargeable batteries with conversion-type chemistry.

INTRODUCTION

Aprotic lithium-oxygen (Li-O2) batteries with ultrahigh theoretical energy density (\sim 3,500 Wh kg⁻¹) have attracted much attention as next-generation batteries.^{1–8} The typical structure of these batteries consists of a lithium anode, a porous cathode, and a separator wetted with a non-aqueous electrolyte.⁹ During discharge reaction processes, O₂ is reduced into Li₂O₂ with lithium ions by accepting electrons from the cathode ($2Li^+ + O_2 + 2e \rightarrow Li_2O_2$).¹⁰ However, the discharged Li_2O_2 product has low electrical conductivity and nonhomogeneous coverage on the cathode that could result in slow electron transfer between the cathode and O_{2i} ^{11–15} finally, the oxygen reduction reaction (ORR) is terminated.¹⁶ Moreover, the slow electron transfer between the cathode and Li₂O₂ limits oxygen evolution reaction (OER) kinetics (Li₂O₂ \rightarrow 2Li⁺ + O₂ + 2e) and increases the charge potential (>4.0 V) during cycling. High charge potential not only promotes the production of numerous reactive ${}^{1}O_{2}$ and related side reactions but also triggers the oxidative degradation of the electrolyte and cathode.¹⁷ Therefore, the slow electron transfer between the cathode and Li₂O₂/O₂ during the ORR and OER is the most notable challenge, causing short cycle lives that consequently restrict the fundamental development and practical application of Li-O₂ batteries.^{18–20}

Different strategies developed in efforts to solve these problems include constructing functional electrode materials, $^{21-27}$ regulating electrolyte components, $^{28-32}$ that could promote the electron transfer between the cathode and O₂/Li₂O₂ to extend the battery cycle life. For example, solid catalysts have been developed to

Context & scale

Rechargeable Li-O₂ batteries have high theoretical capacities that are 10 times more than those of the current Li-ion batteries, which could enable the driving range of an electric vehicle to be comparable to the gasoline vehicles. However, the low cycle stability of Li-O₂ batteries is one of the most severe challenges. This work proposes a double-cathode structured Li-O₂ battery, which can enable stable operation for nearly 2 months at a capacity of 0.2 and 5 mAh cm^{-2} , with more than 4- and 10-fold increases in cycle life when compared with conventional single-cathode batteries. These remarkable improvements in the cyclic stability of Li-O₂ batteries with double cathodes provides an interesting concept for improving the operational stability of other metal-rechargeable batteries with conversion-type chemistry.

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accelerate Li₂O₂ reaction kinetics.^{33–36} However, limited by the small contact area between the solid catalyst and Li₂O₂, it is difficult to enable stable electron-transfer pathways for the ORR and OER at the cathode.^{20,37,38} Furthermore, the catalytic selectivity of most solid catalysts is relatively poor, leading to undesired side reactions between the cathode and electrolyte.^{20,39,40} In this sense, supplementing soluble redox mediator (RM) catalysts as electron carriers into the electrolyte has been proposed to achieve fast electron transfer between the cathode and O_2/Li_2O_2 .^{41–46} For instance, 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) and 2,2,6,6-tetramethyl-1piperidinyloxy (TEMPO) are potential candidates utilized as ORR and OER RM catalysts, respectively.^{9,41} In principle, soluble RMs improve the energy efficiency of the battery, thanks to the stable electron transfer among O₂/Li₂O₂, RMs, and the cathode. They also simultaneously suppress the production of reactive oxygen intermediates, such as superoxide radical ($O_2^{\cdot-}$) and singlet oxygen (1O_2), thus reducing the chemical degradation of battery components and enhancing the battery stability.⁴¹ However, Li-O₂ batteries assembled with hybrid OER and ORR RM catalysts still fall short of achieving long-term cycle life. The underlying reason is that, during battery operation, the continuous accumulation of Li₂O₂ through O₂ reduction and by-products on the cathode passivates its surface, typically in the late stage of cell operation or large capacities,^{18,47} blocking electron transfer between the cathode and RMs. Therefore, the RM catalysts cannot effectively and continuously exchange electrons with the cathode, resulting in an inevitable increase in the charge overpotential. The high charging potential in turn triggers undesired electron transfer between the cathode and electrolyte, resulting in severe side reactions, especially the degradation of RM catalysts. Hence, maintaining stable and continuous electron transfer among the cathode, RM catalysts, and Li_2O_2/O_2 is critical for achieving long cycle life and high energy efficiency in Li-O₂ batteries. Unfortunately, this battery chemistry and the associated electron-transfer pathways have yet to be established.

In this work, we demonstrate a proof of concept that the O2 mass transport and electron transfer for cathodic reactions ($2Li^+ + O_2 + 2e \leftrightarrow Li_2O_2$) can be decoupled in a double-cathode structured electrode design, where the cell consists of a lithium anode, a separator, an electrolyte with RM catalysts (DBBQ and TEMPO), an inner cathode, an O_2 barrier layer, and an outer cathode (Figure 1). The functions of the O₂ barrier layer are to prevent O₂ mass transport to the inner cathode, and the solution-mediated ORR process and Li₂O₂ nucleation/storage can be realized at the outer cathode. Simultaneously, the inner cathode can realize stable electron transfer with RM catalysts. Such a structure ensures stable and continuous electron transfer between the cathode, RM catalysts, and Li₂O₂/O₂ during battery cycling, which provides a continuous driving force for Li₂O₂ reactions at low overpotentials, thereby preventing side reactions. Remarkably, it achieves more than 4- and 10-fold increases in cycle life at capacities of 0.2 and 5 mAh cm^{-2} , respectively, when compared with single-cathode batteries, enabling stable operation to approximately 2 months, a record-high value among the existing Li-O₂ batteries containing RM catalysts. This work opens a door for the fundamental development and practical use of aprotic Li-O₂ and Li-air batteries and has a key value for upgrading the operational stability of other metal-rechargeable batteries with conversion-type chemistry, such as Li-CO₂ and Li-organic positive electrodes.

RESULTS

The working principle of an aprotic Li-O₂ battery

Figure 1A shows a conventional $Li-O_2$ battery (denoted as type A), which is composed of a lithium anode, a separator with an electrolyte, and a porous cathode.

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Figure 1. Schematics and performance of the different types of Li-O₂ batteries

(A) Conventional Li-O₂ battery without a RM catalyst (type A).

(B) Single-cathode Li-O₂ battery with RM catalysts (type B).

(C) Double-cathode Li-O₂ battery with RM catalysts (type C).

(D) Full discharge-charge curves for three types of Li-O₂ batteries at a current density of 0.1 mA $\rm cm^{-2}.$

(E) The corresponding cycle number and voltage for the three types of batteries at a current density of 0.2 mA cm⁻² with a 0.1 mAh cm⁻² capacity cutoff.

(F) Voltage versus cycle number on the discharge terminal of type A (black), type B (green), and type C (orange) batteries at a current density of 0.2 mA cm⁻² in a fixed capacity mode (fixed capacity: 0.1 mAh cm^{-2}).

(G and H) Galvanostatic voltage profiles of the (G) type B and (H) type C batteries with a cutoff capacity of 5 mAh cm⁻² at a current density of 0.1 mA cm⁻². All measurements were conducted with 1 M LiTFSI, 50 mM DBBQ, and 200 mM TEMPO in TEGDME electrolyte solutions.

During cell operation, the high charge voltage caused by slow electron transfer between Li_2O_2 and the cathode usually induces side reactions involving the electrolyte and carbon electrode, resulting in the accumulation of by-products on the cathode (Scheme S1A). Therefore, the cycle life of this type of cell design is limited. In response to these problems, soluble OER and ORR RM catalysts are introduced into the Li- O_2 battery as electron-transfer carriers (denoted as type B, Figure 1B). RM catalysts can promote electron transfer between Li_2O_2 and the cathode in the solution phase, which substantially inhibits electrolyte degradation and reduces byproduct formations. However, due to cathode passivation caused by the gradual accumulation of a product and by-product after long-term cycling, RM catalysts cannot be effectively reduced/oxidized by the cathode. The charge voltage

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continues to increase, leading to intensified side reactions and battery instability in a long-term run (Scheme S1B). We, therefore, construct a double-cathode structured Li-O₂ battery (denoted as type C, Figure 1C), featuring an inner cathode and an outer cathode with an O_2 barrier layer in between with a hope to solve mass transport and electron transfer simultaneously. The inner cathode in this cell design provides a new and stable electron-transfer channel for the reduction/oxidation of RM catalysts. When the outer cathode is passivated due to the coverage of the discharge product Li₂O₂ and/or the by-product, the inner cathode can continuously exchange electrons with RM catalysts, and the activated RM catalysts immediately migrate to the outer cathode to promote solution-mediated nucleation/storage and decomposition of Li_2O_2 . Importantly, to prevent the inner cathode from being covered by Li₂O₂, an O₂ barrier layer is placed between the two cathodes. This layer acts as a membrane to block the O2 mass transport to the inner cathode (Schemes S1C and S1D). The combination of barrier layers and the inner cathode realizes the decoupling of O₂ mass transport and electron transfer at the cathode part of a double-cathode structured Li-O2 cell, which enables stable and continuous electron transfer among the cathode, RM catalysts, and Li₂O₂/O₂, and maintains low overpotential during a long cycling test.

The performance of Li-O₂ cells

First, we assembled the three types of batteries, as shown in Figures 1A-1C, and the most representative DBBQ and TEMPO molecules were selected as the ORR and OER redox catalysts. An artificial membrane close to the anode is applied to inhibit the diffusion of RM catalysts (if used) to the lithium anode (see Figure S1 and Note S1). To eliminate the influence of the inner cathode on the battery performance, the cathodes of type A and B cells are the superposition of two carbon electrodes (the inner and outer parts of a single cathode are referred to as SC-IC and SC-OC, respectively, Figures S1A and S1C). In contrast, the cathode in type C is composed of inner and outer cathodes separated by an O₂ barrier layer (the inner and outer parts of double cathodes are referred to as DC-IC and DC-OC, respectively, Figures S1B and S1D). A polypropylene film is selected as the barrier layer owing to its low surface porosity (percentage of the pore area per unit area, ~15%), pore size (\sim 250 nm), and suitable thickness (\sim 10 μ m); more detailed information is shown in Table S3. Galvanostatic discharge-charge tests were first performed with these three types of cells. As shown in Figure 1D, type B cells exhibit lower charging potentials and higher capacities than type A (without RM catalysts). Clearly, the RM catalysts promote Li₂O₂ reaction kinetics, which has been well documented previously.^{9,41} Notably, the type C battery also shows a lower overpotential with over a 3-fold increase in capacity when compared with type B. In addition, the rate capability of the type C cell at current densities of 0.1-1 mA cm⁻² is also much better than that of type B with a single cathode (Figure S2). From the cyclic voltammetry curves of type B and C cells, the redox peak currents from RM catalysts are similar (Figure S3). This verifies that the difference in the cathode structure does not affect the original redox properties of RM catalysts.

The cycle performance and overpotential of the type C cell with a capacity of 0.1 mAh cm^{-2} were further evaluated. Figure 1E shows that the charge voltage of the type C cell in the initial 120 cycles is stable and well below 3.8 V, while the charge voltages of type B and A cells increase to 4.0 V and 4.5 V after 98 cycles, respectively. This illustrates that the type C battery with double cathodes exhibits a voltage plateau and Li₂O₂ reaction kinetics superior to those of type A and B batteries. More importantly, the cycle life of type C is approximately 3 and 6 times that of type B and A, respectively, achieving 1,100 cycle numbers (approximately 2 months)



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Figure 2. Qualitative and quantitative analyses of discharge products

(A and B) Schematics and SEM images of the cathode of (A) type B and (B) type C batteries with a 5 mAh cm⁻² discharge capacity, where 1 refers to the inner cathode and 2 refers to the outer cathode (scale bar, 2 μ m).

(C) XRD pattern of the discharged cathodes in (A) and (B). SC-OC and SC-IC refer to the outer cathode and inner cathode, respectively, in a single-cathode type B battery; DC-OC and DC-IC refer to the outer cathode and inner cathode, respectively, in a double-cathode type C battery. (D) Li₂O₂ deposition quantities obtained from iodometric titration performed on discharged outer (orange) and inner (green) cathodes with a limited capacity of 5 mAh cm⁻², wherein the yield is defined as the percentage of the titrated peroxide quantity on the inner cathodes or outer cathodes to the total titration quantity. The Li₂O₂ yield of the outer cathodes is the sum of the outer cathode and O₂ barrier layer for the double-cathode Li-O₂ battery.

at a capacity of 0.1 mAh cm⁻² (Figure 1F). To further confirm our concept, we tested the cycle stability in the case of a higher areal capacity on type B and C batteries. At a capacity of 5 mAh cm⁻² (Figures 1G and 1H), the type B battery cannot completely discharge in the second cycle, and the type C battery can still cycle stably at a lower overvoltage. As a result, the double-cathode type C battery shows excellent cycle life over 1,100 h, which is much higher than that of the single-cathode type B battery (Figure S4). Clearly, it is feasible to enhance the cell cycle life with the double-cathode structure design.

Analysis of the battery performance difference

To explore the enormous difference in cell performance between type B and C batteries, we monitor the morphologies of discharge products on the two cathodes with the same capacities (5 mAh cm⁻²) by scanning electron microscopy (SEM). Pristine outer cathodes and inner cathodes are shown in Figure S5. Figure 2A shows a large number of discharge products deposited on both the inside and outside of the cathode in the type B cell (with a single cathode). In contrast, many discharge products can also be found in the outer cathode in the type C cell, but the inner cathode remains relatively clean (Figure 2B). We note that the double-cathode structure design (type C) promotes the solution-mediated ORR and Li₂O₂ nucleation/storage on the outer cathode. The X-ray diffraction (XRD) pattern reveals that the discharge products on the cathode to be Li₂O₂^{43,48} and can be reversibly decomposed after recharging (Figures 2C and S6). The difference between type B and C batteries is the absence and presence of an O₂ barrier layer between the two cathodes. Then,

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we observed the Li₂O₂ deposition on the O₂ barrier layer, as indicated in Figure S7. SEM shows that the side of the barrier layer near the outer cathode deposits a large amount of Li₂O₂, while the side near the inner cathode deposited less. This result indicates that the O₂ barrier layer can effectively prevent the O₂ mass transport to the inner cathode region. After recharging, Li₂O₂ on the O₂ barrier layer disappears, indicating that the formation and decomposition of Li₂O₂ in the double-cathode type C battery is reversible.

To further confirm the influence of the O_2 barrier layer on the storage of Li₂O₂, the quantity of Li₂O₂ deposited on the inner and outer cathodes of the two type of cells is quantitatively analyzed by iodometric titration experiments. Figure 2D shows that approximately 48% and 52% of Li₂O₂ is detected on the inner and outer cathodes, respectively, in the type B cell. In sharp contrast, only 19% of Li₂O₂ is deposited on the outer cathode and most of the Li₂O₂ (approximately 81%) is deposited on the outer cathode and on the O₂ barrier layer in the type C cell. These results demonstrate that the existence of an O₂ barrier layer can greatly block O₂ mass transport to the inner cathode, preventing the discharge product Li₂O₂ from depositing on the inner cathode can proceed stably and efficiently. Therefore, the O₂ barrier layer is the key factor to decouple the electron transfer on the inner cathode and Li₂O₂ nucleation/storage on the outer cathode.

To study the effect of the barrier layer on O_2 mass transport and deposition process of Li₂O₂ on the cathode, we used COMSOL software to simulate the quantities of transported O₂, diffused RMs, and deposited Li₂O₂ during the discharge process of type B and C cells.⁴⁹ Figures 3A and 3B show the models of the cathode structure in type B and C batteries, which are used to simulate the changes in the quantity of chemical substances (O₂, Li₂O₂, and RMs) inside the battery (see the Supplemental information and Table S3 for detailed information on the simulation data). Herein, the type B cell consists of superposed outer and inner cathodes, and the type C cell consists of an outer cathode, an O₂ barrier layer, and an inner cathode. In both type B and C cells, the initially saturated concentration of O₂ in the electrolyte is approximately 3.8 mM, and the inner and outer cathodes are flooded with electrolyte (50 mM DBBQ and 200 mM TEMPO) to reflect the real operating condition of the cell.

Figures 3C–3H show the simulated O₂, DBBQLi, and Li₂O₂ concentrations of type B and type C cells. In the type B cell, O₂ is consumed to generate Li₂O₂ on the cathode when the discharge starts. Meanwhile, a concentration gradient of O₂ is established from the outer cathode near the electrolyte/gas interface to the inner cathode (Figure 3C). After discharging to 1,000 s, the concentrations of O₂, DBBQ, and DBBQLi reach a steady state and remain constant (Figure S8). However, there is still about 0.7 mM O₂ at the deepest inner cathode region (240 μ m), indicating that the O₂ mass transport rate can keep up with the discharge current. Excess O₂ is immediately reduced in the cathode region. The simulation result in Figure 3G shows that the discharge product Li₂O₂ distributed on the inner cathode and outer cathode is comparatively even, which is consistent with the SEM observation and Li₂O₂ iodometric titration experiments in Figure 2.

In the type C cell, the simulation results show that Li_2O_2 mainly forms in the outer cathode and only a small amount in the inner cathode (Figure 3H). At the beginning of the discharge, the dissolved O_2 in the inner cathode region forms a small amount

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Figure 3. Modeling and simulation study of the discharge process on the cathode side with COMSOL software

(A and B) Schematics of the cathode structure used for the modeling study of (A) a single cathode and (B) double cathodes in type B and C batteries.

(C–H) Simulated profiles of O₂, DBBQLi, and Li₂O₂ quantities (concentrations) in Li-O₂ batteries during discharge at 0.2 mA cm⁻² for 1,000 s. (C) O₂, (E) DBBQLi, and (G) Li₂O₂ quantities of single cathodes in type B batteries, and (D) O₂, (F) DBBQLi, and (H) Li₂O₂ quantities of double cathodes in type C batteries. A depth of 0–130 μ m represents the outer cathode, and a depth of 130–240 μ m represents the inner cathode for the single-cathode battery. A depth of 0–130 μ m represents the outer cathode, and a depth of 130–240 μ m represents the inner cathode for the single-cathode battery. A depth of 0–130 μ m represents the outer cathode, 130–140 μ m represents the O₂ barrier layer, and 140–250 μ m represents the inner cathode for the double-cathode battery. The pressure of the gas diffusion layer of type B and C batteries is 1 bar.

of discharge products. Since the O_2 barrier layer has a significant effect on preventing O_2 transport to the inner cathode, the O_2 concentration gradient between the inner and outer cathode becomes higher and higher as the ORR reaction progresses (Figure 3D). When the discharging time reaches 680 s, the O_2 concentration in the inner cathode region is close to 0 mM; therefore, the ORR mainly occurs in the outer cathode region after 680 s.

The O_2 barrier layer prevents the deposition of the discharge product on the inner cathode to a large extent. The relatively clean inner cathode ensures efficient electron transfer from/to RM catalysts. Nevertheless, the O_2 barrier layer has no

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selectivity for O_2 and the oxidized or reduced RMs. Similar to the O_2 diffusion in Figure 3D, the barrier layer is also resistant to DBBQLi diffusion (Figure 3F). However, it is worth noting that there is still about 7 mM DBBQLi that can pass through the barrier layer to maintain stable electron transfer when discharging to 1,000 s (Figure S9). Such positive results attribute to a higher concentration of RMs (50 mM DBBQ and 200 mM TEMPO is much larger than 3.8 mM O_2). A higher concentration of DBBQLi accumulates in the inner cathode during battery operation, and this high concentration gradient can provide a strong driving force for the diffusion of DBBQLi. Therefore, enough DBBQLi can penetrate the O_2 barrier layer, thereby ensuring that a sufficient quantity of DBBQLi on the outer cathode participates in the chemical reduction reaction of O_2 .

To further verify the results of the experiment, we used H-type cells to conduct a simple penetration experiment on O_2 and DBBQ (Figures S10 and S11). The results show that the O_2 barrier layer can effectively prevent O_2 transport from left to right. After 12 h, the O_2 concentration in the right chamber was only 0.9 mg/L, much lower than that in the left chamber (~8.1 mg/L) (Table S1). This confirms the blocking effect of the O_2 barrier layer (surface porosity of 15%, denoted as SP 15%) in the type C cell inhibiting O_2 transport to the inner cathode. For the DBBQ penetration experiment (Figure S11), the DBBQ concentration in the left chamber was 50 mM. After 12 h, the solution in the right bottle turned yellowish, indicating that DBBQ can penetrate through the O_2 barrier layer. Quantitative analysis (Figure S12; Table S2) showed that the concentration of DBBQ was 10.9 mM. Such a concentration difference indicates that the quantities of RM catalysts are more than sufficient to reduce O_2 and decompose Li₂ O_2 under these conditions.

To simulate the true state of the battery during operation, we further simulated the subsequent Li_2O_2 accumulation when the outer cathode was passivated to different levels in type C cells (Figure S13). The results show that the subsequent Li_2O_2 still deposits on the outer cathode at different passivation levels, which further proves the stable and continuous electron transfer with the double-cathode structure. In conclusion, the simulation results illustrate that the double-cathode type C battery changes O_2 mass transport and electron transfer during cell cycling, especially at the late stage of cell operation and large capacities, thereby fully guaranteeing efficient electron transfer between RM catalysts and the inner cathode.

Side reactions in type B and C cells

The above research results clarify that the double-cathode structure can decouple O_2 mass transport and electron transfer with the O_2 barrier layer and inner cathode, leading to stable and effective electron transfer between the cathode, RM catalysts, and Li₂ O_2/O_2 . To further evaluate the efficacy of double-cathode structure cells in enabling efficient electron transfer, we used differential electrochemical mass spectrometry (DEMS) to analyze the quantity of O_2 consumption and production during discharge and charge. In Figure 4A, the type B cell has lower discharge potentials, with a $2e^{-7}/O_2$ rate of 1.09 during the discharge process. It indicates that undesired electron transfer occurs between the cathode and electrolyte, which can be ascribed to side reactions induced by oxygen intermediates (Scheme 1A).^{43,50,51} In contrast, the discharge potentials of a double-cathode type C cell are stable, and the $2e^{-7}/O_2$ rate is closer to 1 (1.02), indicating that the double-cathode structure can promote stable and effective electron transfer and avoid side reactions (Figure 4C; Scheme 1B).

During cell recharge, the type B cell exhibits higher charging potentials with a ratio of $2e^{-}/O_2$ to be 1.08 (Figure 4B), showing that significant side reactions occur on the

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Figure 4. The O_2 consumption/evolution profiles measured by DEMS in single-cathode and double-cathode Li- O_2 batteries

(A–D) DEMS analysis of the Li-O₂ battery. (A and B) Type B battery. (C and D) Type C battery. O₂ consumption (A and C) during discharge at 2 mA cm⁻² and O₂ evolution (B and D) during charge at 1 mA cm⁻² in a fixed capacity mode (fixed capacity: 2 mAh cm⁻²). OCV refers to open circuit voltage; SC refers to the single-cathode type B battery; SP refers to the surface porosity of the O₂ barrier layer; DC-SP15% refers to the double-cathode type C battery with the SP15% O₂ barrier layer.

cathode side during the decomposition of Li₂O₂. The RM catalyst cannot be effectively activated due to limited electron exchange with the passivated cathode, resulting in an increase in the charge voltage, which triggers a series of side reactions (Scheme 1A). The charging curves of the type C cell are relatively stable with a $2e^{-}/O_2$ rate close to 1 (1.01), indicating that there are minimum side reactions in the type C cell (Figure 4D). When the outer cathode cannot stably and continuously transfer electrons owing to Li₂O₂ coverage, the clean inner cathode accepts electrons from the RM catalysts, which reduces the charging potentials (Scheme 1B). The extremely low $2e^{-}/O_2$ rate is due to the double-cathode structure, which decouples Li₂O₂ nucleation/storage and electron transfer at space scale, makes electron transfer fluid among the RM catalysts, cathode, and O₂/Li₂O₂, and enhances Li₂O₂ reaction kinetics. As a result, side reactions due to undesired electron transfer are inhibited.

To further confirm the positive benefits of using double-cathode structures to inhibit side reactions, we characterized inner and outer cathode morphologies for type B and C cells after 170 cycles. Figures 5A and 5D show the original morphology of the outer and inner cathodes, respectively. After cycling, a thick passivation layer on the carbon electrode surface in type B cells can be clearly observed (Figures 5B and 5E). The existence of a passivation layer makes it difficult to realize the stable and continuous electron-transfer process between the cathode and RM catalysts, resulting in early cell failure. For the type C cell, the inner and outer cathodes are still smooth and clean after 170 cycles (Figures 5C and 5F). This is because the inner cathode can continuously activate the RM catalysts to promote the nucleation/storage and decomposition of Li₂O₂ on the outer cathode, thereby reducing charging potentials and associated side reactions. We then further analyzed compositions at the electrode surface by Raman spectroscopy. After the same number of cycles, undecomposed Li_2O_2 and typical by-products, such as CH₃COOLi and Li_2CO_3 , were detected on both the inner and outer cathodes of type B cells (Figure 5G). In contrast, no product/by-product peaks were detected on the inner and outer cathodes in type C cells. In addition, we also analyzed the inner and outer cathodes in the case of high areal capacity (5 mAh cm^{-2}). The SEM results show that a large amount

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Scheme 1. Schematics of the working mechanism in single-cathode and double-cathode $\rm Li-O_2$ batteries

(A and B) Type B battery with a single cathode (A) during discharge (left) and charge (right). Type C battery with a double cathode (B) during discharge (left) and charge (right). ORR and OER refer to oxygen reduction reaction and oxygen evolution reaction, respectively. RM refers to redox mediator.

of undecomposed products and by-products accumulates on the inner and outer cathodes in the single-cathode battery (Figure S14). In contrast, the cathode of the double-cathode battery is relatively clean. The situation is similar to that of Li- O_2 batteries cycling at low capacity (0.2 mAh cm⁻²) after 170 cycles. Whether in a long-term cycle or large-capacity cycle, the side reactions are severe in a conventional Li- O_2 battery. A great difference in the cathode morphology reveals the reason why the single-cathode type B battery cannot completely discharge in the second cycle, but the double-cathode type C battery can operate stably.

We also monitor the morphologies of single cathodes and double cathodes in type B and C cells after 1, 100, 150, and 170 cycles. By SEM observations, it can be clearly seen that some of the products/by-products gradually accumulate on the inner and outer cathodes in type B cells (Figure S15). In contrast, the surfaces of the inner and outer cathodes in type C cells are clean (Figure S16). In addition, Raman spectra further confirm that the species on the inner and outer cathodes in type B cells are CH₃COOLi, Li₂CO₃, and undecomposed Li₂O₂. However, the corresponding substances cannot be detected on the electrode of type C cells (Figures S17 and S18). This further proves that double-cathode structured batteries can inhibit side reactions by enabling the stable and effective electron transfer among the cathode, RM catalysts, and Li₂O₂/O₂ during cycling.

To verify the stable state of inner and outer electrodes after cycling, we removed and cleaned the inner and outer cathodes of type B and C batteries after different cycle numbers (1, 100, 150, and 170) and reassembled the cell with RM catalysts (without O_2). By analyzing the cyclic voltammetry curves of DBBQ redox molecules on electrodes, the electron-transfer ability between the electrode and RM catalysts was verified. As shown in Figures 5H and 5I, when the numbers of cycles experienced by the cathodes of the type B cell increase, its redox peak current values gradually decrease. This indicates that the products/by-products gradually accumulate on

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Figure 5. Morphological composition and electrochemical analysis

(A–F) SEM images of the outer and inner cathodes (scale bar, 200 nm). (A) Outer and (D) inner cathodes made of pristine. (B and E) The cathodes in a type B battery with a single cathode and (C and F) those in a type C battery with double cathodes after 170 cycles at a current density of 0.2 mA cm^{-2} in fixed capacity mode (fixed capacity: 0.2 mAh cm⁻²).

(G) Raman spectroscopy of the outer and inner cathodes after 170 cycles in (B, C, E, and F). (H and I) CV curves of 10 mM DBBQ within 1 M LiTFSI/TEGDME in a Li-C battery at 2 mV s⁻¹ under an argon atmosphere. The positive electrodes come from the cathodes of (H) type B and (I) type C batteries after 1 (green), 100 (dark gray), 150 (dark cyan), and 170 (orange) cycles at a current density of 0.2 mA cm⁻² in fixed capacity mode (fixed capacity: 0.2 mAh cm⁻²). SC refers to the single-cathode type B battery; SP refers to the surface porosity of the O₂ barrier layer; DC-SP15% refers to the double-cathode type C battery with the SP15% O₂ barrier layer.

the surface of the inner and outer cathodes of the type B cell as the cycles progress, resulting in a decrease in the electrochemically active area. In sharp contrast, the cyclic voltammetry peak current values from the type C cell remain constant, showing that the electrochemically active areas of the inner and outer cathodes in the type C cell are stable. No accumulation of products/by-products is found on the surface of the double cathodes in the type C cell. This further proves the much-enhanced activation ability of the double-cathode structure for RM catalysts. DEMS analysis was further performed to clarify this point. The cathodes of the type B cell after 150 cycles show low voltage on discharge and high voltage on charge, indicating that the accumulated products from side reactions on the electrode surface affect the formation and decomposition of Li_2O_2 . The ratios of $2e^-/O_2$ during discharge and charge of type B cells are 1.23 and 1.22, respectively, which are much greater than 1.00 (Figure S19). After 170 cycles in type C cells, the overpotentials for Li₂O₂ formation and decomposition reactions are still small, and the charge voltages are maintained at ~4.0 V (Figure S20). The 2e⁻/ O_2 ratios of type C (1.09 during discharge and 1.07 during charge) are much lower than those of type B.

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Figure 6. Morphology of O₂ barrier layers with different surface porosities and their effect on battery stability

(A–C) SEM images of O₂ barrier layers with different surface porosities (scale bar, 1 μ m). Surface porosity (SP) values of (A) 80%, (B) 50%, and (C) 15%.

(D) Full discharge-charge curves of single-cathode type B batteries (green) and double-cathode type C batteries with SPs of 80% (blue), 50% (dark cyan), and 15% (orange) at a current density of 0.1 mA cm^{-2} . SC and DC refer to the single-cathode type B battery and the double-cathode type C battery, respectively.

(E) Voltage versus cycle number on the discharge terminal of type B and C batteries at a current density of 0.2 mA cm⁻² in a fixed capacity mode (fixed capacity: 0.2 mAh cm⁻²).

(F) Li₂O₂ quantities obtained from iodometric titration experiments performed on the discharged outer (dark colors) and inner (light colors) cathodes, wherein the yield is defined as the percentage of the titrated peroxide quantity on the inner or outer cathodes to the total titration quantity. (G) Voltage versus cycle number on the discharge terminal of the single-cathode (green) and double-cathode (orange) Li-air batteries with an air humidity of 25% at 0.2 mA cm⁻² of current density in fixed capacity mode (fixed capacity: 0.2 mAh cm⁻²).

Influence of O₂ membrane surface porosity on battery performance

According to the abovementioned results, the O_2 membrane has a decisive effect on battery performance by decoupling O_2 mass transport and electron transfer. To further study the mechanism of the O_2 barrier layer on battery cycle stability, we investigate the influence of O_2 membrane surface porosity on battery performance. To obtain barrier layers with different surface porosities, a polypropylene film was treated with Harrick plasma at different time intervals. O_2 barrier layers with different surface porosities (Figures 6A–6C) were assembled. As shown in Figure 6D, when the surface porosities are 80%, 50%, and 15% in type C cells, the discharge capacities reach 10.5, 13.8, and 20.8 mAh cm⁻², respectively, indicating that the cell capacity is highly related to O_2 membrane surface porosity. Figure 6E shows the cycle stability of type C cells containing an O_2 barrier layer with different surface porosities. As the surface porosity of the O_2 barrier layer decreases, the cycle life of the battery is substantially extended as well. To analyze the above process, we further used iodometric titrations to quantitatively analyze Li₂ O_2 deposits on the inner and outer cathodes of the type C cell (Figure 6F). When the O_2 membrane surface porosity is 80%,

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50%, and 15%, the ratios of deposited Li₂O₂ on the outer/inner cathode are 57%/ 43%, 66%/34%, and 81%/19%, respectively. Notably, when the surface porosity of the O₂ barrier layer is only 15%, the quantity of Li₂O₂ deposited on the inner cathode is the lowest (19%) with the longest cycle life (684 cycles compared with 171 cycles of the type B battery). Obviously, using an O₂ membrane with low surface porosity could ensure the maximum decoupling of Li₂O₂ nucleation/storage and electron transfer, which is significant for extending the cycle life of cells.

Furthermore, we used COMSOL software to simulate O2 mass transport and the quantity of deposited Li₂O₂ during the discharge process of type C cells containing O_2 membranes with different surface porosities. As the O_2 membrane surface porosity decreases, the O₂ concentration difference between the inner cathode and the outer cathode gradually increases, implying that the surface porosity of the O_2 membrane can adjust the rate and level of O_2 transport to the inner cathode (Figure S21). Correspondingly, from a simple O_2 permeability experiment, as the surface porosity of the O₂ membrane decreases, the transport rate and quantity of O₂ from left to right can be significantly reduced. This also reflects changes in O₂ barrier effects of membranes with different surface porosities on the inner cathode in type C cells (Figure S10). Similarly, the diffusion simulation of DBBQLi and the permeability experiment of DBBQ also illustrate the inter-relationship between surface porosity and diffusion rate, which is consistent with O2 barrier transport rate trends (Figures S11, S22, and S23). The simulated quantities of deposited Li₂O₂ on the inner cathode also decrease as the surface porosities decrease, which matches the iodometric titration results (Figure S24). We then tested type C cells with surface porosities of 80% and 50% by operating them for 170 cycles. A passivation film is observed on the electrode after cycling, and the thickness of the passivation film increases with increasing surface porosity (Figures 5, S25, and S26). This shows that surface porosity regulation for the O₂ barrier layer has a definite effect on ensuring the electron-transfer ability of the inner cathode.

The above results confirm that a Li-O₂ battery with a double-cathode structure is significant for improving the battery capacity and cycle stability. O₂ membranes with low surface porosity can prevent O₂ transport to the inner cathode and protect the ability of the inner cathode to transfer electrons to activate RM catalysts. Then, the activated RM catalysts migrate to the outer cathode to promote the reaction rate and stability of Li₂O₂ formation and decomposition. This innovative cell structure design ensures efficient activation of liquid RM catalysts and reduces charging potentials through new electron-transfer channels. Therefore, undesired electron transfer is reduced, and cell cycle life is improved. To further verify the application of double-cathode structured type C cells in a relatively practical process, we tested them in air atmosphere with a humidity of 25%. As shown in Figure 6G, the cycle life of a lithium-air (Li-air) battery with a double-cathode structure reaches 486 cycles, which is 4 times that of type B cells. This further confirms the key role of the double-cathode structure in Li-O₂ and Li-air batteries.

DISCUSSION

In summary, to address short cycle life in Li-O₂ batteries due to non-conductive discharge products and severe side reactions, we propose that O₂ mass transport and cathodic electron-transfer reactions could be decoupled at space scale in a double-cathode structured battery. This structure can continuously and effectively enable stable electron transfer among the cathode, RM catalysts, and Li₂O₂/O₂, solve the accumulation of products/by-products, and improve Li₂O₂ reaction

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kinetics. As a result, double-cathode Li-O₂ batteries exhibit superior cycle life compared with single-cathode batteries. The current problems of double-cathode-structured Li-O₂ batteries mainly come from the degradation reaction of RM catalysts on the lithium anode, causing deactivation of the RM catalysts in the later stage of battery cycling. However, these issues can be resolved by developing efficient membrane materials. Therefore, we strongly believe that decoupling mass transport and electron transfer within double-cathode structures represents an important advancement in the fundamental development and practical application of these batteries. In future studies, this innovative cell design could provide important reference values for upgrading the operational stability of other metal-rechargeable batteries whose discharge products are non-conductive and insoluble.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Yong Zhao (zhaoyong@henu.edu.cn).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The datasets generated in this study are available from the lead contact on reasonable request.

Materials and methods

Materials preparation

Anhydrous tetraethylene glycol dimethyl ether (TEGDME), diethylene glycol dimethyl ether (DME), and lithium bis(trifluoromethane)sulfonimide (LiTFSI) were purchased from Suzhou Dodochem, China. The water content was below 20 ppm for solvents and 40 ppm for Li salts. Then, 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) was purchased from Aladdin, China. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) was purchased from Macklin, China. Carbon nano-membranes (CNMs) were purchased from NanoTechLabs Inc. (NTL-12211), United States. Glass microfiber filters (GFs) were purchased from Whatman (GF/C, 1822), Britain. Polypropylene (PP) membranes were purchased from Celgard (2500), United States. Carbon nano-tubes (CNTs) were obtained from Tianjin Aiweixin, China. All materials for battery assembly were stored in an Ar-filled glove box.

Electrochemical cyclic voltammetry

Cyclic voltammetry (CV) tests of lithium-carbon (Li-C) cells were performed using Metrohm Autolab. The measurements were carried out at room temperature (25°C) under an argon atmosphere. Carbon electrodes were used as the working electrodes. Metallic lithium was employed as both reference and counter electrodes.

Li-O₂ cell assembly

Li-O₂ batteries were assembled in an Ar-filled glove box. The outer cathode was prepared through conventional methods with powder CNTs. In detail, 90 wt % of CNTs and 10 wt % of poly(vinylidene fluoride) (PVDF) in methyl-2-pyrrolidone (NMP) were mixed homogeneously and then coated on the stainless steel substrate (1 cm²). Subsequently, the electrodes were heated at 110°C for 10 h under vacuum. The loading mass of CNTs was controlled at 0.45 \pm 0.1 mg cm⁻². The O₂ barrier layer was from

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the PP membrane treated with Harrick plasma (model: PDC-32G-2). After plasma treatment for 0, 5, and 10 min, O₂ barrier layers with surface porosities of 15%, 50%, and 80% can be obtained, respectively. The surface porosity and thickness of the O_2 barrier layer were measured and calculated by analysis of surface pore area using a scanning electron microscope. The inner cathode was CNM with a diameter of 1.6 cm, and the part outside the circle was 0.2 cm wide and 0.5 cm long. The O₂ barrier layer was employed to separate the outer and inner cathode, and they were wetted with an electrolyte containing RMs (30 µL). The electrolyte was prepared by mixing LiTFSI (1 M), DBBQ (0.05 M), TEMPO (0.2 M), and TEGDME in an Ar-filled glove box. During the cell assembly process, the anode and cathode were separated by a PSS-Li/GO-Li/GF membrane and a glass fiber separator infiltrated with an electrolyte containing RMs. To protect the lithium anode, the PSS-Li/GO-Li/GF membrane is placed between the lithium anode and the glass fiber separator. The detailed procedure for synthesizing the PSS-Li/GO-Li/GF membrane has been described in our previous reports.⁵² For the Li- O_2 with double cathodes, the electrolyte was dropped into the glass fiber on the surface of the PSS-Li/GO-Li/GF membrane by pipetting with a solution dosage of 60 µL. To keep the experimental conditions consistent, 90 µL of an electrolyte containing RMs was dropped on the glass fiber in the Li-O₂ battery with a single cathode. All the batteries were tested at room temperature (30°C) with a potential range of 2.0–4.9 V. Li-O₂ batteries were measured at a gas mixture of O_2/Ar (4/1, v/v) in a sealed chamber. Li-air batteries were measured under air atmosphere with 25% of the humidity under realistic conditions. A gas pressure of 1 bar is applied in the Li-O₂ and Li-air batteries.

Physical characterization

To investigate discharge products on the cathodes, the batteries were disassembled in an Ar-filled glove box, and the cathodes were washed with glycol DME three times. Then, the electrode was dried for further characterization. The X-ray diffraction (XRD) test was conducted with a powder XRD system using Cu K α radiation (D8-ADVANCE, Bruker, Germany). The electrode morphology was observed using a field emission scanning electron microscope (Gemini500, Carl Zeiss, Germany). Raman spectra were recorded with a Renishaw inVia spectrometer (10 mW, 532 nm).

Chemical titration

The discharged cathodes were disassembled in an Ar glove box and cleaned with DME solvents. Then, bases formed on the cathodes were titrated with a standard 0.005 M HCl solution (phenolphthalein was used as the end-point indicator). After finishing titration, three reagents were added to the existing solution in turn: 1 mL of 2 wt % Kl in H₂O, 1 mL of 3.5 M H₂SO₄, and 50 μ L of a molybdate-based catalyst solution. The peroxide solution color turned yellow upon adding a reagent due to I₂ formation, and I₂ is immediately titrated to a faint straw color using 0.005 M NaS₂O₃. At this point, ~0.5 mL of a 1% starch indicator was added to the solution, and the color turned dark blue. The titration was continuously operated until the solution turned transparent. The Li₂O₂ yield is defined as the percentage of titrated peroxide quantities on the inner cathodes or outer cathodes to the total titration quantity. The Li₂O₂ yield of outer cathodes is the sum of the outer cathode and the O₂ barrier layer in the Li-O₂ batteries with double cathodes. Detailed procedures for titration of Li₂O₂ are described in previous reports.⁵³

UV-vis analysis

UV-vis absorption spectra were recorded with a UV-visible near infrared spectrophotometer (PE Lambda 950) with a wavelength range of 200–800 nm. TEGDME



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electrolytes containing 50 mM DBBQ were used as the original solution. After maintaining a static state for 1 and 12 h, the permeated solution in the right bottle was diluted with TEGDME (1:20). Then, UV absorption spectra were recorded.

Differential electrochemical mass spectrometry

A differential electrochemical mass spectrometry (DEMS) system was built in-house based on a commercial quadrupole mass spectrometer (Hiden HPR-40) with a turbomolecular pump (Edwards EXT75DX). The DEMS cell had a customized Swagelok design with two PEEK (polyetheretherketone) capillary tubes as a purge gas inlet and outlet. The cell assembly was carried out in an Ar glove box. For DEMS testing, a mixture gas of O₂/Ar (4/1, v/v) with a flux of 0.5 mL min⁻¹ controlled using a digital flow meter (Bronkhorst) was used. During the discharge process, the cells were discharged at a current density of 2 mA cm⁻² with a cutoff capacity of 2 mAh cm⁻². During the charging process, pure Ar with a flux of 0.5 mL min⁻¹ was used as the carrier gas, and the cells were charged at a current density of 1 mA cm⁻².

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.joule. 2022.01.003.

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AUTHOR CONTRIBUTIONS

Q.H. and Y.Z. developed the concept. Q.H. and W.G. designed the experiment. Q.H., W.G., X.H., X.L., X.Z., and T.B. carried out the electrochemical and physical characterizations. Q.H., T.L., J.L., Y.Z., and L.J. discussed the results and co-wrote the paper. All of the authors discussed the results and reviewed the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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