Uniform MnO$_2$ nanostructures supported on hierarchically porous carbon as efficient electrocatalyst for rechargeable Li-O$_2$ batteries

Xiaopeng Han, Fangyi Cheng(✉), Chengcheng Chen, Yuxiang Hu and Jun Chen(✉)

Nano Res., Just Accepted Manuscript • DOI: 10.1007/s12274-014-0604-y
http://www.thenanoresearch.com on October 8 2014

© Tsinghua University Press 2014

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.
Uniform MnO$_2$ nanostructures supported on hierarchically porous carbon as efficient electrocatalyst for rechargeable Li-O$_2$ batteries

Xiaopeng Han, Fangyi Cheng*, Chengcheng Chen, Yuxiang Hu and Jun Chen*

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China.

MnO$_2$ nanostructures supported on hierarchically porous carbon was synthesized and exhibited much enhanced Li-O$_2$ battery performance, owning to the improved catalytic activity and favorable transportation of ions, oxygen and electrons.

Provide the authors’ website if possible.

Author 1, website 1
Author 2, website 2
Uniform MnO₂ nanostructures supported on hierarchically porous carbon as efficient electrocatalyst for rechargeable Li-O₂ batteries

Xiaopeng Han, Fangyi Cheng, Chengcheng Chen, Yuxiang Hu and Jun Chen

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China.

Received: day month year
Revised: day month year
Accepted: day month year (automatically inserted by the publisher)

© Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2014

KEYWORDS
Lithium-oxygen batteries, manganese oxide, nanocomposite, catalyst, oxygen electrochemistry

ABSTRACT
Through in situ redox deposition and growth of MnO₂ nanostructures on hierarchically porous carbon (HPC), a MnO₂/HPC hybrid was synthesized and employed as cathode catalyst for non-aqueous Li-O₂ batteries. Owning to the mild synthetic condition, MnO₂ was uniformly distributed on the surface of the carbon support, without destroying the hierarchical porous nanostructure. As a result, the as-prepared MnO₂/HPC nanocomposite exhibits much enhanced Li-O₂ battery performance, including low charge overpotential, good rate capacity and long cycle stability up to 300 cycles with controlling capacity of 1000 mAh g⁻¹. The combination of multi-scale porous network of the shell-connected carbon support and the high-dispersion MnO₂ nanostructure benefits the transportation of ions, oxygen and electrons and contributes to the superior electrode performance.

1 Introduction

Rechargeable lithium-oxygen (Li-O₂) batteries have stimulated extensive interest due to their high theoretical specific energy far exceeding that of current lithium-ion batteries [1-4]. However, formidable challenges need to be addressed before the Li-O₂ systems could realize commercial deployment [5, 6]. One of the most important parameters that critically determine the battery performance is the reversible formation/decomposition of discharged products in the oxygen electrodes. The severe sluggish kinetics of both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) not only decrease the energy efficiency but also limit the rate capability. In addition, the irregular precipitation of insoluble and insulating discharge species (mainly Li₂O₂) is

Address correspondence to Fangyi Cheng, fycheng@nankai.edu.cn; Jun Chen, chenabc@nankai.edu.cn
prone to block the pores of the cathode, thus resulting in low capacity and poor cycling stability. Therefore, to build advanced Li-O2 batteries, it is desirable to develop efficient cathode that allows fast, reversible redox reactions between gaseous oxygen and solid peroxide. An ideal cathode should possess several critical properties: high activity for catalyzing dual ORR/OER, large surface area for providing abundant active sites, high electrical conductivity for fast electron transfer, robust porous structure to accommodate discharge products and facilitate transportation of oxygen and electrolyte [7-12].

Recent studies on the catalysts materials of oxygen electrodes are mainly focused on noble metals or alloys [13-19], metal oxides [20-29], sulfides [30] and nanostructured carbonaceous materials [7, 31-34]. Among the nonprecious catalysts, manganese oxides are attractive because of many advantages such as low cost, natural abundance, considerable electrocatalytic activity and environmental friendliness [20-26]. However, manganese oxides suffer from low electronic conductivity. Although mixing with carbon additive is a common strategy to enhance electron conduction in metal oxide-based electrode, the side reaction of carbon with LiO2 or electrolyte will form Li2CO3 and degenerate the electrochemical performance [35, 36]. Peculiar architectures materials with a metal oxide shell and carbon core (e.g., carbon nanotubes@RuO2 [28]) could alleviate the unwanted reaction while combine the merits of two components. By taking advantages of carbon and cheap metal oxides and bearing in mind the above-discussed rational design of air cathode, herein we develop an oxygen electrocatalyst that consists of homogeneous MnO2 nanostructures supported on hierarchically porous carbon matrix (designated as MnO2/HPC), which, to the best of our knowledge, has never been employed in Li-O2 system. The MnO2/HPC composite materials are fabricated by in situ self-sacrificed template method and provide several virtues, as illustrated in Fig. 1. Along with the numerous exposed MnO2 catalytic sites, the multiscale (micro/meso/macro) pores offer sufficient space and interface for O2 diffusion, LiO2 accommodation, and electrolyte immersion, while the interconnected carbon matrix serves as electron conducting network. Otherwise, the MnO2 wrapped HPC hybrid hinders the reduced oxygen species (O2−)

2 Experimental

2.1 Materials Synthesis

The honeycomb-like structure hierarchically porous carbon (HPC) was firstly prepared via a self-assembly template strategy. Typically, 0.5 g of phenolic resin was ground into powder and added to 20 mL of absolute ethanol at 50 °C. After completely dissolved, 2 mL of tetraethyloxysilicate (TEOS) was added and stirring for 15 min to form a transparent light yellow solution. 50 mL mixture of 25 wt% aqueous ammonia and ethanol (2:1, volume ratio) was quickly poured into the solution and then reacted at 50 °C for 3h. The mixed slurry was evaporated at 60 °C and the obtained solid was carbonized at 700 °C for 2h in an argon atmosphere. The black product was treated with 10 wt % HF to remove the silica, then washed with distilled water and dried to obtain HPC spheres.

The MnO2/HPC nanocomposite was synthesized via a direct redox reaction between the obtained porous carbon and the KMnO4 solution. In this case, the hierarchically carbon acts not only as a sacrificial reducing agent but also as a substrate for the growth of MnO2. In brief, 30 mg as-prepared porous carbon was firstly ultrasonically dispersed in 30 mL KMnO4 solution (0.05 M) in an ice bath. Then, the mixed solution was reacted for 90 min at 50 °C and the final
product was obtained by centrifugation and washed with distilled water before drying in vacuum at 80 °C overnight. Pure MnO₂ was obtained by prolonging the reaction time to 3 h.

For comparison, the composites of loading MnO₂ on other types of carbon (Vulcan carbot XC-72 and Super P, designated as MnO₂/Vc-72 and MnO₂/Super P, respectively) were prepared through similar procedures using the corresponding carbon supports.

2.2 Materials Characterization

The structures and morphologies of the as-prepared samples were respectively characterized by powder X-ray diffraction (XRD, Rigaku/MiniFlex600 with Cu Kα radiation), Raman microscope (DXR, Thermo-Fisher Scientific at 532 nm excitation), field-emission scanning electron microscopy (SEM, JEOL JSM7500F) and transmission electron microscopy (TEM, Philips Tecnai-F20). The carbon content of the composite was determined by elemental analyser (Elementar, vario El cube) and energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) results were collected on a Perkin Elmer PHI 1600 ESCA system. X-ray absorption (XAS) was performed on Shanghai Synchrotron Radiation Facility (SSRF). Surface area analysis was measured by using the N₂ adsorption/desorption isotherms at 77 K on a BELsorp-Mini instrument. Thermogravimetric (TG) tests were performed using a Netzsch STA 449 F3 Jupiter analyzer. Fourier Transform Infrared (FTIR) spectroscopies were performed on a FTIR-650 spectrometer (Tianjin Gangdong) at a resolution of 2 cm⁻¹.

2.3 Cell assembly and electrochemical measurements

The electrochemical performance of non-aqueous Li-O₂ cell was analyzed by a 2023-type coin cell. All the cells were fabricated in an argon-filled glove box (Mikrouna Universal 2440/750) using a lithium metal anode, a glass fiber separator, a catalyst contained oxygen cathode and an electrolyte of 1 M LiTFSI (lithium bis-(trifluoromethanesulfonyl) imide) in TEGDME (tetaethylene glycol dimethyl ether). The oxygen cathodes were prepared by casting a homogenous ink of 90 wt% catalyst materials and 10 wt% polyvinylidene fluoride (PVdF) onto the Ni foam current collector with a catalyst mass loading of about 0.8 mg cm⁻². After completing assembly, the cells were placed in a sealed container filled with 1 atm high-purity oxygen.

Electrochemical tests were performed at room temperature after 5 h rest on a Land-CT2001A battery system. All the specific capacity and current density were calculated based on the total amount of the catalyst. The cyclic voltammograms (CVs) were conducted within 2.0-4.6 V on Parstat 263A workstation (AMTEC). Electrochemical impedance spectroscopy (EIS) was tested using Parstat 2273 potentiostat/galvanostat workstation within a frequency range of 100 kHz to 100 mHz.

3 Results and discussions

Fig. 2a displays the typical scanning electron microscopy (SEM) image of MnO₂/HPC. The hybrid maintains the morphology of the honeycomb-like, shell-connected hollow HPC microspheres (Fig. S1 in the Electronic Supplementary Material (ESM)). Transmission electron microscopy (TEM) image (Fig. 2b) clearly reveals that uniform MnO₂ is homogeneously supported on the porous carbon. The high-resolution TEM imaging (Fig. 2c) shows lattice fringes with interlayer distance of 0.7 nm, which agrees with the neighbouring spacing of the (001) plane of birnessite-type MnO₂. The texture of MnO₂/HPC is analyzed by nitrogen adsorption-desorption isotherms. The determined Brunauer-Emmett-Teller (BET) specific surface area is 95.7 m²/g (Fig. 2d). The corresponding pore size distribution data calculated by the BJH method (inset in Fig. 2d) shows hierarchical pore features with micropores diameter below 2.0 nm, mesopores centered at 4 nm and macropores located in a wide range of 20–100 nm. In our synthesis, it is noted that a higher reaction temperature and a longer deposition time would lead to overconsumption of the carbon substrate and destruction of the hierarchically porous nanostructure (Fig. S2 in the ESM).

The formation of birnessite-type MnO₂ in MnO₂/HPC is confirmed by X-ray diffraction (XRD, Fig. S3 in the ESM). Broad peaks imply poorly
crystallized property, which may originate from the small particle size and amorphous nature of the powders as a result of the mild synthesis condition [37]. Raman spectra (Fig. S4 in the ESM) indicate the presence of both carbon and MnO₂. Beside the two characteristic signals of carbon, two peaks are observed at 570 cm⁻¹ and 640 cm⁻¹ in the low wavelength region, which can be attributed to the Mn-O stretching and the symmetric stretching vibration of the MnO₆ groups, respectively. In addition, the peak splitting width of 4.85 eV in Mn 3s X-ray photoelectron spectroscopy (XPS, Fig. S5a in the ESM) and the X-ray absorption near edge structure (XANES, Fig. S5b in the ESM) suggest the presence of oxygen vacancies and a multiple valence (+3 and +4) of Mn, which could contribute to enhanced electrochemical activity [24, 38, 39]. Furthermore, elemental mapping evidences the homogenous dispersion of MnO₂ in the carbon framework matrix (Fig. 2e). The weight percentage of manganese oxide is determined to be about 46% in the synthesized MnO₂/HPC nanocomposite by combining energy dispersive spectroscopy (EDS), element analysis, and thermogravimetric analysis (TGA) in air (Fig. S6 in the ESM).

Figure 2 (a) SEM and (b, c) TEM images of the synthesized MnO₂/HPC composite materials. (d) Nitrogen adsorption-desorption isotherms and pore size distribution (inset) of MnO₂/HPC. (e) Elemental mapping of MnO₂/HPC.

The synthesized MnO₂/HPC was employed as an ORR/OER bifunctional cathode catalyst in Li-O₂ batteries. Fig. 3a shows the first discharge-charge voltage profiles of the Li-O₂ cells assembled with MnO₂/HPC and the comparative HPC and conventional Super P carbon with the restricting capacity of 1000 mAh g⁻¹. The composite-based cell exhibits a significantly lowered charge plateau voltage and slightly increased discharge plateau voltage, resulting in an overpotential of 0.68 V. This is ca. 0.75 V and 1.01 V smaller than those of the cells made with HPC and Super P cathodes, respectively. The round-trip efficiency (the ratio of discharge to charge voltages) of MnO₂/HPC cell attains a remarkably high value of about 80%. The kinetics of the three electrodes were also investigated by cyclic voltammetry (CV) in TEGDME (tetraethylene glycol dimethyl ether)-based electrolyte (Fig. 3b). The MnO₂/HPC hybrid shows a higher ORR onset potential (~ 2.75 V), a much lower OER peak potential (~ 3.80 V), and much larger cathodic/anodic peak currents compared with HPC and Super P.
These results indicate superior electrocatalytic activity of MnO$_2$/HPC.

The rate capability of prepared catalysts was tested at various current densities, as shown in Fig. 3c and Fig. S7 in the ESM. The Li$_2$O$_2$ cell with MnO$_2$/HPC exhibits higher discharge capacity than those with HPC and Super P to the terminal discharge voltage of 2.0 V. Specially, even at a high current density of 5000 mA g$^{-1}$, the MnO$_2$/HPC-based battery can deliver a discharge capacity of 2260 mAh g$^{-1}$, which is 4- and 75-fold larger than those of HPC (554 mAh g$^{-1}$) and Super P (30 mAh g$^{-1}$), respectively. At a current density of 500 mA g$^{-1}$, the Li$_2$O$_2$ battery with MnO$_2$/HPC maintains a specific capacity of >2000 mAh g$^{-1}$ for 60 cycles over a wide voltage window of 2.0–4.4 V (Fig. S8 in the ESM). In contrast, the discharge capacity of HPC or Super P rapidly decreases to < 150 mAh g$^{-1}$ after 10 cycles. When restricting a cycling capacity of 1000 mAh g$^{-1}$, the MnO$_2$/HPC cell sustains 300 cycles with the discharge terminal above 2.0 V while the HPC and Super P cells can merely afford 66 and 34 cycles, respectively (Fig. 3d and Fig. S9 in the ESM). The performance of MnO$_2$/HPC is also much better than pure MnO$_2$, MnO$_2$/Vc-72 and MnO$_2$/Super P counterparts (Fig. S10 in the ESM), suggesting the advantages of the hierarchically porous carbon support. The battery performance presented here is among the best results reported in Li-air systems with manganese oxides electrocatalysts (Table S1 in the ESM) [20-23].

The cathodes of Li$_2$O$_2$ cells were disassembled and characterized at discharged and charged states. Among the discharged electrodes, there is much difference in morphology. The precipitate on Super P (Fig. 4a) presents typical toroid shape [8, 40]. In comparison, mossy species composed of nanosheets uniformly covers the surface of MnO$_2$/HPC (Fig. 4b).

TEM imaging (Fig. S11a in the ESM) reveals porous structure of the discharged mossy solid. The concentric rings in electron diffraction pattern (Fig. S11b in the ESM) are unambiguously indexed to Li$_2$O$_2$ and indicate polycrystalline nature of the generated Li$_2$O$_2$. After recharged, the super P-based electrode contains aggregated particles and is
clogged by a dense layer (Fig. 4c) whereas the mossy discharged species disappears and the honeycomb-like hierarchically porous morphology is fully regained for MnO₂/HPC electrode (Fig. 4d and Fig. S11c, d in the ESM). XRD analysis (Fig. 4e) clearly indicates the formation of Li₂O₂ which disappears in the recharged cathodes. Fourier Transform Infrared (FTIR) spectroscopies (Fig. 4f) of the recharged electrodes further evidence the presence of Li₂CO₃, HCO₂Li (Li formate) or CH₃CO₂Li (Li acetate). Especially, the formation of carbonate and carboxylate lithium on Super P electrode is much more obvious than the case of MnO₂/HPC hybrid after the same 30 cycles. The accumulation of these species upon cycling would retard the mass transportation and charge transfer, leading to increased electrode polarization and performance degradation of the cell. This conjecture is verified by the electrochemical impedance spectroscopy (Fig. S12 and Table S2 in the ESM) that show gradual increase of electrode resistance. Compared with neat Super P, the increase rate of charge transfer resistance is much slower in the hybrid electrode. Thus, the MnO₂ wrapped HPC hybrid can effectively suppress the side reaction of carbon.

Figure 4 Characterization of the discharged/charged electrodes after 5 cycles at terminal capacity of 1000 mAh g⁻¹ and constant current density of 350 mA g⁻¹. SEM images of discharged Super P (a) and MnO₂/HPC (b) electrodes. SEM images of charged Super P (c) and MnO₂/HPC (d) electrodes. (e) XRD patterns of MnO₂/HPC, Super P electrodes and the reference Li₂O₂. The peaks of MnO₂ and Super P are marked with * and #, respectively. (f) FTIR of the 5th-cycle and 30th-cycle MnO₂/HPC, Super P cathodes and the standard lithium carbonates and carboxylate.

The above results clearly indicate the superior activity of MnO₂/HPC in catalyzing the reversible formation/decomposition of Li₂O₂ during the discharge/charge process of Li-O₂ cells. Possibly, the remarkable performance of MnO₂/HPC could be attributed to the combined benefits of MnO₂ and HPC. The interconnected hierarchically porous structure of carbon network not only favors electron conduction, oxygen diffusion and electrolyte permeation, but also provides abundant sites and larger room for Li₂O₂ precipitation (Fig. 1). Manganese oxide itself is known to have considerable activity for the ORR/OER [38, 41-45]. Also, the metal oxide surfaces have been shown to be less “sticky” than pure carbon surfaces riddled with dangling bonds [46], which could weaken the binding of the intermediate superoxide to the substrate and facilitating the transport of superoxide species, leading to a thin and uniform nucleation/crystallization of discharged product (i.e., Li₂O₂) on the hybrid electrode. These two factors might contribute to the homogeneous distribution of
peroxides. Compared to the dense toroid-shaped LiO$_2$ (Fig. 4a), the formed porous and loose solid (Fig. 4b) could provide more exposed surfaces and interfaces, enabling easy decomposition of discharged product on recharging (Fig. 4d). Consequently, the LiO$_2$ batteries assembled with MnO$_2$/HPC manifest high round-trip efficiency and good rechargeability.

4 Conclusions

In summary, hierarchically porous MnO$_2$/HPC nanocomposite was synthesized and catalytically investigated as cathode electrocatalyst in aprotic Li-O$_2$ batteries. Compared with neat HPC and conventional Super P carbon electrodes, the obtained MnO$_2$/HPC electrodes exhibit lower overpotential (~0.68 V at 100 mA g$^{-1}$), better rate capability (2260 mAh g$^{-1}$ at 5 A g$^{-1}$) and longer operational life (~300 cycles with a fixed terminal capacity of 1000 mAh g$^{-1}$). The remarkable performance of MnO$_2$/HPC was ascribed to a combination of positive effects including intrinsic ORR/OER catalytic activity, the unique architecture, the favorable morphology of LiO$_2$ and the reduced side reactions. Our results would enlighten the rational design of multifunctional porous carbon/metal oxide hybrid materials as cheap yet efficient cathode electrocatalysts for advanced Li-O$_2$ batteries.

Acknowledgements

This work was supported by the National 973 (2011CB935900), NSFC (21322101 and 21231005), and MOE (ACET-13-0296 and B12015).

Electronic Supplementary Material:
Supplementary material (additional material characterizations and electrochemical tests, such as XRD, Raman, SEM, TEM, XPS, TGA, EIS results etc) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-****-**** (automatically inserted by the publisher).

References


[39] Han, X. P.; Cheng, F. Y.; Zhang, T. R.; Yang, J. G.; Hu, Y. X.; Chen, J. Hydrogenated uniform Pt clusters supported on porous CaMnO₃ as a bifunctional electrocatalyst for...


Electronic Supplementary Material

Uniform MnO₂ nanostructures supported on hierarchically porous carbon as efficient electrocatalyst for rechargeable Li-O₂ batteries

Xiaopeng Han, Fangyi Cheng(✉), Chengcheng Chen, Yuxiang Hu and Jun Chen(✉)

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China. Fax: 86-22-23509571; Tel: 86-22-23504482.

Supporting information to DOI 10.1007/s12274-****-****-* (automatically inserted by the publisher)

Figure S1 SEM (a, b) and TEM (c, d) images of HPC. e) Elemental mapping and EDS spectra of HPC. SEM images display the macroporous honeycomb-like monolith morphology, which is made up of shell-connected carbon hemispheres. The inset of (b) shows the diameter distribution of carbon spheres (diameter about 410 nm). TEM images reveal the macroporous inner structure and the inter-connected carbon framework of the as-prepared HPC. No obvious Si signal was observed from the EDS spectra, indicating the silica template has been completely removed.
**Figure S2** SEM images of MnO$_2$/HPC samples with different preparation procedures. (a) reaction temperature 50 ºC, deposition time 180 min; (b) reaction temperature 65 ºC, deposition time 90 min.

**Figure S3** XRD patterns of synthesized pure HPC, MnO$_2$/HPC samples. The broad diffraction peaks at 2θ around 11.8º, 37.2º and 66.0º in the MnO$_2$/HPC composite can be readily indexed to the birnessite-type MnO$_2$ (Joint Committee on Powder Diffraction Standards, JCPDS card No. 42-1317).

**Figure S4** Raman spectra of prepared HPC and MnO$_2$/HPC.
Figure S5 (a) Mn 3s XPS spectra and (b) Mn K-edge XANES of synthesized MnO$_2$/HPC composite. Mn K-edge XANES of β-Mn$^{IV}$O$_2$ and Mn$^{II,III}$O$_4$ are shown as reference standards. The Mn 3s XPS splitting peaks energies locate at 88.5 eV and 83.65 eV, respectively, with separation of 4.85 eV, which indicates a mixed valence of Mn between +3 and +4 [1, 2]. This result is also confirmed by comparing the K-edge absorption position to those of β-Mn$^{IV}$O$_2$ and Mn$^{II}$O$_4$ reference standards.

Figure S6 EDS spectra (a) and TG profile (b) of as-prepared MnO$_2$/HPC hybrid at heating rate of 5 °C min$^{-1}$ in air flow at speed of 50 mL min$^{-1}$. In EDS spectra, the signal of potassium (K) element can be found. The presence of K cations in the formed birnessite-type MnO$_2$ originates from the KMnO$_4$ precursor, which could stabilize the lattice structure of manganese oxides [3, 4]. In TG profile, the mass loss before 150 °C can be attributed to the removal of physi-adsorbed water. The following rapid mass loss, peaked at 380 °C, correspond to the carbon combustion in the MnO$_2$/HPC composite.
Figure S7 Rate performance of (a) HPC and (b) Super P electrodes.

Figure S8 Cycling performance of three catalysts at 500 mA g\(^{-1}\) over a wide voltage window from 2.0 to 4.4 V.

Figure S9 Discharge-charge curves of the Li-O\(_2\) batteries with three cathode catalysts at selected cycles at a current density of 350 mA g\(^{-1}\) with controlling cycling capacity of 1000 mAh g\(^{-1}\). (a): MnO\(_2\)/HPC hybrid, (b): pure HPC, (c): conventional Super P carbon.
Figure S10 TEM images of prepared MnO$_2$/Vc-72 (a) and MnO$_2$/Super P (b). (c) First discharge/charge profiles at 100 mA g$^{-1}$ and (d) Cyclability and terminal discharge voltages at a current density of 350 mA g$^{-1}$ based on pure MnO$_2$, MnO$_2$/Vc-72 and MnO$_2$/Super P. To overcome the poor electronic conductivity, the pure MnO$_2$ electrode was prepared by mixing pure MnO$_2$ with the Vulcan carbot XC72 (weight ratio, 3:7). As for MnO$_2$/Vc-72 and MnO$_2$/Super P, MnO$_2$ nanowires were grown on the carbon supports. The morphologies of deposited MnO$_2$ on Vc-72 and Super P are much different from the case of HPC that confines homogenous surface growth of MnO$_2$. With the cut-off capacity of 1000 mAh g$^{-1}$, the charge/discharge overpotentials are 1.56 V, 1.36 V and 1.20 V and the cycling number are 33, 64 and 74 for pure MnO$_2$, MnO$_2$/Super P and MnO$_2$/Vc-72 cathodes, respectively. The superior performance of MnO$_2$/HPC can be clearly seen, indicating the advantages of the hierarchically porous carbon support which not only facilitates the transportation of oxygen and electrolyte but also offers empty space to accommodate the discharge product, thus leading to enhanced electrode performance.
Figure S11 (a) TEM image of discharged MnO$_2$/HPC cathode and (b) the corresponding electron diffraction pattern. (c) TEM image of recharged MnO$_2$/HPC cathode. (d) Raman spectra of pristine MnO$_2$/HPC cathode and the electrodes after five cycles. Raman results indicate that the Li$_2$O$_2$ generates after discharging and disappears in the recharged electrode, whereas there is no signal showing structural change of the MnO$_2$/HPC catalyst before and after cycling.

Figure S12 Electrochemical impedance spectroscopies (EIS) of (a) MnO$_2$/HPC and (b) Super P of discharged/recharged cathodes of pristine, the 5th and 30th cycles. At 5th discharged state, the increase extent of charge transfer resistance ($R_{ct}$) of MnO$_2$/HPC electrode (72.8 $\Omega$ to 144.1 $\Omega$) is slightly lower than that of Super P (192.1 $\Omega$ to 571.2 $\Omega$), which is in consistent with the different case of deposited discharged products and the restrained ability towards the side reaction. After 5th recharging, the resistance of MnO$_2$/HPC-based batteries could recover to that of the fresh batteries to a large extent (96.0 $\Omega$ vs. 72.8 $\Omega$), whereas the Super P electrodes cannot recover absolutely (441.5 $\Omega$ vs. 192.1 $\Omega$). This phenomenon becomes much more apparent for extended
30th cycle (see Table S2 for details). The EIS results here again suggest a relatively reversible reaction for Li₂O₂ formation/decomposition during the repeated discharge/charge process over the MnO₂/HPC cathode as well as the suppressed side reaction with the carbon.

Table S1 Summary of electrochemical performance of Li–O₂ batteries based on manganese oxides catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>maximum capacity based on total mass / mAh g⁻¹</th>
<th>rate capability / mAh g⁻¹</th>
<th>cycle performance / controlling capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MnO₂ [5]</td>
<td>730</td>
<td>----</td>
<td>10 cycles/2000 mAh g⁻¹</td>
</tr>
<tr>
<td>α-MnO₂/Graphene [6]</td>
<td>2304</td>
<td>----</td>
<td>25 cycles/3000 mAh g⁻¹</td>
</tr>
<tr>
<td>δ-MnO₂ [7]</td>
<td>7000</td>
<td>1900 at 800 mA g⁻¹</td>
<td>120 cycles/&gt;1000 mAh g⁻¹</td>
</tr>
<tr>
<td>3D-Graphene-MnO₂ [8]</td>
<td>3660</td>
<td>770 at 387 mA g⁻¹</td>
<td>132 cycles/1000 mAh g⁻¹</td>
</tr>
<tr>
<td>MnCo₂O₄/Graphene [9]</td>
<td>3780</td>
<td>2743 at 800 mA g⁻¹</td>
<td>40 cycles/1000 mAh g⁻¹</td>
</tr>
<tr>
<td>La₀.₇₅Sr₀.₂₅MnO₃ [10]</td>
<td>7333</td>
<td>6666 at 133 mA g⁻¹</td>
<td>124 cycles/1000 mAh g⁻¹</td>
</tr>
<tr>
<td>manganese oxide nanowires [11]</td>
<td>~5000</td>
<td>----</td>
<td>47 cycles/2000 mAh g⁻¹ carbon</td>
</tr>
<tr>
<td>our sample</td>
<td>9283</td>
<td>2260 at 5000 mA g⁻¹</td>
<td>300 cycles/1000 mAh g⁻¹</td>
</tr>
</tbody>
</table>

Table S2 Comparison of the fitted charge transfer resistance (Rct, Ω) at different discharged/recharged states with prolonged cycles based on MnO₂/HPC and Super P cathodes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>States</th>
<th>5th discharge</th>
<th>5th recharge</th>
<th>30th discharge</th>
<th>30th recharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂/HPC</td>
<td>Pristine</td>
<td>72.8</td>
<td>144.1</td>
<td>96.0</td>
<td>188.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>119.0</td>
</tr>
<tr>
<td>Super P</td>
<td></td>
<td>192.1</td>
<td>571.2</td>
<td>441.5</td>
<td>755.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>605.0</td>
</tr>
</tbody>
</table>

Supplementary References


Address correspondence to Fangyi Cheng, fycheng@nankai.edu.cn; Jun Chen, chenabc@nankai.edu.cn