Realizing the Embedded Growth of Large Li$_2$O$_2$ Aggregations by Matching Different Metal Oxides for High-Capacity and High-Rate Lithium Oxygen Batteries

Peng Zhang, Shoufeng Zhang, Mu He, Junwei Lang, Aimin Ren, Shan Xu,* and Xingbin Yan*

Large Li$_2$O$_2$ aggregations can produce high-capacity of lithium oxygen (Li-O$_2$) batteries, but the larger ones usually lead to less-efficient contact between Li$_2$O$_2$ and electrode materials. Herein, a hierarchical cathode architecture based on different discharge characteristics of $\alpha$-MnO$_2$ and Co$_3$O$_4$ is constructed, which can enable the embedded growth of large Li$_2$O$_2$ aggregations to solve this problem. Through experimental observations and first-principle calculations, it is found that $\alpha$-MnO$_2$ nanorod tends to form uniform Li$_2$O$_2$ particles due to its preferential Li$^+$ adsorption and similar LiO$_2$ adsorption energies of different crystal faces, whereas Co$_3$O$_4$ nanosheet tends to simultaneously generate Li$_2$O$_2$ film and Li$_2$O$_2$ nanosheets due to its preferential O$_2$ adsorption and different LiO$_2$ adsorption energies of varied crystal faces. Thus, the composite cathode architecture in which Co$_3$O$_4$ nanosheets are grown on $\alpha$-MnO$_2$ nanorods can exhibit extraordinary synergetic effects, i.e., $\alpha$-MnO$_2$ nanorods provide the initial nucleation sites for Li$_2$O$_2$ deposition while Co$_3$O$_4$ nanosheets provide dissolved LiO$_2$ to promote the subsequent growth of Li$_2$O$_2$. Consequently, the composite cathode achieves the embedded growth of large Li$_2$O$_2$ aggregations and thus exhibits significantly improved specific capacity, rate capability, and cyclic stability compared with the single metal oxide electrode.

1. Introduction

Rechargeable lithium-oxygen (Li-O$_2$) batteries are triggering worldwide interest due to their ultrahigh theoretical energy density (3505 Wh kg$^{-1}$ based on lithium peroxide (Li$_2$O$_2$)), thus exhibiting significant potential to meet the demand of long-range electric vehicles.$^{[1,2]}$ In a typical Li-O$_2$ battery, during the discharging process, O$_2$ reacts with Li$^+$ to form Li$_2$O$_2$ with insulating and insoluble characteristics that lead to the gradual increase of electrode impedance until the electron transport cannot match the current density.$^{[3–5]}$ For this reason, if conformal Li$_2$O$_2$ film or small Li$_2$O$_2$ aggregation is formed, the electrode surface will be passivated early and thus yield a low capacity.$^{[6,7]}$ If large-sized Li$_2$O$_2$ aggregation is produced, the passivation of electrode surface will be prolonged and result in a relatively high capacity.$^{[8–10]}$ Therefore, the capacity of Li-O$_2$ batteries is strongly related to the size of Li$_2$O$_2$ aggregation. For instance, Bruce and co-workers found that the size of Li$_2$O$_2$ toroids could be adjusted by changing the solvent or electrolyte additive, and the battery capacity could be increased with Li$_2$O$_2$ sizes.$^{[6,8]}$ Han and co-workers reported that Li$_2$O$_2$ with large sheet-like morphology provided a higher capacity than the small Li$_2$O$_2$ nanoparticles.$^{[11]}$ Amine and co-workers also found that large Li$_2$O$_2$ toroids delivered higher capacity than Li$_2$O$_2$ film.$^{[12]}$ Thus, a large size is a desirable feature for Li$_2$O$_2$ in Li-O$_2$ batteries.

However, Chen and co-workers and Byon and co-workers both demonstrated that upsizing Li$_2$O$_2$ would result in a higher charging plateau and low charging rate.$^{[13,14]}$ That is, for large Li$_2$O$_2$ aggregations, a contradiction between high capacity and low oxygen evolution reaction (OER) overpotential is found. To solve this problem, many studies have focused on the development of OER catalysts. For example, Han co-workers reported a PdCu/Super P cathode yielding large sheet-like Li$_2$O$_2$ as well as low OER overpotential.$^{[11]}$ Liu and co-workers designed a carbon-dotted/CoO/Super P cathode that could produce large Li$_2$O$_2$ toroids and perform lower overpotentials.$^{[15]}$ Moreover, Peng and co-workers have proved that the OER reaction interface of Li-O$_2$ batteries is electrode/Li$_2$O$_2$ instead of Li$_2$O$_2$/electrolyte.$^{[4]}$ Basing on this result, further increasing...
contact sites between the catalyst and Li$_2$O$_2$, the decomposition of the large Li$_2$O$_2$ aggregations should become more easily and quickly. Meanwhile, large Li$_2$O$_2$ aggregations usually randomly deposit on the electrode surface,[16–20] leading to the less effective contact between Li$_2$O$_2$ and electrode material. In this regard, confining the large Li$_2$O$_2$ aggregations in a hierarchical cathode/catalyst matrix should be an effective strategy to produce sufficient contact sites between them. Although many studies have focused on the construction of hierarchically structured cathodes,[21–25] these reported structures still did not realize the strategy.

For the construction of the cathode architecture toward the embedded growth of Li$_2$O$_2$, using metal oxides is one of the ideal choices due to their scientific and practical values compared with noble metals, and their variety and better stability compared with carbon materials.[22,26–30] Among various metal oxides, MnO$_2$ and Co$_3$O$_4$ are the most studied materials,[28,31–36] and the corresponding results have shown that MnO$_2$ and Co$_3$O$_4$ are promising active materials for constructing ideal cathode architecture.

Herein, we demonstrate that the embedded growth of large Li$_2$O$_2$ aggregations can be realized by constructing a hierarchical cathode architecture wherein Co$_3$O$_4$ nanosheets are grown on the surfaces of $\alpha$-MnO$_2$ nanorods on a conductive carbon paper (CP). First, the different discharge characteristics of Co$_3$O$_4$ nanosheet and $\alpha$-MnO$_2$ nanorod are analyzed through experimental observations and first-principles calculations. $\alpha$-MnO$_2$ nanorod tends to produce the uniform Li$_2$O$_2$ nucleation due to its preferential Li$^+$ adsorption characteristic, resulting in the formation of uniform Li$_2$O$_2$ particles; whereas Co$_3$O$_4$ nanosheet tends to produce Li$_2$O$_2$ crystal seeds through the surface and solution due to its preferential oxygen adsorption characteristic, resulting in the separate formation of Li$_2$O$_2$ film and Li$_2$O$_2$ nanosheets. The composite cathode architecture wherein Co$_3$O$_4$ nanosheets are grown on $\alpha$-MnO$_2$ nanorods exhibits extraordinary synergistic effects: $\alpha$-MnO$_2$ can offer the initial Li$_2$O$_2$ nucleation sites and produce enough sites to grow ultrathin Co$_3$O$_4$ nanosheets, and Co$_3$O$_4$ nanosheets are conducive to yield dissolved LiO$_2$. Thus, large mooncake-like Li$_2$O$_2$ and sheet-like Li$_2$O$_2$ both possessing embedded structures are formed on CP-MnO$_2$-Co$_3$O$_4$ electrode at low and high current densities, respectively. As a consequence, such composite cathode exhibits remarkably improved electrochemical performance compared with the single ones, in terms of a large capacity (5950 mAh g$^{-1}$ at 51 mA g$^{-1}$), outstanding rate capability (2574 mAh g$^{-1}$ at 1.03 A g$^{-1}$), as well as good cyclic stability (54 cycles at the limited capacity of 1000 mAh g$^{-1}$).

2. Results and Discussion

2.1. Structure Characterization of CP-MnO$_2$ and Its Discharge Products in Li-O$_2$ Cells

In this study, $\alpha$-MnO$_2$ and Co$_3$O$_4$ were directly grown on CP substrates as freestanding electrodes to avoid using any binder that will increase the resistance and induce the possible side reactions in Li-O$_2$ cells.[37,38] Specifically, CP-MnO$_2$ was prepared via a facile hydrothermal method and its microstructure and morphology are shown in Figure 1. X-ray diffraction (XRD) pattern presented in Figure 1a reflects that the diffraction peaks

![Figure 1](image_url)

**Figure 1.** a) XRD pattern and b) SEM image of CP-MnO$_2$. c) TEM image of an individual MnO$_2$ nanorod. Insets are the HRTEM image and its corresponding Fourier transform image. d) Charge–discharge curves of CP-MnO$_2$ at different currents. SEM images of CP-MnO$_2$ electrode discharged at e) 104 mA g$^{-1}$ and f) 311 mA g$^{-1}$. The insets in b), c), and f) are the corresponding magnified images.
can almost be well indexed to tetragonal $\alpha$-MnO$_2$ (PDF#44-0141) except the carbon peaks (26° and 53°). As shown in Figure 1b, scanning electron microscopy (SEM) images exhibit a uniform growth of highly ordered nanorods array on the CP substrate. The transmission electron microscopy (TEM) image further confirms the nanorod-like morphology (Figure 1c) and the selected area electron diffraction (SEAD, Figure S1a, Supporting Information) suggests the single-crystal structure of $\alpha$-MnO$_2$ nanorod. Lattice fringes displayed in the high-resolution TEM (HRTEM) are $\approx$ 0.5 and 0.27 nm, corresponding to the (200) and (101) planes, respectively. Combined with the Fourier transform image (inset of Figure 1c), the growth direction of $\alpha$-MnO$_2$ nanorod can be confirmed to be at the [001] axis with the exposed planes of (020) and (110). When employed as the cathode for Li-O$_2$ battery, the CP-MnO$_2$ electrode delivers specific capacities of 2195, 1543, and 648 mAh g$^{-1}$ at 52, 104, and 311 mA g$^{-1}$, respectively. Correspondingly, the ORR (OER) voltage plateaus are $\approx$ 2.63 V (4.05 V), 2.52 V (4.15 V), and 2.40 V (4.11 V) at different currents (Figure 1d).

As mentioned before, the morphology of Li$_2$O$_2$ can reflect the electrochemical performance of a Li-O$_2$ battery. Here, the discharge products were examined by SEM and XRD. Figure 1e,f shows CP-MnO$_2$ electrode morphology discharged specific capacities of 2195, 1543, and 648 mAh g$^{-1}$ at 52, 104, and 311 mA g$^{-1}$, respectively. Correspondingly, the ORR (OER) voltage plateaus are $\approx$ 2.63 V (4.05 V), 2.52 V (4.15 V), and 2.40 V (4.11 V) at different currents (Figure 1d).

As shown in Figure 1b, the major XRD peaks of CP-Co$_3$O$_4$ sample are consistent with the pure Co$_3$O$_4$ phase (PDF#43-1003) except for the diffraction peaks of CP. SEM images show the uniform and vertical growth of Co$_3$O$_4$ nanosheets on the CP skeleton, and these nanosheets interconnect into a 3D framework (Figure 2b). TEM images verify that such a Co$_3$O$_4$ nanosheet has an obvious low crystallinity and low content in this sample, which is also reflected by other metal oxide electrodes. Furthermore, the obvious peak shift of MnO$_2$ to the low angle direction can be detected from the discharged electrode, suggesting the volume increase of the lattice. The increased lattice volume should be attributed to the storage of Li$_2$O$_2$ in 2 $\times$ 2 MnO$_6$ octahedron tunnels of $\alpha$-MnO$_2$ instead of Li$^+$ insertion, which is due to the insertion of Li$_2$O$_2$ clogging the channels and Li$_2$O$_2$ on the surfaces of MnO$_2$ further covering the channels. After recharging, these peaks can shift back to their original positions, suggesting the reversible extraction of the Li$_2$O$_2$ in the tunnels. Additionally, the electrochemical performance of the pure CP substrate was also investigated to confirm the major contribution of the loading active materials on battery capacity (Figure S3, Supporting Information).

2.2. Structure Characterization of CP-Co$_3$O$_4$ and Its Discharge Products in Li-O$_2$ Cells

CP-Co$_3$O$_4$ electrode was synthesized via a simple electro-deposition method followed by an annealing process (Figure S4, Supporting Information). Its structure characteristics and electrochemical performance were analyzed and the corresponding results are presented in Figure 2. As shown in Figure 2a, the major XRD peaks of CP-Co$_3$O$_4$ sample are consistent with the pure Co$_3$O$_4$ phase (PDF#43-1003) except for the diffraction peaks of CP. SEM images show the uniform and vertical growth of Co$_3$O$_4$ nanosheets on the CP skeleton, and these nanosheets interconnect into a 3D framework (Figure 2b). TEM images verify that such a Co$_3$O$_4$ nanosheet has an obvious
surface-porous structure (Figure 2c and Figure S5a, Supporting Information) and the nitrogen adsorption–desorption isotherms prove the large specific surface area of Cp-Co₃O₄ sample (74.73 m² g⁻¹, Figure S6b, Supporting Information). The diffraction rings in the SEAD pattern (Figure S1b, Supporting Information) of the Co₃O₄ nanosheet indicate its polycrystalline structure, and the HRTEM and Fourier transform images (insets of Figure 2c) further show that the polycrystalline nanosheet is composed of numerous Co₃O₄ monocrystals. When employed as the cathode for a Li₂O₂ battery, the CP-Co₃O₄ electrode exhibits specific capacities of 2080, 1445, and 551 mAh g⁻¹ at 51, 102, and 306 mA g⁻¹, respectively (Figure 2d). These profiles also reveal that the discharge (charge) plateau voltages are 2.59 V (3.92 V), 2.60 V (3.98 V), and 2.27 V (3.95 V). The electrochemical properties shown here are similar to previously reported freestanding Co₃O₄ electrodes.[44-46] XRD results of discharged and charged CP-Co₃O₄ electrodes prove the reversible formation and decomposition of Li₂O₂ (Figure S2b, Supporting Information). Moreover, as displayed in Figure 2e, after the electrode discharged at 100 mA g⁻¹, numerous Li₂O₂ nanosheets are generated on the electrode surfaces with a randomly floating state. Simultaneously, film-like Li₂O₂ is also formed on the surfaces of Co₃O₄ nanosheets (seen from the inset). In comparison, when the current increases to 300 mA g⁻¹, such nanosheet-like morphology disappears from the electrode. Instead, film-like Li₂O₂ and discrete nanoparticle aggregations occupy the electrode surface.

2.3. Discharge Characteristics of CP-MnO₂ and CP-Co₃O₄

The morphology of the discharge product depends on the electrode material morphology, current density, and the intrinsic discharge characteristic of used electrode material. For the influence of electrode morphology, previous studies have reported that carbon nanotubes and granular KB carbon can both produce toroidal Li₂O₂. The morphology of electrode material is not the critical factor to determine its discharge characteristic.[9,47] Our recent study also reported that flower-like Li₂O₂ assembled by Li₂O₂ sheets was both produced on Ni/Co₃O₄ nanowires and Ni/Co₃O₄ rectangular nanosheet electrodes.[48] In this study, aside from setting the same mass current density for testing CP-MnO₂ and CP-Co₃O₄ electrodes, we also compared the discharged morphology of the two electrodes at the same current density of ~1.40 mA m⁻² SSA based on the specific surface area (Table S1 and Figure S7, Supporting Information). As a result, the morphology of the discharged CP-MnO₂ electrode still exhibits uniform granular Li₂O₂ coating on α-MnO₂ nanorod surface. Thus, the intrinsic characteristic of metal oxides determines the growth process of Li₂O₂ in an operated Li-O₂ cell. Then, we deeply analyzed the different discharge characteristics of α-MnO₂ nanorod and Co₃O₄ nanosheet, respectively.

Schematic illustrations of the discharging process of α-MnO₂ (Figure S8a, Supporting Information) and Co₃O₄ (Figure S8b, Supporting Information) and the corresponding equations were outlined. For α-MnO₂, the first ORR step was proven to be a Li⁺ adsorption process with desolvation (Equation (S1) in Figure S8 of the Supporting information).[31,32,49] obtaining an electron and further adsorbing O₂ to form LiO₂α⁺ ("α" represents adsorbed species) at the MnO₂ surface (Equation (S2) in Figure S8 of the Supporting information).[50,51] Then, LiO₂α⁺ transforms to Li₂O₂ through an electrochemical reduction or a disproportionation reaction (Equation (S3) in Figure S8 of the Supporting information).[50,52] Owing to the single crystal structure of α-MnO₂ nanorods, the accommodation of Li₂O₂ in 2 × 2 MnO₂ octahedron tunnels, and close Li₂O₂ adsorption energy for exposed crystal face of α-MnO₂ nanorod (Figure 3c,d)[31,42] the formed Li₂O₂ seeds can be uniformly distributed on the MnO₂ surface and act as the desired seeds for subsequent Li₂O₂ growth. After the nucleation process of Li₂O₂ on α-MnO₂ surface, Li₂O₂ can be adsorbed on the Li₂O₂ surface or dissolved into electrolyte due to the close adsorption energy of Li₂O₂ on Li₂O₂ (~1.27 eV, Figure 3a) and the salvation energy of Li₂O₂ (~1.35 eV, Figure 3b) (Equation (S4) in Figure S8 of the Supporting information). Thus, the uniform Li₂O₂ nucleus can induce the subsequent growth of Li₂O₂ simultaneously through surface and solution, finally resulting in the formation of Li₂O₂ particles (Equations (S5) and (S6) in Figure S8 of the Supporting information).

For CP-Co₃O₄ electrode, the first ORR step is oxygen adsorption followed by oxygen reduction to form O₂⁺ on the electrode surface, and then O₂⁺ transfers to electrolyte due to solvation (Equations (S7) and (S8) in Figure S8 of the Supporting information).[10,11,33] The dissolved O₂sol ("sol" represents solvated species) and Li⁺ form LiO₂(sol) by coupling (Equation (S9) in Figure S8 of the Supporting information).[54] Near the electrode surface, the coupled LiO₂(sol) can be adsorbed on Co₃O₄ nanosheet surfaces owing to the larger adsorption energy between them (~3.10 to ~4.63 eV on different crystal planes, Figure 3e–h) compared to the salvation energy of LiO₂ in electrolyte (~1.35 eV, Equation (S10) in Figure S8 of the Supporting information). Then, the adsorbed LiO₂α⁺ undergoes a second reduction or disproportionation to form Li₂O₂ as surplus ("sur-seeds" represent the seeds formed through surface), Equation (S11) in Figure S8 of the Supporting information).[55] Simultaneously, in the bulk electrolyte, LiO₂(sol) transforms to Li₂O₂ through disproportionation (Equation (S12) in Figure S8 of the Supporting information).[12] When Li₂O₂ cluster reaches a supersaturated state, solid Li₂O₂ deposits on the electrode surface as sol-seeds ("sol-seeds" represent the seeds formed through solution).[10,11,19] Thus, for Co₃O₄ material, the nucleation occurs simultaneously through surface and solution, which leads to further growth of Li₂O₂ on the surface and in the electrolyte.

2.4. Design Philosophy for the Composite Cathode

Basing on the above analyses, the nucleation processes of Li₂O₂ for α-MnO₂ and Co₃O₄ are quite different. α-MnO₂ undergoes Li⁺ adsorption and O₂ reduction to directly form LiO₂ on MnO₂ surfaces. Co₃O₄ undergoes O₂ adsorption, O₂ reduction, O₂⁺ solvation, coupling of O₂⁻ and Li⁺, and then forms dissolved LiO₂ oligomer or being adsorbed on electrode surfaces. Thus, the nucleation rate of α-MnO₂ should be faster than Co₃O₄ at the initial discharge process. Meanwhile, for Co₃O₄ electrode, the growth of Li₂O₂ through surface and electrolyte
occurs at the same time. Taking these findings into account, the composite electrode, i.e., CP-MnO$_2$-Co$_3$O$_4$ (Figure 4e), may combine the discharge characteristics of $\alpha$-MnO$_2$ and Co$_3$O$_4$ (Figure 4a–d), of which $\alpha$-MnO$_2$ nanorods function as the initial growth sites of Li$_2$O$_2$ acting as the seeds for subsequent Li$_2$O$_2$ growth and simultaneously provide plenty of sites for Co$_3$O$_4$ nanosheets deposition inducing the formation of sufficient activity area to provide a large amount of dissolved LiO$_2$. Then, as shown in Figure 4f, Li$_2$O$_2$ produced on the composite cathode architecture probably possesses a large size and an embedded structure, resulting in the remarkable improvement of battery performance.

2.5. Structure Characterization of CP-MnO$_2$-Co$_3$O$_4$

As shown in Figure 5a, the CP-MnO$_2$-Co$_3$O$_4$ composite electrode was synthesized through electro-depositing Co$_3$O$_4$ on the

---

Figure 3. a) The adsorption energy of LiO$_2$ on (111) plane of Li$_2$O$_2$. b) The solvation energy of LiO$_2$ in Tetraethylene glycol dimethyl ether (TEGDME). c,d) The adsorption energies of LiO$_2$ on (110) and (020) planes of $\alpha$-MnO$_2$. e–h) The adsorption energies of LiO$_2$ on O-(111), (112), (110), and (311) planes of Co$_3$O$_4$.

Figure 4. e) Schematic illustration of designing the composite cathode architecture f) with ideal discharge product morphology based on different discharge characteristics of a,b) CP-MnO$_2$ and c,d) CP-Co$_3$O$_4$. 

---

Adv. Sci. 2017, 4, 1700172 © 2017 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
CP-MnO₂ substrate followed by an annealing process. Figure 5b displays the XRD pattern of as-prepared composite electrode, presenting the diffraction peaks of both MnO₂ and Co₃O₄. X-ray photoelectron spectroscopy (XPS) survey also confirms the coexistence of MnO₂ and Co₃O₄ (Figure 5c and Figure S9, Supporting Information). For Mn 2p spectrum, the Mn 2p₃/2 (642.1 eV) and Mn 2p₁/2 (653.8 eV) peaks have a spin-energy separation of 11.7 eV, reflecting the +4 oxidation state for Mn.[56] For Co 2p spectrum, peaks at 780.5 and 796.6 eV correspond to Co 2p₃/2 and Co 2p₁/2, respectively, indicating the characteristic of Co₃O₄ phase. [57] Fitting using Gaussian method, the Co 2p spectrum can be well fitted into two spin orbits with features of Co²⁺ and Co³⁺. From the top view of SEM images, Co₃O₄ nanosheets interconnect each other to form numerous matrices for the accommodation of Li₂O₂ during the discharge process (Figure 5d and inset). From the side view (Figure S10, Supporting Information), Co₃O₄ nanosheets grow on the surface of each MnO₂ nanorod from bottom to top, but these nanosheets do not cover the whole surface of MnO₂ nanorods. The microstructure of Co₃O₄ nanosheets grown on a MnO₂ nanorod was further revealed by TEM (Figure 5e and Figure S11, Supporting Information). As shown in a typical interface area marked with a blue circle in Figure 5e, the main lattice fringes spacing are 0.48 and 0.54 nm, corresponding to the (002) plane of MnO₂ and the (110) plane of Co₃O₄, respectively. Moreover, as seen from the crystal planes of the Co₃O₄ nanosheet (their boundaries are marked with a dashed line), their crystal orientations are the same (marked with a red solid line). Nevertheless, the Co₃O₄ nanosheets in composite electrode still exhibit polycrystalline structure (Figure S12, Supporting Information).

Furthermore, mesopores on Co₃O₄ nanosheet in the composite electrode are larger than those in CP-Co₃O₄ electrode (Figure S5b, Supporting Information). The formation of these larger mesopores is due to much thinner Co₃O₄ nanosheets in CP-MnO₂-Co₃O₄ sample compared with the ones in CP-Co₃O₄ under the same annealing process (Figure S13, Supporting Information).[58] With the consideration of the identical mass of Co₃O₄ on the two electrodes, the decreased thickness of Co₃O₄ nanosheets is linked to the significantly increased height derived from more depositing sites on the CP-MnO₂ substrate than those on the pure CP substrate (Figure S14, Supporting Information). As a result, the composite electrode exhibited a large surface area of 71.18 m² g⁻¹ (Figure S6c, Supporting Information), which would be in favor of producing a large amount of dissolved LiO₂sol. Furthermore, the abundant mesoporous structure of the Co₃O₄ nanosheets may also facilitate the transport of electrolyte, oxygen, superoxide, and peroxide species. The surface area of the composite electrode is slightly lower than that of CP-Co₃O₄ electrode (74.73 m² g⁻¹), mainly because of the low specific surface area (21.31 m² g⁻¹), high mass loading of MnO₂ (0.85 mg cm⁻² for MnO₂; 0.51 mg cm⁻² for Co₃O₄), larger mesoporous size of Co₃O₄, and partially overlapped surface of MnO₂ and Co₃O₄ in the composite electrode.

2.6. Performance Comparison of CP-MnO₂, CP-Co₃O₄ and CP-MnO₂-Co₃O₄ Cathodes, and the Discharge Products of CP-MnO₂-Co₃O₄ Electrode

The electrochemical performance of Li-O₂ battery with CP-MnO₂-Co₃O₄ electrode was then investigated and the results are shown in Figure 6. By comparing the charge–discharge curves of the three electrodes, it is clearly seen that CP-MnO₂-Co₃O₄ electrode exhibits a much higher capacity (4850 mAh g⁻¹) than the two other electrodes (CP-MnO₂ and...
CP-Co₃O₄) at ~103 mA g⁻¹. SEM image of the discharged CP-MnO₂-Co₃O₄ electrode was investigated. As expected, mooncake-like Li₂O₂ is uniformly embedded in the given matrices (Figure 6b) and the formation of a large amount of Li₂O₂ aggregation endows the higher capacity of CP-MnO₂-Co₃O₄ electrode. Such capacity improvement is more obvious at a high current density. As shown in Figure 6c, the composite electrode can deliver 3543 mAh g⁻¹ at 309 mA g⁻¹, almost six times higher than the two other electrodes. After discharging, numerous large Li₂O₂ sheets form on the surface of CP-MnO₂-Co₃O₄ electrode with an inlaid structure (Figure 6d). Moreover, as shown in Figure 6e,f, the CP-MnO₂-Co₃O₄ electrode exhibits superior rate capability. For instance, the discharge capacity is 3401 mAh g⁻¹ at 618 mA g⁻¹, 57.3% of the capacity at 51 mA g⁻¹ (5940 mAh g⁻³). When the current increases to 1236 mA g⁻¹, the capacity still reaches 2592 mAh g⁻¹, 43.6% of the initial capacity. Additionally, we also compared the electrochemical performance of the three samples normalized by their electrode area, and the related results are shown in Table S2 and Figure S15 (Supporting Information). The results show that the performance improvement of the composite electrode is more remarkable when the test results are normalized by the electrode area, further reflecting the effectivity of this cathode architecture.

We believe that the remarkably improved electrochemical performance should be attributed to the synergistic effect of the different discharge characteristics of MnO₂ and Co₃O₄ through the scientific design of the cathode architecture. In detail, the obviously increased height of Co₃O₄ nanosheets in the vertical direction can significantly increase the amount of LiO₂sol and boost the growth of Li₂O₂, resulting in the formation of large aggregations (mooncake-like and large sheet-like Li₂O₂). Simultaneously, these Li₂O₂ aggregations are embedded in the cathode architecture, which can increase the contact sites between electrode materials and Li₂O₂ with a resulted potential and significantly improved rate capability of Li-O₂ cell. Furthermore, during the discharge process, Li⁺ can intercalate into MnO₂ crystal structure, as proven from the weaker peak shift in XRD pattern of discharged CP-MnO₂-Co₃O₄ electrode than that in XRD pattern of discharged CP-MnO₂ electrode (Figures S16 and S2, Supporting Information). The decreased peak shift to the low angle indicates the reduced volume change during the discharge process, suggesting the decreased amount or shrinking volume of insert species. As seen from Figure S17 (Supporting Information), the close capacity values between CP-MnO₂ and CP-MnO₂-Co₃O₄ tested in argon atmosphere indicate that Li⁺ can diffuse across the Co₃O₄ nanosheets (the specific capacity values of two electrodes were both calculated based on the mass of MnO₂). Simultaneously, the O₂ adsorption characteristic of Co₃O₄ can lead to the low availability of O₂ on MnO₂ surfaces. Thus, in this case, the inserted Li₂O₂ is partially replaced by Li⁺ due to the overlapped interface that can allow Li⁺ diffusion but prevent O₂ transmission. Fortunately, the lithiated MnO₂ was proved to be a better electronic conductor than the pristine MnO₂, facilitating the charge transfer during electrochemical reactions.[11] Additionally, to confirm the key role of MnO₂ in the composite structure, another composite electrode with a higher Co₃O₄ loading was prepared and its SEM images are presented in Figure S18a,b (Supporting Information). When the deposition quantity of Co₃O₄ increases from 1 to 2.5 C cm⁻², the surface of MnO₂ sample is completely covered by Co₃O₄ nanosheets. After discharging, this electrode can also form abundant Li₂O₂, resulting in a high discharge capacity (Figure S18c, Supporting Information).

Figure 6. Charge–discharge curves of three electrodes at a) ~103 mA g⁻¹ and c) ~309 mA g⁻¹, respectively. SEM images of discharged CP-MnO₂-Co₃O₄ electrode at b) 103 mA g⁻¹ and d) 309 mA g⁻¹, respectively. e) Rate capability of the Li-O₂ battery with CP-MnO₂-Co₃O₄ electrode at different current densities. f) The capacity retention of CP-MnO₂-Co₃O₄ electrode at different current densities.
Information). However, the discharge products do not embed in the matrices of the electrode, leading to a larger OER overpotential compared with the composite electrode with an appropriate Co$_3$O$_4$ loading (Figure S18c,d, Supporting Information).

As shown in Figure 7a, CP-MnO$_2$-Co$_3$O$_4$ electrode exhibits the lowest overpotential among the three electrodes during the limited capacity test. Meanwhile, no obvious change exists in the cyclic charge–discharge profile (Figure 7b), reflecting its good cycle stability. In comparison, CP-MnO$_2$-Co$_3$O$_4$ electrode is able to perform over 50 cycles before the terminal voltage decreases below 2 V, while CP-MnO$_2$ and CP-Co$_3$O$_4$ electrodes can only achieve approximately ten cycles at a limited capacity of 1030 mAh g$^{-1}$ (Figure 7c). Fourier Transform in frared (FTIR) spectra of the three electrodes at the eighth cycle were measured to investigate the reversibility of the three electrodes. As shown in Figure 7d, the obvious existence of the peaks around 400 to 600 cm$^{-1}$ indicates the reversible formation and decomposition of Li$_2$O$_2$ for the CP-MnO$_2$-Co$_3$O$_4$ composite electrode. For CP-MnO$_2$-Co$_3$O$_4$ electrode, the weakest intensity of organic lithium salt peaks suggests the slightest electrolyte decomposition. Also, the peak of Li$_2$CO$_3$ at 870 cm$^{-1}$ is observed for CP-MnO$_2$ and CP-Co$_3$O$_4$ electrodes. The formation of Li$_2$CO$_3$ is mainly due to the oxidation of carbon during the charge process.[59] Thus, this peak may derive from the side reaction related to CP substrate. As seen from FTIR spectra of CP-MnO$_2$-Co$_3$O$_4$ electrode at the 30th cycle (Figure S19, Supporting Information), the reversible decomposition of Li$_2$O$_2$ can also be detected. However, the intensity of peaks for organic lithium salt increases at the same time, indicating the gradual accumulation of the byproducts on the composite cathode, which further leads to the passivated electrode surfaces and the limited cycle life (54 cycles for CP-MnO$_2$-Co$_3$O$_4$ electrode).

Because the discharge depth can also affect the cycling performance of Li-O$_2$ batteries, we further compared the cyclic stability of the three electrodes under the identical rate of limited discharge capacity to their full capacities. In detail, the capacity of CP-MnO$_2$-Co$_3$O$_4$ electrode was 4850 mAh g$^{-1}$ at 103 mA g$^{-1}$ and 1030 mAh g$^{-1}$ (21% of the full capacity) was chosen as the limited capacity during the cyclic tests. Here, this discharge ratio was also applied in CP-MnO$_2$ and CP-Co$_3$O$_4$ electrodes (1543 mAh g$^{-1}$ × 21% = 323 mAh g$^{-1}$, with the value of 320 mAh g$^{-1}$ chosen for the two electrodes). As shown in Figure S20 (Supporting Information), the cyclic stability of CP-MnO$_2$ and CP-Co$_3$O$_4$ electrodes can be remarkably improved compared with that of the electrodes under the limited capacity setting at 1030 mAh g$^{-1}$. Even so, their cycle lives are still inferior to CP-MnO$_2$-Co$_3$O$_4$ electrode. Moreover, we compared the morphologies of the three electrodes after discharging (Figure S21, Supporting Information). α-MnO$_2$ nanorods are entirely covered by byproducts after
being charging at the 25th cycle (may have some unde-composed Li₂O₂, Figure S21a, Supporting Information) and Co₃O₄ surfaces are partially covered by byproducts (Figure S21b, Supporting Information). Fortunately, no obvious byproduct was found on the charged CP-MnO₂-Co₃O₄ electrode at 25th cycle (Figure S21c, Supporting Information). However, after recharging at the 54th cycle, undesired byproducts also covered on CP-MnO₂-Co₃O₄ electrode surfaces (Figure S21d, Supporting Information). These results show that the composite electrode is conducive to alleviate the accumulation of byproducts, thus exhibiting enhanced cyclic stability. Consequently, when the composite electrode was tested at the limited capacity of 320 mAh g⁻¹, it can achieve 142 cycles before the discharged terminal voltage decreases below 2 V (Figure S22, Supporting Information).

3. Conclusions

In summary, a cathode architecture composed of nanostructural α-MnO₂ and Co₃O₄ was developed to achieve embedded growth of discharge product Li₂O₂. To this end, the inherent catalytic characteristics of α-MnO₂ and Co₃O₄ are first studied through experimental observations and first-principle calculations. For the single MnO₂ and Co₃O₄, the CP-MnO₂ electrode produces Li₂O₂ with granular morphology due to its preferential Li⁺ adsorption property, accommodating Li₂O₂ in 2 × 2 MnO₂ octahedron channels and similar Li₂O₂ adsorption energy of exposed crystal faces. The CP-Co₃O₄ electrode produces nanosheet-like Li₂O₂ as well as film-like Li₂O₂ on the electrode surface owing to its preferential O₂ adsorption characteristic and the difference in Li₂O₂ adsorption energy of exposed crystal faces. On this basis, a hierarchical cathode architecture where Co₃O₄ nanosheets attach on MnO₂ nanorods array was fabricated, and the as-made composite electrode exhibits a distinct synergistic effect between α-MnO₂ and Co₃O₄. On the one hand, α-MnO₂ acts as the initial growing sites. On the other hand, ultrathin Co₃O₄ nanosheets with obviously increased height further produce a large amount of dissolved Li₂O₂. Thus, uniform mooncake-like Li₂O₂ and large sheet-like Li₂O₂ can be generated on the composite electrode with an embedded structure at low and high current densities, respectively. As a consequence, this composite electrode can offer remarkably improved electrochemical performance when compared to the single α-MnO₂ or Co₃O₄ electrode, in terms of high reversible capacity, superior rate capability, and outstanding cycle stability. This study develops a feasible strategy to design reasonable cathode architectures for realizing the embedded growth of Li₂O₂. It also provides valuable information for understanding the discharge mechanism of Li-O₂ batteries and designing high-performance Li-O₂ cathodes. Notably, this design philosophy may also be interesting for other energy storage devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (Grant Nos. 21573265, 51501208, and 21741071), China Scholarship Council (Grant No. 201500090190), and the Natural Science Foundation of Gansu Province of China (Grant No. 1606RJA258).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

discharge characteristics, Li₂O₂, LiO₂ adsorption energy, Li-O₂ batteries, metal oxides

Received: April 17, 2017
Revised: June 22, 2017
Published online: July 20, 2017

[1] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, Nat. Mater. 2012, 11, 19.
[2] S. Wu, J. Tang, F. Li, X. Liu, Y. Yamauchi, M. Ishida, H. Zhou, Adv. Funct. Mater. 2016, 26, 3291.
[3] D. G. Kwabi, M. Tufodziecki, N. Pour, D. M. Iktis, C. V. Thompson, Y. Shao-Horn, J. Phys. Chem. Lett. 2016, 7, 1204.
[4] J. Wang, Y. Zhang, L. Guo, E. Wang, Z. Peng, Angew. Chem., Int. Ed. 2016, 55, 5201.
[5] M. Noked, M. A. Schroeder, A. J. Pearse, G. W. Rubloff, S. B. Lee, J. Phys. Chem. Lett. 2016, 7, 211.
[6] L. Johnson, C. Li, Z. Liu, Y. Chen, S. A. Freunberger, P. C. Ashok, B. B. Praveen, K. Dholakia, J. M. Tarascon, P. G. Bruce, Nat. Chem. 2014, 6, 1091.
[7] B. D. Adams, C. Radtke, R. Black, M. L. Trudeau, K. Zaghib, L. F. Nazar, Energy Environ. Sci. 2013, 6, 1772.
[8] N. B. Aetukuri, B. D. McCloskey, J. M. Garcia, L. E. Krupp, V. Viswanathan, A. C. Luntz, Nat. Chem. 2015, 7, 50.
[9] B. Horstmann, B. Ballant, R. Mitchell, W. G. Bessler, Y. Shao-Horn, M. Z. Bazant, J. Phys. Chem. Lett. 2013, 4, 4217.
[10] C. Shen, Z. Wenn, F. Wang, K. Rui, Y. Lu, X. Wu, J. Power Sources 2015, 294, 593.
[11] R. Choi, J. Jung, G. Kim, K. Song, Y. I. Kim, S. C. Jung, Y. K. Han, H. Song, Y. M. Kang, Energy Environ. Sci. 2014, 7, 1362.
[12] J. Lu, L. Cheng, K. C. Lau, E. Tyo, X. Luo, J. Wen, D. Miller, R. S. Assary, H. H. Wang, P. Redfern, H. Wu, J. B. Park, Y. K. Sun, S. Vajda, K. Amine, L. A. Curtiss, Nat. Commun. 2014, 5, 4895.
[13] Y. Hu, X. Han, F. Cheng, Q. Zhao, H. Zhe, J. Chen, Nanoscale 2014, 6, 177.
[14] E. Yilmaz, C. Yogi, K. Yamanaka, T. Ohta, H. R. Byon, Nano Lett. 2013, 13, 4679.
[15] R. Gao, Z. Li, X. Zhang, J. Zhang, Z. Hu, X. Liu, ACS Catal. 2016, 6, 400.
[16] M. Olivares-Marín, A. Sorrentino, R. C. Lee, E. Pereiro, N. L. Wu, D. Tonti, Nano Lett. 2015, 15, 6932.
[17] B. Sun, S. Chen, H. Liu, G. Wang, Adv. Funct. Mater. 2015, 25, 4436.
[18] S. Ma, L. Sun, L. Cong, X. Gao, C. Yao, X. Guo, L. Tai, P. Mei, Y. Zeng, H. Xie, R. Wang, J. Phys. Chem. C 2013, 117, 25890.
[19] P. Tan, L. Shi, W. Shyy, T. Zhao, Energy Technol. 2016, 4, 393.
[20] X. Lin, Y. Cao, S. Cai, J. Fan, Y. Li, Q. H. Wu, M. Zheng, Q. Dong, J. Mater. Chem. A 2016, 4, 7788.
