Reversible LiOH chemistry in Li-O₂ batteries with free-standing Ag/ δ -MnO₂ nanoflower cathode

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ABSTRACT The low energy efficiency and poor cycle stability arising from the high aggressivity of discharge products toward organic electrolytes limit the practical applications of Li-O₂ batteries (LOBs). Compared with the typical discharge product Li₂O₂, LiOH shows better chemical and electrochemical stability. In this study, a free-standing cathode composed of hydrangea-like δ -MnO₂ with Ag nanoparticles (NPs) embedded in carbon paper (CP) (Ag/ δ -MnO₂@CP) is fabricated and used as the catalyst for the reversible formation and decomposition of LiOH. The possible discharge mechanism is investigated by *in situ* Raman measurement and density functional theory calculation. Results confirm that δ -MnO₂ dominantly catalyzes the conversion reaction of discharge intermediate LiO₂^{*} to LiOH and that Ag particles promote its catalytic ability. In the presence of Ag/ δ -MnO₂@CP cathode, the LOB exhibits enhanced specific capacity and a high discharge voltage plateau under humid O₂ atmosphere. At a current density of 200 mA g⁻¹, the LOB with the Ag/ δ -MnO₂@CP cathode presents an overpotential of 0.5 V and an ultra-long cycle life of 867 cycles with a limited specific capacity of 500 mA h g⁻¹. This work provides a fresh view on the role of solid catalysts in LOBs and promotes the development of LOBs based on LiOH discharge product for practical applications.

Keywords: Li-O₂ batteries, Ag nanoparticles, δ -MnO₂, reversible LiOH, *in situ* Raman

INTRODUCTION

The growing demand in electric vehicles and consumer electronics calls for high-energy-density batteries as an alternative to the prevailing Li-ion batteries (LIBs) [1–4]. Rechargeable aprotic Li-O₂ batteries (LOBs) are a promising option because of their ultra-high theoretical energy density [5]. Traditional LOBs achieve energy conversion based on the overall reaction of $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$; the corresponding reaction kinetics is sluggish, and the discharge product Li₂O₂ is highly aggressive toward the electrolyte and the cathode, leading to high polarization and poor cycle stability [6,7]. Hence, enormous efforts

have been devoted to investigating efficient catalysts, chemically stable electrolytes and additives [8–11].

Recent studies have shown that changing the discharge product from Li₂O₂ to LiOH can mitigate side reactions from active oxygen species and improve the energy efficiency of LOBs [12,13]. Moreover, traditional LOBs are discharged and charged in a strictly dry O₂-filled atmosphere [14–16], making the large-scale application difficult. In response, several researchers have exerted substantial efforts to explore various electrolyte additives and catalysts for LOBs to tune the formation and decomposition of LiOH as the discharge product. In these studies, water or other electrolyte additives in the electrolyte usually dominate the formation of LiOH. For example, Grey's group [17] found that LiOH can serve as the reversible discharge product during the cycling process with a LiI redox mediator (RM). The high specific capacities, ultra-low charge voltage platform of 3.0 V, and long-term cycle lifespan can be achieved. However, RMs such as LiI show an inevitable shuttle behavior in the electrochemical process, which consumes the RM⁺ and accelerates the decay of Li anode [18]. Adding the cation additive of sodium ions into the electrolyte has been recently proposed by Amine's group [19]; they found that LiOH can be reversible at a low charge voltage of 3.4 V under the competing solvation environment. Understanding the formation and decomposition mechanisms of LiOH is challenging owing to the complex reaction process dominated by electrolyte additives [20].

Therefore, solid catalysts for LOBs must be designed to catalyze the formation and decomposition of LiOH, which have been demonstrated with the nanoparticles (NPs) of Ru/ γ -MnO₂ [21], Mn-metal-organic framework-74@carbon nanotubes (Mn-MOF-74@CNTs) [22] and Co₃O₄ [20]. Mn-based catalysts are widely applied in LOBs because of their advantages, such as low cost and good intrinsic catalytic activity [23–26], regardless if the discharge product is Li₂O₂ or LiOH. δ -MnO₂ exhibits a layered crystalline structure, and some small cations (e.g., K⁺, H⁺) and molecules (e.g., H₂O) are located in the interlayer spaces [24], establishing the foundation for catalyzing the formation of LiOH. Meanwhile, embedding noble metal particles or clusters in the transition metal oxides is efficient to boost the catalytic effect synergistically [27,28]. Moreover, designing a free-stand-

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ing three-dimensional (3D) porous structure plays a key role in improving the catalytic ability and avoiding side reactions caused by the carbon substrate or polymer binder [29,30].

In this study, a free-standing cathode composed of hydrangea-like δ - MnO_2 loaded with Ag NPs embedded in carbon paper ($\text{Ag}/\delta\text{-MnO}_2\text{@CP}$) was designed and fabricated. The free-standing O_2 cathode with composite catalysts can induce the formation of flake-like LiOH during the discharge process. The porous structure provides abundant active sites and spaces for the growth of flake-like LiOH. Ag NPs embedded in δ - MnO_2 exhibit a positive effect on adsorbing H_2O molecules. LOBs with the $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ cathode show good rate capacity at selected humid O_2 atmosphere (relative humidity (RH) 2.5%). Moreover, LOBs with the $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ cathode present an ultra-long cycle life of 867 cycles at a current density of 200 mA g^{-1} with a specific capacity of 500 mA h g^{-1} . Scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results at different states during a deep discharge/charge process were obtained to reveal the formation and decomposition process of flake-like LiOH. Importantly, *in situ* Raman experiment and density functional theory (DFT) calculation were carried out to analyze the formation mechanism of LiOH. The obtained free-standing cathode provides an alternative choice for high-performance LOBs.

EXPERIMENTAL SECTION

Fabrication of electrode materials

$\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ was fabricated by *in situ* growth of Ag NPs and hydrangea-like $\delta\text{-MnO}_2$ on CP *via* a one-step hydrothermal method. First, CP was cut into $2.8\text{ cm} \times 4\text{ cm}$ pieces and then immersed into a 100-mL Teflon-lined stainless autoclave with 50 mL of concentrated nitric acid (HNO_3) solution (69 wt%). Superficial impurities of CPs were removed after maintaining the autoclave at 120°C for 1.0 h. They were rinsed with deionized (DI) water and ethanol, and then dried at 60°C for 12 h. Second, 3.3 mg of manganese(II) sulfate monohydrate ($\text{MnSO}_4\cdot\text{H}_2\text{O}$) and 23.4 mg of potassium permanganate (KMnO_4) were dissolved completely in 40 mL of DI water to form a precursor solution. After a piece of CP was soaked into the precursor solution for 20 min with stirring, 1 mL of solution containing 2 mg of silver nitrate (AgNO_3) was added into the above solution slowly and stirred for 20 min to thoroughly mix the two solutions. The hydrothermal reaction was carried out at 140°C for 6 h. Finally, $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ was acquired by washing with DI water and ethanol at least three times followed by drying at 60°C for 10 h. Then, oblong CP was cut into rounded electrodes of 14 mm in diameter, and the total mass of each $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ electrode was in the range of 0.3–0.5 mg. The fabrication process of $\delta\text{-MnO}_2\text{@CP}$ was the same as that of the above product but without the addition of AgNO_3 solution. $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ -200, 300, and 400 were obtained by calcining $\text{Ag}/\delta\text{-MnO}_2$ at 200, 300, and 400°C , respectively, under Ar atmosphere for 1 h at a ramp rate of 2°C min^{-1} . LOBs with Ketjenblack (KB) and Ag powder catalysts were adopted as the control groups. The total loading mass of them was approximately 0.4–0.6 mg. The cathode of Ag powder was prepared by mixing Ag powder, KB, and poly(vinyl difluoride) at a weight ratio of 3:6:1 into *N*-methyl-2-pyrrolidone (NMP). The slurries were casted on CPs with a diameter of 14 mm and then dried at 80°C under vacuum for 12 h.

Characterization

The crystal phases of the above samples and discharge products were characterized by XRD patterns collected on a Rigaku Miniflex 600 powder diffractometer at scan rates of 5° and 2° min^{-1} , respectively. Superficial element composition and valence states were analyzed through XPS (AXIS SUPRA). The morphologies of the $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ electrodes at different states were observed using field-emission SEM (FE-SEM, Hitachi SU-70). The microstructure and specific crystal structure were investigated using high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100). The ratio of Ag in Ag/MnO_2 composites was determined *via* inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 725). The electron structure changes in $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ and $\delta\text{-MnO}_2\text{@CP}$ were characterized using Raman spectroscopy on a Renishaw InVia Reflex (532 nm laser). The generation and disappearance of the intermediate and final products during the cycling process were also recorded by *in situ* Raman spectroscopy (633 nm laser). The power of the laser light was 1.7 mW.

DFT calculations

DFT calculations were conducted through the Vienna *ab initio* Simulation Package (VASP) with the projector augmented wave method. Generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) functional was used as the exchange-correlation functional. The cutoff energy was set as 500 eV, and structure relaxation was performed until the convergence criteria of energy and force reached $1 \times 10^{-4}\text{ eV}$ and $0.03\text{ eV \AA}^{-1}$, respectively. The Brillouin zone was sampled with a Kmesh-resolved value of $0.04\text{ 2PI \AA}^{-1}$. A vacuum layer of $15\text{ \AA}$ was constructed to eliminate interactions between periodic structures of surface models. The van der Waals (vdW) interaction was amended using the DFT-D3 method of Grimme. The formation energy of the interface was determined by: $E_{\text{inter}} = (E_{\text{A|B}} - E_{\text{A}} - E_{\text{B}})/S$, where E_{inter} , $E_{\text{A|B}}$, E_{A} and E_{B} represent the formation energy of the interface, the total energy of A|B, A and B, respectively. The Gibbs free energy for the intermediates of the formation of LiOH or Li_2O_2 was calculated as $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S$, where ΔE , ΔE_{ZPE} , and ΔS are the electronic energy, zero-point energy, and entropy difference between the products and the reactants. The zero-point energies of the isolated and adsorbed molecules were calculated from the frequency analysis. The entropies of molecules in the gas phase were obtained from the National Institute of Standards and Technology (NIST) database.

Electrochemical measurements

A total of 2032 coin-type LOBs were assembled in an argon-filled glove box ($\text{H}_2\text{O} < 0.1\text{ ppm}$, $\text{O}_2 < 0.1\text{ ppm}$) using free-standing $\text{Ag}/\delta\text{-MnO}_2\text{@CP}$ or $\delta\text{-MnO}_2\text{@CP}$ cathodes, glass fiber separators (Whatman GF/D), and lithium foil anodes with 1 mol L^{-1} lithium bis(trifluoromethane) sulfonamide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) as the electrolyte. The H_2O content in the electrolyte was $\sim 46\text{ ppm}$, as measured using a Karl Fisher coulometer (AKF-1 plus) with a sample volume of 10 mL of electrolyte. The electrolyte volume for each cell was 150 μL , and all coin cells were placed in a sealed box filled with O_2 and rested for 8 h before testing. Specific capacity and cycle performance were conducted on a LAND testing system. Cyclic voltammetry (CV) was performed on a CHI 660e electrochemical workstation (Chenhua, Shanghai).

over the voltage window of 2.0–4.4 V at 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed on an Autolab (Metrohm) within the frequency range of 0.01–100 kHz. As shown in Fig. S1, the electrochemical performances of LOBs in humid O₂ atmosphere with different levels of moisture were measured using a home-made equipment. The corresponding RH in the O₂ atmosphere was controlled *via* a precise COS-03-X USB thermohydrometer.

RESULTS AND DISCUSSION

The Ag/ δ -MnO₂ catalyst was grown directly on the CP by using a one-step hydrothermal method. Fig. S2a shows the XRD patterns of Ag/ δ -MnO₂@CP and δ -MnO₂@CP. The characteristic peaks at 12.5°, 25.2° and 37.3° can be ascribed to the (001), (002) and ($\bar{1}11$) lattice planes of δ -MnO₂ (PDF#80-1098). The characteristic peaks of Ag/ δ -MnO₂@CP possess lower intensity than δ -MnO₂@CP, indicating that the addition of Ag has an effect on tuning the grain size of δ -MnO₂. Peaks of Ag cannot be detected because of the high background peaks of CP and its low content or nanoscale particle size [31]. Fig. S2b shows the Raman spectra of the above samples. The peaks at approximately 566 and 645 cm⁻¹ can be assigned to the Mn–O–Mn stretching vibration in the [MnO₆] octahedral lattice and symmetric Mn–O stretching modes of the [MnO₆] group, respectively [32]. The red shift in Ag/ δ -MnO₂@CP demonstrates the interaction between Ag and δ -MnO₂, corresponding to the intensity change of XRD peaks, which also introduces local distortions into the steady crystal structure and thus provides more catalytic sites [33]. XPS was used to investigate the chemical structure differences between the two samples (Fig. S2c, d). XPS spectra of Ag 3d present that Ag exists in two forms. The peaks at approximately 368.3 and 374.3 eV result from the metallic Ag, whereas the peaks at approximately 367.8 and 373.7 eV should be referred to Ag⁺ [34,35]. In the XPS spectra of O 1s, the peaks at approximately 529.9, 531.1 and 532.7 eV are related to the anhydrous lattice oxygen (Mn–O–Mn), hydrated group (–OH), and adsorbed H₂O molecule, respectively [36,37]. The larger ratio of the hydrated groups and adsorbed H₂O molecules in Ag/ δ -MnO₂@CP than that in δ -MnO₂@CP (21.91% *vs.* 19.15%) indicates that the incorporation of Ag increases the affinity of δ -MnO₂ toward them.

The detailed morphologies and microstructures of free-standing Ag-loaded hydrangea-like δ -MnO₂ can be observed from the SEM and TEM images. Fig. 1a shows that hydrangea-like Ag/ δ -MnO₂ distributes uniformly on CP fibers without any apparent Ag NPs, indicating that Ag is very small, which is consistent with the XRD result. The uniform coverage of Ag/ δ -MnO₂ is beneficial to improving the charge process with reduced carbonate side reaction products [38]. The SEM image in Fig. 1b presents clear distributions of hydrangea-like Ag/ δ -MnO₂. The following energy dispersive X-ray spectroscopy (EDS) mapping results of O, Mn and Ag provide evidence for the existence of Ag on δ -MnO₂. ICP result shows that the ratio of Ag in Ag/MnO₂ composites is 6.17 wt%. The 3D porous structure provides adequate spaces for discharge products. Moreover, δ -MnO₂ possesses a layered stacking structure consisting of edge-sharing MnO₆ octahedra in the layers (Fig. 1c), which provides active sites and space for oxygen reduction reaction/oxygen evolution reaction (ORR/OER). Meanwhile, some small cations (K⁺, H⁺) and molecules (such as H₂O) can be located in the interlayer gaps [39,40]. As presented in Fig. 1d, the boundary is unclear

and the thickness of Ag/ δ -MnO₂ is supposed to be approximately 1.2 μ m because of the limited penetrating power of the electron beam and thick CP fiber background. Fig. 1e shows that MnO₂ has a thin-sheet structure with Ag NPs embedded firmly even after the sonication. The compact structure plays an important role in synergistical catalysis in the discharging and charging processes. Two diffraction lattice fringes can be clearly observed in Fig. 1f, which further prove the crystal structure of the Ag NP-loaded δ -MnO₂. The sheet-like structure of δ -MnO₂ at the magnified image of the inset area shows regular and uniform lattice fringes. Its profiled result indicates that the lattice spacing is approximately 0.23 nm (Fig. 1h), which corresponds to the (111) crystal plane of δ -MnO₂. Selected area electron diffraction (SAED) patterns of Ag NPs in Fig. 1g and SAED patterns of δ -MnO₂ in Fig. S3 further confirm the successful fabrication of the composite catalyst Ag/ δ -MnO₂. The diffraction rings of Ag NPs can be assigned to the crystal planes of (422), (420), (400), (222), (311), (220), (211) and (111), consistent with the standard PDF card of Ag (PDF#04-0783).

The initial typical discharge and charge profiles of several relative control cathodes were studied, including KB, Ag/ δ -MnO₂@CP, δ -MnO₂@CP, and Ag powder. As shown in Fig. 2a, the Ag/ δ -MnO₂@CP cathode leads to the highest specific capacity (~4570 mA h g⁻¹) compared with other cathodes. In specific, the discharge platform is relatively high (~2.85 V). Without Ag, δ -MnO₂@CP shows a specific capacity of approximately 2740 mA h g⁻¹, indicating that the Ag/ δ -MnO₂@CP cathode provides more active sites. KB and Ag powder cathodes exhibit low specific capacities of ~2910 and 1650 mA h g⁻¹, respectively. The XRD patterns in Fig. 2b reveal that LiOH is the only discharge product of Ag/ δ -MnO₂@CP and δ -MnO₂@CP (PDF#32-0564). With the same electrolyte and under the same measurement environment, KB and Ag powder cathodes lead to Li₂O₂ as the discharge product (PDF#73-1640). This result suggests that δ -MnO₂ is the key factor for generating LiOH as the discharge product, whereas the residual water in the electrolyte is not decisive. CV curves of the Ag/ δ -MnO₂@CP cathode in dry oxygen and Ar at a scan rate of 0.1 mV s⁻¹ were compared to verify the effects of electrochemical environments (Fig. S4). The intensities of the reduction and oxidation peaks in Ar are considerably weaker than those in O₂, suggesting the significant effect of O₂ and the critical role of δ -MnO₂.

Fig. 2c–f show the morphologies of discharge products on the KB, Ag/ δ -MnO₂@CP, δ -MnO₂@CP and Ag powder cathodes, respectively. The spherical Li₂O₂ with a diameter of ~500 nm covers the surface of the KB cathode, whereas Li₂O₂ on the surface of the Ag powder cathode exhibits a large toroid-like structure. Interestingly, the surface of Ag/ δ -MnO₂@CP exhibits a flake-like LiOH, but δ -MnO₂@CP shows a film-like LiOH. The above results reveal that the catalyst component and structure play important roles in tuning discharge products in LOBs, which agrees with the results of a previous work [3]. As shown in Fig. 2g, h, the XPS spectra of Li 1s (~55.1 eV) and O 1s (531.9 eV) of discharged Ag/ δ -MnO₂@CP match the spectra of standard LiOH, further proving that the main discharge product LiOH is formed during the discharge process. The peaks of Li 1s (~55.6 eV) and O 1s (~532.2 and 532.9 eV) indicate that small amounts of Li₂CO₃ and other by-products cover the surface of the discharged cathode, which can be ascribed to the decomposition of the electrolyte [41,42]. In addition, the optical images of the 0.1 mmol L⁻¹ KMnO₄ solution soaked with discharged KB

Figure 1 Morphological characterization of Ag/ δ -MnO₂@CP. (a, b) SEM images and the corresponding EDS mapping of O, Mn and Ag. (c) Crystal structure of δ -MnO₂. (d) TEM image of Ag/ δ -MnO₂@CP. (e) TEM image and (f) HRTEM image of Ag/ δ -MnO₂. The inset image is the magnified rectangle area. (g) SAED pattern of Ag NPs. (h) Lattice spacing profile of the magnified rectangle area in (f).

and Ag/ δ -MnO₂@CP cathodes show a sharp difference (Fig. 2i). The discharge product Li₂O₂ formed on the KB cathode causes the purple to fade quickly, but obvious purple fading is hardly observed after soaking the discharged Ag/ δ -MnO₂@CP cathode into the same solution, indicating that peroxide and superoxide barely exist.

Ex situ SEM, XRD, and XPS were conducted at selected states to understand the formation and decomposition of LiOH on the surface of Ag/ δ -MnO₂@CP during the deep discharging and charging processes (Fig. 3a). When the Ag/ δ -MnO₂@CP cathode is discharged by 30% (stage I), dense and thin LiOH flakes (~1.0 μ m in diameter, ~150 nm in thickness) grow on the surface (Fig. 3c). The corresponding XRD pattern (Fig. 3b-I) shows weak characteristic peaks of LiOH. The XPS spectrum of Li 1s (Fig. 3g-I) displays obvious LiOH peak (55.1 eV) and the XPS spectrum of Mn 2p shows strong signals (Fig. 3h-I), implying that LiOH forms on the electrode surface and the catalyst can still provide many active catalytic sites. However, the peak of Li 1s at ~55.7 eV indicates that Li₂CO₃ also forms during the

process. After full discharging (stage II), the size of LiOH flakes increases sharply, and large and thick flakes (~1.3 μ m in diameter, ~350 nm in thickness) cover the cathode surface (Fig. 2d). This result indicates that Ag/ δ -MnO₂ can effectively promote the formation and growth of LiOH. Conversely, as shown in Fig. 3b-II, the peak intensity of LiOH increases without the appearance of impurity peaks, suggesting that few side reactions are involved in the discharge process. The XPS spectra show a stronger Li 1s signal (Fig. 3g-II), and the Mn 2p signal disappears (Fig. 3h-II). This result implies that the discharge product LiOH has completely covered the surface of the Ag/ δ -MnO₂@CP cathode, which agrees with the SEM observation in Fig. 2d. The intensity of Li 1s signal at ~55.7 eV increases because of Li₂CO₃ accumulation with the further degradation of electrolyte (Fig. 3g-II).

The charge process was also studied to understand the OER ability of the Ag/ δ -MnO₂@CP cathode. As shown in Fig. 3d, when the cathode is charged by ~5%, LiOH flakes retain a similar shape but at a slightly decreased size (1.2 μ m in the diameter, ~250 nm in thickness) compared with the LiOH flakes

Figure 2 The characterization for discharge products of different cathodes. (a) The initial discharge profiles of KB, Ag/δ-MnO₂@CP, δ-MnO₂@CP and Ag powder cathodes at a current density of 200 mA g⁻¹. (b) XRD patterns of different discharged cathodes. SEM images of discharged (c) KB, (d) Ag/δ-MnO₂@CP, (e) δ-MnO₂@CP and (f) Ag powder cathodes in dry atmosphere at the current density of 200 mA g⁻¹. XPS spectra of (g) Li 1s and (h) O 1s of discharge products for Ag/δ-MnO₂@CP and standard LiOH. (i) Optical image of KB and Ag/δ-MnO₂@CP cathodes soaked in 0.1 mmol L⁻¹ KMnO₄ solution after discharge.

on the fully discharged cathode (Fig. 2d). The reduction in LiOH peak intensity further confirms that LiOH is being decomposed (Fig. 3b-III). Correspondingly, the XPS spectrum of Li 1s presents a slightly decreased signal (Fig. 3g-III) along with a weak Mn 2p signal (Fig. 3h-III). When the LOB is further charged to ~50% (stage IV), the LiOH flakes shrink dramatically (800 nm in diameter, ~200 nm in thickness) and some hydrangea-like Ag/δ-MnO₂ particles are exposed, indicating that the periphery of LiOH is catalytically decomposed first by Ag/δ-MnO₂ (Fig. 3e). Meanwhile, XRD peaks of LiOH have almost disappeared because of its decreased size and content. XPS spectra exhibit that Li 1s signal continuously decreases compared with the last stage (Fig. 3g-IV) and the signal of Mn 2p is strong (Fig. 3h-IV). When the LOB is fully charged (stage V), as shown in Fig. 3f, the surface of Ag/δ-MnO₂ is free of LiOH flakes, but a few side reaction products cover the partial area. This phenomenon could be verified by the XPS spectra of Li 1s at stage V, and the peaks at 55.7 and 56.5 eV indicate the irreversibility Li₂CO₃ and carbonate side reaction products [43]. Fortunately, the XRD pattern of the fully charged cathode retains the same state as its pristine pattern (Fig. 3b-V), and the XPS spectrum of Mn 2p shows the

strongest intensity (Fig. 3h-V), illuminating that the side reaction product is very thin or exists in an amorphous status (Fig. 3b-V). In Fig. 3h, the XPS spectra of Mn 2p show negligible changes, indicating that the catalyst can remain stable during the discharge/charge process.

Control experiments were performed to investigate whether the formation of LiOH comes from embedded H₂O molecules on the catalyst surface [44,45]. Thermogravimetric analysis (TGA) was used to characterize the weight of the covered catalyst and embedded H₂O molecules on the free-standing cathodes. As shown in Fig. 4a, two cathode materials overlap within ~150°C, and their weights do not show obvious descending (blank area), which means they possess good thermal stability until ~150°C. In the orange area, the weight of Ag/δ-MnO₂@CP increases in a small scale, which can be ascribed to the oxidation of Ag NPs. This result is also in line with the TGA curve of Ag powders in the air atmosphere (Fig. S5b). However, the weight of δ-MnO₂ begins to decrease at 300°C, indicating that embedded H₂O molecules and O atoms gradually lose. With the temperature rising (purple area), both of them lose weight because of the consumption of CP in air atmosphere. The result

Figure 3 Characterization of freestanding Ag/δ-MnO₂@CP cathode at different states during the electrochemical process. (a) Full discharge and charge profiles of LOBs with the freestanding Ag/δ-MnO₂@CP cathode at the current density of 200 mA g⁻¹. Five typical states were indicated with I–V. (b) Corresponding XRD patterns, (c–f) SEM images obtained on the Ag/δ-MnO₂@CP cathode surface at those states. (g) Li 1s XPS and (h) Mn 2p XPS spectra of the freestanding Ag/δ-MnO₂@CP cathode at different states.

shows that the mass ratio of catalysts covered on the CP is ~20 wt%. TGA curves of Ag, Ag/δ-MnO₂ and δ-MnO₂ powders in Ar atmosphere were obtained (Fig. S5a, b). The mass of Ag/δ-MnO₂ decreases more than that of δ-MnO₂ before 300°C, indicating that it possesses more adsorbed H₂O on the surface. Thereafter, Ag/δ-MnO₂@CP prepared at different temperatures was fabricated to confirm the effects of the intrinsic H₂O molecules located in the interlayer gaps. As presented in Fig. 4b, Ag/δ-MnO₂@CP can retain the same crystal phase until the calcination temperature rises to 300°C, which is consistent with the above TGA result. Ag/δ-MnO₂@CP-300 and Ag/δ-MnO₂@CP-400 were selected to conduct further investigations. The heat treatments exert no obvious effect on the morphological structure of Ag/δ-MnO₂@CP (Fig. S6a, b). Fourier transformed infrared spectroscopy (FTIR) spectra confirm that Ag/δ-MnO₂@CP-300 possesses a lower intensity of –OH groups at ~3383 cm⁻¹ than Ag/δ-MnO₂@CP, and Ag/δ-MnO₂@CP-400

possesses different bonds and the lowest content of –OH groups (Fig. 4c). Correspondingly, the Li foil of Ag/δ-MnO₂@CP-300-based cell shows a shinier surface than that of Ag/δ-MnO₂@CP (Fig. S7). The strong peak at 500 cm⁻¹ is attributed to Mn–O bending, and the peaks at ~1538 and 1411 cm⁻¹ can be ascribed to the symmetric –COO⁻ vibration with Mn ions [46,47]. Fig. 4d shows that the Ag/δ-MnO₂@CP-300 cathode still induces the formation of LiOH, which presents a film-like morphology (Fig. 4e). However, the discharge product of Ag/δ-MnO₂@CP-400 is not LiOH and shows a sphere-like structure (Fig. 4d, f). Therefore, the formation of LiOH is related to the H₂O molecules and the active sites of Ag/δ-MnO₂.

In situ Raman measurement is often used to detect the evolution of non-crystalline species (LiO₂) or other electrochemically generated products because it could offer a relatively sensitive and undisturbed probe [48–50]. Therefore, it was applied to investigate the formation and decomposition

Figure 4 The analysis of the influential factors impacting the discharge product. (a) TGA curves of Ag/δ-MnO₂@CP and δ-MnO₂@CP in air atmosphere. (b) XRD patterns of Ag/δ-MnO₂@CP and other samples treated at different temperatures. (c) FTIR spectra of Ag/δ-MnO₂@CP and Ag/δ-MnO₂@CP-300/400. (d) XRD patterns of discharged Ag/δ-MnO₂@CP-300 and Ag/δ-MnO₂@CP-400 cathodes. SEM images of discharged (e) Ag/δ-MnO₂@CP-300 cathode and (f) Ag/δ-MnO₂@CP-400 cathode.

mechanism of LiOH. The schematic of *in situ* Raman electrochemical LOB cell is shown in Fig. 5a. The cell was performed under the discharge specific capacity of 500 mA h g⁻¹ with a total time of 5 h to avoid the error resulting from the long-term electrochemical process. The corresponding discharge/charge profiles are presented in Fig. 5b. The discharge/charge curves are as usual as the 2032-type cell, and even the overpotential decreases with abundant O₂ flow. After *in situ* Raman measurement, the corresponding XRD pattern of Li foil does not present the characteristic peak of Li₂CO₃, different from the pristine Li foil, and Li foil presents a shiny surface (Fig. S8), indicating that the *in situ* Raman measurement system is independent of external environment. As shown in Fig. 5c, at the beginning of discharge, no signal peaks of intermediate products appear because of their low concentration. Moreover, the three peaks of TEGDME-based electrolyte in the range of 2800–2900 cm⁻¹ are apparent, which can be assigned to the vibration peaks of –CH₂ and –CH₃ groups [51]. After being discharged for 50 min, *in situ* Raman spectra show weak signals at approximately 1140 cm⁻¹, confirming the formation of LiO₂* on the catalyst surface [48,52]. Simultaneously, the peaks of electrolyte begin to change, indicating that the active LiO₂* is aggressive to the electrolyte. Moreover, no apparent evidence of discharge products of Li₂O₂ (~790 cm⁻¹) or LiOH (~230 cm⁻¹) is found [20], indicating that the overall reaction proceeds in a stepwise pathway. During the subsequent discharge process, the intensity of LiO₂* increases, two peaks of LiOH near ~230 cm⁻¹ appear, the peaks of electrolyte continue changing, and even the peaks of the –CH₂ group disappear. Meanwhile, some peaks in the range of 1200–1500 cm⁻¹ appear at a similar rate, corresponding to the C–H stretching vibration and C–C stretching

vibration modes [53], which should arise from the side reaction products. The peak at ~720 cm⁻¹ exhibits a decreased intensity with the discharge reaction ongoing, which suggests that a layer of discharge products covers the surface of the cathode. The peaks of Li₂O₂ at ~790 cm⁻¹ and HO₂⁻ at ~820 cm⁻¹ cannot be observed in the overall process [12]. Thus, LiOH may not be formed from Li₂O₂ via the formation of H₂O₂. Fig. 5d shows the Raman spectra during the charge process. The peaks of LiOH disappear gradually in the early charge stage. The peaks of LiO₂* and other impurity products disappear completely in the later stage (after being charged for ~100 min). Importantly, the peaks of electrolyte show a decreasing trend. Then, the spectra have hardly changed in the subsequent stage.

DFT calculations were conducted to understand the catalytic mechanism of Ag/δ-MnO₂ toward LiOH formation. As shown in Fig. S9a, the rate-determining step (RDS) for the formation of LiOH on Ag is the conversion of *LiO to *LiOH (*LiO + H⁺ + e⁻ → *LiOH) with an energy barrier of 0.12 eV. It is thermodynamically inclined to the formation of Li₂O₂ on Ag (ΔG < 0), corresponding to the discharge product Li₂O₂ on the Ag cathode (Fig. 2b). The formation energy of the Ag|Li₂O₂ interface is -1.46 eV, lower than that of Ag|LiOH (-0.62 eV), which further confirms the growth preference of Li₂O₂ on Ag (Table S1). The free energy diagram for OER on Ag also verifies that the dissociation energy of Li₂O₂ to Li (1.94 eV) is lower than that of LiOH (2.43 eV) (Fig. S9b). The result further proves that Li₂O₂ easily forms on the Ag cathode.

The free energy diagrams for ORR and OER on the surface of δ-MnO₂ are exhibited in Fig. 6a, b. As shown in Fig. 6a, the RDS of the formation of Li₂O₂ and LiOH is the conversion of *Li⁺ to *LiO₂ (*Li⁺ + O₂ → *LiO₂) with an energy barrier of 0.48 eV.

Figure 5 *In-situ* Raman characterizations. (a) *In situ* Li-O₂ cell schematic for Raman spectroscopy. (b) Discharge/charge profiles of *in situ* Li-O₂ cell with a Ag/ δ -MnO₂@CP cathode at the current density of 200 mA g⁻¹ within a limited specific capacity of 500 mA h g⁻¹. Detailed *in situ* Raman spectra of Ag/ δ -MnO₂@CP cathode during (c) discharge and (d) charge processes.

However, Fig. S10 and Table S1 show that the interface formation energy of δ -MnO₂|LiOH (-2.68 eV) is lower than that of δ -MnO₂|Li₂O₂ (-2.61 eV), illustrating that LiOH more easily grows on δ -MnO₂ than Li₂O₂. Meanwhile, the free energy diagram of OER on δ -MnO₂ shows that the dissociation energy barrier of LiOH (1.79 eV) is lower than that of Li₂O₂ (2.37 eV) (Fig. 6b). Thus, δ -MnO₂ plays a key role in the formation of LiOH, and the formation of LiOH ameliorates the discharge and recharge processes of the δ -MnO₂ cathode. Remarkably, a small amount of Ag particles embedded in δ -MnO₂ enhance the electroconductibility of Ag/ δ -MnO₂. As shown in Fig. 6c, the calculated DOS of Ag/ δ -MnO₂ is higher than that of pure δ -MnO₂ at the Fermi level, indicating that the embedded Ag particles can elevate conductivity [54]. Moreover, the charge density difference (CDD) displays that Ag and δ -MnO₂ are surrounded with cyan and yellow regions, manifesting an electron transfer from Ag to δ -MnO₂ (Fig. 6d). Meanwhile, the planar-averaged CDD of Ag/ δ -MnO₂ shows a positive CDD value on δ -MnO₂ and a negative CDD value on Ag, further evidencing that Ag loses electrons and δ -MnO₂ obtains electrons during the formation of the Ag/ δ -MnO₂ interface. Bader charge analysis demonstrates that the electron transfer from Ag to δ -MnO₂ is ~ 1.6 e (Fig. 6e). The accelerated electron transportation and low energy barrier of Ag/ δ -MnO₂ facilitate the formation and dissociation of LiOH during the discharge and recharge processes [55].

On the basis of the above discussions, a possible formation mechanism of the flake-like LiOH on the surface of the Ag/ δ -MnO₂ cathode is illustrated in Fig. 6f. The formation of LiOH relies on the H₂O content in the electrolyte, adsorbed H₂O of the catalyst, and electrolyte consumption. The specific steps are demonstrated as follows. Once the cell initializes discharging,

the Ag/ δ -MnO₂ catalyst with strong affinity to oxygen adsorbs O₂ molecules, which are subsequently reduced to O₂⁻. O₂⁻ are dissolved in the electrolyte and couple with Li⁺ to form a certain amount of LiO₂^{*}. These two steps are the same as the reactions in the process of Li₂O₂ formation [56]. Moreover, O₂⁻ seizes a proton from the electrolyte, whereas the unstable electrolyte decomposes to form H₂O and other side products (e.g., HCO₂Li and CH₃CO₂Li) in the presence of Ag/ δ -MnO₂ [57]. Finally, LiO₂^{*} can react with H⁺ from H₂O dissociation to form LiOH in the presence of the Ag/ δ -MnO₂ catalyst. Combining the above experimental results and previous studies [17], the related reactions can be described in Fig. 6g.

The above results indicate that Ag/ δ -MnO₂@CP promotes the formation and decomposition of LiOH, although it induces extra consumption of the electrolyte. Thus, the catalytic ability of Ag/ δ -MnO₂@CP at different levels of moisture must be investigated. CV measurements were carried out to help decipher the ORR and OER of LOBs with the Ag/ δ -MnO₂@CP cathode. As shown in Fig. 7a, the Ag/ δ -MnO₂@CP and δ -MnO₂@CP cathodes present two oxygen reduction peaks and one oxygen evolution peak. The reaction pathways are consistent with the above analyses. Moreover, the δ -MnO₂@CP cathode shows a stronger peak than Ag/ δ -MnO₂@CP at ~ 2.8 V, indicating that more active O₂⁻ gather at the surface of δ -MnO₂ than the Ag/ δ -MnO₂@CP cathode [22]. Subsequent reactions occur at the surface, corresponding to the surface-mediated growth mode. For LOBs with the Ag/ δ -MnO₂@CP cathode, most O₂⁻ diffuse into the electrolyte, and the final product grows *via* a solution-mediated mode [52]. The result is consistent with the above mentioned morphological structures of discharge products. The peak at ~ 2.5 V can be ascribed to the formation of the final discharge product. For OER, two cathodes present a peak at

Figure 6 DFT calculation results and possible discharge mechanism. The free energy diagrams for (a) ORR and (b) OER on δ -MnO₂. “*” indicates the surfaces of catalysts. (c) Calculated density of states (DOS) of Ag/ δ -MnO₂ and δ -MnO₂. (d) Side and top views of the CDD of Ag/ δ -MnO₂ interface with an isosurface of 2.7×10^{-3} e Å⁻³. The charge accumulation and depletions are depicted as the yellow and cyan region. (e) Planar-averaged CDD $\Delta\rho(z)$ for Ag/ δ -MnO₂ interface. (f) Schematic illustration and (g) reaction processes of the possible formation mechanism of LiOH via Ag/ δ -MnO₂@CP cathode during the discharge/charge process.

~3.2 V, but the onset potential of the Ag/ δ -MnO₂@CP cathode is lower. The higher cathodic and anodic peaks of the Ag/ δ -MnO₂@CP cathode demonstrate that Ag plays important roles in enhancing LOB reversibility [58,59].

Galvanostatic discharge/charge measurements in dry and humid atmospheres were carried out to verify the catalytic ability of the Ag/ δ -MnO₂@CP cathode toward LiOH. As shown in Fig. 7b, the specific capacity at the current density of 200 mA g⁻¹ initially increases and then decreases with increasing RH. When the RH is 2.5%, the Ag/ δ -MnO₂@CP cathode achieves the highest specific capacity of 8401 mA h g⁻¹. As shown in Fig. S11, LiOH flakes fully cover the surface of the Ag/ δ -MnO₂@CP cathode after discharging in humid O₂ atmosphere (RH 2.5%). LiOH flakes (2.2 μ m in diameter, ~400 nm in thickness) are thicker and larger than the flakes that formed in dry atmosphere (Fig. 2d, ~1.3 μ m in diameter, ~350 nm in thickness). Subsequently, the rate capacities of the Ag/ δ -

MnO₂@CP and δ -MnO₂@CP cathodes were measured at the selected current densities of 300 and 500 mA g⁻¹ under humid O₂ atmosphere (RH 2.5%) (Fig. 7c). The Ag/ δ -MnO₂@CP cathode shows the specific capacity of 8228 and 6041 mA h g⁻¹, respectively. However, the δ -MnO₂@CP cathode presents lower specific capacities of 6475, 5731 and 3886 mA h g⁻¹ at the corresponding current densities, further promoting the advantages of the Ag/ δ -MnO₂@CP cathode on catalyzing the formation and decomposition of LiOH under humid O₂ atmosphere. Details about the discharge and charge profiles are exhibited in Fig. S12. The increased capacity indicates that the Ag/ δ -MnO₂@CP cathode is a potential material to catalyze LOBs in the practically humid environment. The cycle stability of the Ag/ δ -MnO₂@CP cathode at the current density of 200 mA g⁻¹ under dry and selected humid O₂ atmosphere with RH 2.5% is displayed in Fig. 7d. When O₂ atmosphere is dry and the specific capacity is limited within 500 mA h g⁻¹, LOB shows an ultra-long cycle

Figure 7 The characterization of electrochemical performances. (a) CV curves of LOBs with the Ag/δ-MnO₂@CP and the δ-MnO₂@CP cathodes at a scan rate of 0.1 mV s⁻¹ in dry O₂ atmosphere. (b) Specific capacity of LOBs with the Ag/δ-MnO₂@CP cathode at the current density of 200 mA g⁻¹ under different levels of moisture (RH 1%, 1.5%, 2.5% and 5%). (c) Rate capacity of LOBs with the Ag/δ-MnO₂@CP and the δ-MnO₂@CP cathodes in an O₂ atmosphere with a moisture level of RH 2.5%. (d) Cycling performance of LOBs with the Ag/δ-MnO₂@CP cathode in dry and humid O₂ atmosphere (RH 2.5%) at the current density of 200 mA g⁻¹ within a specific capacity of 500 mA h g⁻¹. (e) Corresponding discharge and charge curves of LOBs with the Ag/δ-MnO₂@CP cathode at different cycles in dry O₂ atmosphere.

lifespan of 867 cycles. Meanwhile, no obvious fade of the discharge and charge terminal voltages can be observed within 600 cycles, indicating that the LOB with the Ag/δ-MnO₂@CP cathode possesses remarkable reversibility. After 600 cycles, the discharge voltage gradually reduces from ~2.6 to 2.0 V and the charge voltage increases from ~4.1 to 4.5 V, which may be caused by the accumulation of side products, corrosion of Li anode and consumption of electrolyte. Details can be observed in Fig. 7e. The first discharge platform is close to 2.96 V, and its overpotential is ~0.5 V. However, the high discharge platform fades to ~2.75 V rapidly, which may be related to the decrease in available H₂O molecules on the catalyst surface. Fortunately, the charge platform remains stable at ~4.0 V within 400 cycles. The cycling performance of LOBs with the Ag/δ-MnO₂ cathode was also measured at the current density of 400 mA g⁻¹ within a specific capacity of 1000 mA h g⁻¹ in dry atmosphere. As shown in Fig. S13, the cell only retains ~70 cycles. Correspondingly, the electrolyte would not seriously decompose at a small current density within a low specific capacity, but may be decomposed deeply and irreversibly at a large current density within a high specific capacity. Impressively, LOB presents a long cycle lifespan of 261 cycles under humid O₂ atmosphere, which is shorter than that in dry O₂ atmosphere. The charge terminal voltage is lower in early stages, which can be attributed to the effects of H₂O [21]. Simultaneously, the high H₂O content in O₂ can induce the Li anode to corrode seriously, further deteriorating the cycle performance [60,61]. Detailed discharge and charge curves at different cycles are profiled in Fig. S14. Compared with previous research where the discharge product is LiOH or other

free-standing δ-MnO₂, the electrochemical performances of LOB with the cathode, especially cycle lifespan, are still remarkable (detailed information in Table S2). Therefore, H₂O as an electrolyte additive in the presence of the Ag/δ-MnO₂ cathode for LOBs is an alternative strategy to decrease charge overpotential, but an effective method for avoiding Li corrosion is essential.

CONCLUSION

A free-standing porous Ag/δ-MnO₂@CP cathode for LOBs was fabricated *via* a facile one-step hydrothermal method. The Ag/δ-MnO₂@CP cathode can catalyze the formation and decomposition of LiOH during the discharge/charge process. In addition, a possible catalytic mechanism was investigated *via in situ* Raman spectroscopy and DFT calculation. LOBs with the Ag/δ-MnO₂@CP cathodes exhibit excellent specific capacity and rate capability in the optimized humid atmosphere. Moreover, LOBs with the Ag/δ-MnO₂@CP cathodes show an ultra-long cycle lifespan because of its good catalytic ability and the low aggressiveness of LiOH. This work provides a fresh view for investigating the role of solid catalysts in LOBs and promoting the development of practical LOBs with LiOH as the discharge product.

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- 1 Tan L, Sun Y, Wei C, *et al.* Design of robust, lithiophilic, and flexible inorganic-polymer protective layer by separator engineering enables dendrite-free lithium metal batteries with LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ cathode. *Small*, 2021, 17: 2007717

- 2 He B, Wang J, Liu J, *et al.* Superassembly of porous $\text{Fe}_{\text{tet}}(\text{NiFe})_{\text{oct}}\text{O}$ frameworks with stable octahedron and multistage structure for superior lithium-oxygen batteries. *Adv Energy Mater*, 2020, 10: 1904262
- 3 Shu C, Wang J, Long J, *et al.* Understanding the reaction chemistry during charging in aprotic lithium-oxygen batteries: Existing problems and solutions. *Adv Mater*, 2019, 31: 1804587
- 4 Song LN, Zhang W, Wang Y, *et al.* Tuning lithium-peroxide formation and decomposition routes with single-atom catalysts for lithium-oxygen batteries. *Nat Commun*, 2020, 11: 2191
- 5 Zhou Y, Yan D, Gu Q, *et al.* Implanting cation vacancies in Ni-Fe LDHs for efficient oxygen evolution reactions of lithium-oxygen batteries. *Appl Catal B-Environ*, 2021, 285: 119792
- 6 Mahne N, Schafzahl B, Leybold C, *et al.* Singlet oxygen generation as a major cause for parasitic reactions during cycling of aprotic lithium-oxygen batteries. *Nat Energy*, 2017, 2: 17036
- 7 Xiang C, Sheng W, Zhang P, *et al.* RuO_2 nanoparticles supported on Ni and N Co-doped carbon nanotubes as an efficient bifunctional electrocatalyst of lithium-oxygen battery. *Sci China Mater*, 2021, 64: 2397–2408
- 8 Petit YK, Leybold C, Mahne N, *et al.* DABCONium: An efficient and high-voltage stable singlet oxygen quencher for metal- O_2 cells. *Angew Chem Int Ed*, 2019, 58: 6535–6539
- 9 Li J, Shu C, Liu C, *et al.* Rationalizing the effect of oxygen vacancy on oxygen electrocatalysis in Li- O_2 battery. *Small*, 2020, 16: 2001812
- 10 Xu SM, Liang X, Liu X, *et al.* Surface engineering donor and acceptor sites with enhanced charge transport for low-overpotential lithium-oxygen batteries. *Energy Storage Mater*, 2020, 25: 52–61
- 11 Liu B, Xu W, Yan P, *et al.* Enhanced cycling stability of rechargeable Li- O_2 batteries using high-concentration electrolytes. *Adv Funct Mater*, 2016, 26: 605–613
- 12 Qiao Y, Wu S, Yi J, *et al.* From O_2^- to HO_2^- : Reducing by-products and overpotential in Li- O_2 batteries by water addition. *Angew Chem Int Ed*, 2017, 56: 4960–4964
- 13 Li Y, Wang X, Dong S, *et al.* Recent advances in non-aqueous electrolyte for rechargeable Li- O_2 batteries. *Adv Energy Mater*, 2016, 6: 1600751
- 14 Gao J, Cai X, Wang J, *et al.* Recent progress in hierarchically structured O_2 -cathodes for Li- O_2 batteries. *Chem Eng J*, 2018, 352: 972–995
- 15 Leng L, Zeng X, Song H, *et al.* Pd nanoparticles decorating flower-like Co_3O_4 nanowire clusters to form an efficient, carbon/binder-free cathode for Li- O_2 batteries. *J Mater Chem A*, 2015, 3: 15626–15632
- 16 Luo N, Ji GJ, Wang HF, *et al.* Process for a free-standing and stable all-metal structure for symmetrical lithium-oxygen batteries. *ACS Nano*, 2020, 14: 3281–3289
- 17 Liu T, Leskes M, Yu W, *et al.* Cycling Li- O_2 batteries via LiOH formation and decomposition. *Science*, 2015, 350: 530–533
- 18 Park JB, Lee SH, Jung HG, *et al.* Redox mediators for Li- O_2 batteries: Status and perspectives. *Adv Mater*, 2018, 30: 1704162
- 19 Bi X, Li M, Liu C, *et al.* Cation additive enabled rechargeable LiOH-based lithium-oxygen batteries. *Angew Chem Int Ed*, 2020, 59: 22978–22982
- 20 Lu J, Dey S, Temprano I, *et al.* Co_3O_4 -catalyzed LiOH chemistry in Li- O_2 batteries. *ACS Energy Lett*, 2020, 5: 3681–3691
- 21 Li F, Wu S, Li D, *et al.* The water catalysis at oxygen cathodes of lithium-oxygen cells. *Nat Commun*, 2015, 6: 7843
- 22 Zhang X, Dong P, Lee JL, *et al.* Enhanced cycling performance of rechargeable Li- O_2 batteries via LiOH formation and decomposition using high-performance MOF-74@CNTs hybrid catalysts. *Energy Storage Mater*, 2019, 17: 167–177
- 23 Bi R, Liu G, Zeng C, *et al.* 3D hollow $\alpha\text{-MnO}_2$ framework as an efficient electrocatalyst for lithium-oxygen batteries. *Small*, 2019, 15: 1804958
- 24 Zhang P, He M, Xu S, *et al.* The controlled growth of porous $\delta\text{-MnO}_2$ nanosheets on carbon fibers as a bi-functional catalyst for rechargeable lithium-oxygen batteries. *J Mater Chem A*, 2015, 3: 10811–10818
- 25 Luo C, Sun H, Jiang Z, *et al.* Electrocatalysts of Mn and Ru oxides loaded on MWCNTs with 3D structure and synergistic effect for rechargeable Li- O_2 battery. *Electrochim Acta*, 2018, 282: 56–63
- 26 Cao Y, Wei Z, He J, *et al.* $\alpha\text{-MnO}_2$ nanorods grown *in situ* on graphene as catalysts for Li- O_2 batteries with excellent electrochemical performance. *Energy Environ Sci*, 2012, 5: 9765
- 27 Thapa AK, Ishihara T. Mesoporous $\alpha\text{-MnO}_2$ /Pd catalyst air electrode for rechargeable lithium-air battery. *J Power Sources*, 2011, 196: 7016–7020
- 28 Huang Z, Zhang M, Cheng J, *et al.* Silver decorated alpha-manganese oxide nanostructured electrocatalyst for rechargeable lithium-oxygen battery. *Catal Commun*, 2015, 61: 44–47
- 29 Chou SL, Wang JZ, Chew SY, *et al.* Electrodeposition of MnO_2 nanowires on carbon nanotube paper as free-standing, flexible electrode for supercapacitors. *Electrochem Commun*, 2008, 10: 1724–1727
- 30 Hu X, Han X, Hu Y, *et al.* $\epsilon\text{-MnO}_2$ nanostructures directly grown on Ni foam: A cathode catalyst for rechargeable Li- O_2 batteries. *Nanoscale*, 2014, 6: 3522–3525
- 31 Tang C, Sun P, Xie J, *et al.* Two-dimensional IrO_2 /MnO₂ enabling conformal growth of amorphous Li_2O_2 for high-performance Li- O_2 batteries. *Energy Storage Mater*, 2017, 9: 206–213
- 32 Xie Y, Yu Y, Gong X, *et al.* Effect of the crystal plane figure on the catalytic performance of MnO_2 for the total oxidation of propane. *CrystEngComm*, 2015, 17: 3005–3014
- 33 Dai L, Sun Q, Chen L, *et al.* Ag doped urchin-like $\alpha\text{-MnO}_2$ toward efficient and bifunctional electrocatalysts for Li- O_2 batteries. *Nano Res*, 2020, 13: 2356–2364
- 34 Cong Y, Tang Q, Wang X, *et al.* Silver-intermediated perovskite $\text{La}_{0.9}\text{FeO}_{3-\delta}$ toward high-performance cathode catalysts for nonaqueous lithium-oxygen batteries. *ACS Catal*, 2019, 9: 11743–11752
- 35 Sun YF, Zhang YQ, Yang YL, *et al.* Smart tuning of 3D ordered electrocatalysts for enhanced oxygen reduction reaction. *Appl Catal B-Environ*, 2017, 219: 640–644
- 36 Cao C, Lan Z, Yan Y, *et al.* Mechanistic insight into the synergetic catalytic effect of Pd and MnO_2 for high-performance Li- O_2 cells. *Energy Storage Mater*, 2018, 12: 8–16
- 37 Sun Q, Li D, Cheng J, *et al.* Nitrogen-doped carbon derived from pre-oxidized pitch for surface dominated potassium-ion storage. *Carbon*, 2019, 155: 601–610
- 38 Long J, Hou Z, Shu C, *et al.* Free-standing three-dimensional CuCo_2S_4 nanosheet array with high catalytic activity as an efficient oxygen electrode for lithium-oxygen batteries. *ACS Appl Mater Interfaces*, 2019, 11: 3834–3842
- 39 Sun Y, Wang L, Liu Y, *et al.* Birnessite-type MnO_2 nanosheets with layered structures under high pressure: Elimination of crystalline stacking faults and oriented laminar assembly. *Small*, 2015, 11: 300–305
- 40 Li YF, Zhu SC, Liu ZP. Reaction network of layer-to-tunnel transition of MnO_2 . *J Am Chem Soc*, 2016, 138: 5371–5379
- 41 Dai L, Sun Q, Guo J, *et al.* Mesoporous Mn_2O_3 rods as a highly efficient catalyst for Li- O_2 battery. *J Power Sources*, 2019, 435: 226833
- 42 Hu A, Shu C, Xu C, *et al.* Interface-engineered metallic 1T-MoS₂ nanosheet array induced via palladium doping enabling catalysis enhancement for lithium-oxygen battery. *Chem Eng J*, 2020, 382: 122854
- 43 Zhao Z, Huang J, Peng Z. Achilles' heel of lithium-air batteries: Lithium carbonate. *Angew Chem Int Ed*, 2018, 57: 3874–3886
- 44 Zhang L, Zhang F, Huang G, *et al.* Freestanding MnO_2 @carbon papers air electrodes for rechargeable Li- O_2 batteries. *J Power Sources*, 2014, 261: 311–316
- 45 Peng Z, Freunberger SA, Chen Y, *et al.* A reversible and higher-rate Li- O_2 battery. *Science*, 2012, 337: 563–566
- 46 Taguchi Y, Noguchi T. Drastic changes in the ligand structure of the oxygen-evolving Mn cluster upon Ca^{2+} depletion as revealed by FTIR difference spectroscopy. *Biochim Biophys Acta (BBA) - Bioenergetics*, 2007, 1767: 535–540
- 47 Parikh SJ, Chorover J. FTIR spectroscopic study of biogenic Mn-oxide formation by *pseudomonas putida* GB-1. *Geomicrobiol J*, 2005, 22: 207–218
- 48 Johnson L, Li C, Liu Z, *et al.* The role of LiO_2 solubility in O_2 reduction in aprotic solvents and its consequences for Li- O_2 batteries. *Nat Chem*, 2014, 6: 1091–1099
- 49 Gittleson FS, Ryu WH, Taylor AD. Operando observation of the gold-electrolyte interface in Li- O_2 batteries. *ACS Appl Mater Interfaces*, 2014, 6: 19017–19025
- 50 Ze H, Chen X, Wang XT, *et al.* Molecular insight of the critical role of

- Ni in Pt-based nanocatalysts for improving the oxygen reduction reaction probed using an *in situ* SERS borrowing strategy. *J Am Chem Soc*, 2021, 143: 1318–1322
- 51 Shang Y, Chen N, Li Y, *et al.* An “ether-in-water” electrolyte boosts stable interfacial chemistry for aqueous lithium-ion batteries. *Adv Mater*, 2020, 32: 2004017
 - 52 Zhang Y, Zhang X, Wang J, *et al.* Potential-dependent generation of O_2^- and LiO_2 and their critical roles in O_2 reduction to Li_2O_2 in aprotic $Li-O_2$ batteries. *J Phys Chem C*, 2016, 120: 3690–3698
 - 53 Zhai D, Wang HH, Lau KC, *et al.* Raman evidence for late stage disproportionation in a $Li-O_2$ battery. *J Phys Chem Lett*, 2014, 5: 2705–2710
 - 54 Li W, Liu J, Guo P, *et al.* Co/CoP heterojunction on hierarchically ordered porous carbon as a highly efficient electrocatalyst for hydrogen and oxygen evolution. *Adv Energy Mater*, 2021, 11: 2102134
 - 55 Mu X, Xia C, Gao B, *et al.* Two-dimensional Mo-based compounds for the $Li-O_2$ batteries: Catalytic performance and electronic structure studies. *Energy Storage Mater*, 2021, 41: 650–655
 - 56 Song K, Ai W, Zhang Y, *et al.* Three-dimensional self-supported $CoCo_2O_4$ nanowires@NiO nanosheets core/shell arrays as an oxygen electrode catalyst for $Li-O_2$ batteries. *J Mater Chem A*, 2021, 9: 3007–3017
 - 57 Freunberger SA, Chen Y, Drewett NE, *et al.* The lithium-oxygen battery with ether-based electrolytes. *Angew Chem Int Ed*, 2011, 50: 8609–8613
 - 58 Li J, Shu C, Hu A, *et al.* Tuning oxygen non-stoichiometric surface via defect engineering to promote the catalysis activity of Co_3O_4 in $Li-O_2$ batteries. *Chem Eng J*, 2020, 381: 122678
 - 59 Liu S, Zhu Y, Xie J, *et al.* Direct growth of flower-like $\delta-MnO_2$ on three-dimensional graphene for high-performance rechargeable $Li-O_2$ batteries. *Adv Energy Mater*, 2014, 4: 1301960
 - 60 Shen Z-Z, Lang S-, Zhou C, *et al.* *In situ* realization of water-mediated interfacial processes at nanoscale in aprotic $Li-O_2$ batteries. *Adv Energy Mater*, 2020, 10: 2002339
 - 61 Wang C, Guo Z, Zhang S, *et al.* Constructing *in-situ* polymerized electrolyte on lithiophilic anode for high-performance lithium-air batteries operating in ambient conditions. *Energy Storage Mater*, 2021, 43: 221–228

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Conflict of interest The authors declare that they have no conflict of interest.

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

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锂氧电池中基于自支撑Ag/ δ - MnO_2 纳米花正极的可逆LiOH化学

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摘要 因放电产物对有机电解液具有高攻击性, 使得锂-氧电池能量效率低和循环稳定性差的问题一直限制着其实际应用. 与典型放电产物过氧化锂相比, 氢氧化锂(LiOH)具有更好的化学和电化学稳定性. 本文通过在碳纸上原位生长嵌有纳米银的花状二氧化锰作为锂-氧电池的正极(Ag/ δ - MnO_2 @CP), 并证明了它能催化LiOH的可逆生成和分解. 原位拉曼测试和理论计算表明Ag/ δ - MnO_2 催化放电中间体 LiO_2^* 与水分子解离的 H^+ 反应最终生成LiOH. 以Ag/ δ - MnO_2 @CP为正极的锂-氧电池在潮湿氧气环境下表现出更高的比容量和放电平台. 在电流密度为 200 mA g^{-1} 时, 锂-氧电池的过电位仅为 0.5 V , 在 500 mA h g^{-1} 的限制比容量下可循环867圈. 该工作为研究固相催化剂在锂-氧电池中的作用提供了新的思路, 并将促进基于LiOH放电产物的锂-氧电池的实际应用.