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A Co-Doped MnO₂ Catalyst for Li-CO₂ Batteries with Low Overpotential and Ultrahigh Cyclability

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Abstract
Lithium-CO₂ batteries not only capture carbon dioxide to solve the greenhouse effect, but also serve as clean and next-generation energy storage devices on the merits of economical, environmentally-friendly and sustainable aspects. However, the Li-CO₂ batteries are suffering from two main drawbacks: high overpotential and poor cyclability, severely postponing the rhythm of their applications. Herein, we have prepared a new Co-doped alpha-MnO₂ nanowire catalyst for rechargeable Li-CO₂ batteries, which exhibits a high capacity (8160 mA h g⁻¹ at a current density of 100 mA g⁻¹), a low overpotential (~0.73 V) and an ultrahigh cyclability (over 500 cycles at a current density of 100 mA g⁻¹), exceeding those of Li-CO₂ batteries reported so far. The reaction mechanisms are interpreted depending on the in-situ experimental observations in combination with density functional theory calculations. The outstanding electrochemical properties are mostly associated with a high conductivity, a large fraction of hierarchical channels and a unique Co interstitial doping, which might be of benefit for the diffusion of CO₂, the decomposition of Li₂CO₃ discharge product, and the prohibitions of side reactions between electrolyte and electrode. Consequently, these results shed light on both CO₂ fixation and new Li-CO₂ batteries for energy storage.

Keywords: Lithium-air battery; Catalyst; Low overpotential; Cyclability
1. Introduction

Li-ion batteries have dominated the portable electronics market and revolutionized our daily activities in the past decades.\cite{1} However, these traditional Li-ion batteries cannot meet the requirements of high energy density for portable electronic devices and electric vehicles due to their low capacity densities.\cite{2-4} Therefore, the development of a new metal-gas battery with high specific energy density and good cycle stability is believed as a promising strategy to solve this issue. For example, Li-CO$_2$ battery which has been developed on the basis of Li-O$_2$ battery has recently attracted attention. This battery system not only bestows a high energy density in terms of electrochemical energy storage, but also alleviates the greenhouse effect by capturing CO$_2$.\cite{5}

More recently, Li-CO$_2$ batteries have been attempted as new energy carriers to store renewable energy, in which Li$_2$CO$_3$ is the discharge product as indicated as follows:

$$4\text{Li} + 3\text{CO}_2 + 4e^- \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C} \quad (E^0 = 2.80 \text{ V vs. Li/Li})$$\cite{6-8} Unfortunately, this incipient prototype battery can only run about 10 cycles. The main reasons are related to two features. Firstly, the insert decomposition of Li$_2$CO$_3$ discharge product is prone to adhere on the cathode surface, and then remarkably reduces the capacity.\cite{8} Secondly, the aggregation of Li$_2$CO$_3$ product can block the channels of gas diffusion and reduce the conductivity of electrode, resulting in a very high charge potential (>4.3 V).\cite{6} In this regard, an efficient cathode which could provide a high surface area and promote the decomposition of the Li$_2$CO$_3$ discharge product is desirable to achieve the high performance of the Li-CO$_2$ batteries.\cite{9}

Akin to the development of the Li-O$_2$ batteries, there are two approaches to design effective cathodes. On the one hand, the direct modification and optimization of cathode structures have been regarded as a simple method to improve the properties of the Li-CO$_2$ batteries. For instance, Zhou et al.\cite{10,11} successfully examine graphene and carbon nanotubes (CNTs) as the cathodes, in which the Li-CO$_2$ batteries operate for 20
cycles with an overpotential of 1.78 V at 50 mA g\(^{-1}\) under a limitative capacity of 1000 mAh g\(^{-1}\). Dai et al. \cite{12} devise two kinds of graphene-based materials with defective structures for Li-CO\(_2\) batteries—holey graphene and B,N-co-doped holey graphene, which shows a cycling lifetime over 200 cycles at 1 A g\(^{-1}\), but suffer from a large overpotential (about 1.8 V at 1 A g\(^{-1}\)). Liu et al.\cite{13} first introduce CNT decorated with RuO\(_2\) as cathode materials for Li-CO\(_2\) batteries, which can deliver high specific capacity together with a lower overpotential.

On the other hand, the development of new catalysts is another effective method to enhance the electrochemical properties of Li-CO\(_2\) batteries. For example, the cobalt–titanium layered oxide-RuO\(_2\) composite with a low over-potential of 0.6 V has been achieved recently.\cite{14} The nanocomposite of anatase titania nanoparticles (TiO\(_2\)-NPs) has been established as a high efficient catalyst for the Li-CO\(_2\) battery with favorable cycle performance.\cite{15} The porous Mn\(_2\)O\(_3\) catalyst for the Li-CO\(_2\) battery exhibits a durable cyclability for 2000 h (about 50 cycles) at 50 mA g\(^{-1}\) and an overpotential of 1.4 V, due to a highly porous structure and an excellent catalytic activity.\cite{16} The cathode which comprising manganese metal-organic frameworks delivers a high discharge specific capacity of 18022 mA h g\(^{-1}\) at 50 mA g\(^{-1}\), while still undergoes a high overpotential (>1.2 V).\cite{17} Although enormous progress has been made, achieving a highly cycled Li-CO\(_2\) battery with a low overpotential still remains challenging.

In this work, we have prepared a new Co-doped alpha-MnO\(_2\) nanofiber catalyst, which was effective to improve the electrochemical properties of the Li-CO\(_2\) batteries by increasing the conductivity, enhancing the catalytic activity and prohibiting the side reactions. The Li-CO\(_2\) battery with the optimized Co-doped alpha-MnO\(_2\) nanofiber electrode shows a large capacity of 8160 mA h g\(^{-1}\), a low overpotential of ~0.73 V and an ultrahigh cyclability (500 cycles). The catalyst is highlighted by its simplicity and
high-yield production of a well-defined morphology, which is attributed for the industrial development of Li-CO$_2$ batteries.

2. Results and discussion

2.1. Electrode characteristics

An electrode with a Co-doped alpha-MnO$_2$ compound supported by a piece of carbon cloth (CC) was prepared by a simple hydrothermal reaction (the detailed procedure was described in the Experimental Procedure). Specifically, a KMnO$_4$ powder was added to a mixed solution of MnSO$_4$$\cdot$H$_2$O and Co(NO$_3$)$_2$$\cdot$6H$_2$O, and then a CC was immersed in the mixed solution. Subsequently, the reaction mixture was heated in a microwave-assisted reactor at 140 °C for 60 min. Finally, the reacted CC was washed three times with deionized water and dried for 12 hours in a vacuum. The X-ray diffraction (XRD, Figure 1a) patterns shows that a typical (002) peak is detected in the primitive CC sample, which is consistent with our previous result.$^{[18]}$ However, some new peaks are observed after reacting in the single MnSO$_4$$\cdot$H$_2$O solution. The lattice parameters are $a=b=0.98$ nm and $c=0.28$ nm, respectively. They are in agreement with those of pure tetragonal alpha-MnO$_2$ (JCPDS NO. 44-0141). Comparatively, the similar peaks are also confirmed in the mixed solution of MnSO$_4$$\cdot$H$_2$O and Co(NO$_3$)$_2$$\cdot$6H$_2$O. The intensity of XRD diffraction peaks decreases with the increase of Co-doped content (Figure. S1), revealing the crystalline of compounds weaker.

The scanning electron microscopy (SEM, Figure 1b-d) images show that the smooth wires become coarse, and then they are covered by fine nanoscale wires after reacting for 60 min, resulting in the formation of thorn-bush nanofibers. The transmission electron microscopy (TEM, Figure 1e) image reveals that the diameter and length of wires are ~ 50 nm and over 2 µm, respectively. The selected area electron diffraction pattern and high revolution TEM results (Figure. 1f) demonstrate that the growth orientation of nanowires is along $<001>$ direction. The planar parameters are 0.32 nm and 0.27 nm, respectively. Both of them are
similar to those of (310) and (001) planes of pure alpha-MnO2. The low-loss electron energy
loss spectroscopy (EELS) profile shows that some new peaks (13.2, 27.2 and 65.7 eV, Figure. 1g) are observed in contrast to the primitive alpha-MnO2 nanowire, indicating the formation of Co-doping alpha-MnO2 nanowires. Moreover, the Co dopant has also been confirmed by X-ray photoelectron spectroscopy (XPS) analysis (Figure. 1h), in which both Mn peaks and Co peaks are involved. The high-resolution XPS spectra of Mn 2p (Figure. 1i) reveals the concentration of Mn4+ (642 eV) and Mn3+ (645.0 and 654.0 eV) are 56% and 44%, respectively. The Co-doping increases the amount of Mn3+. Comparatively, Co3+, Co2+ and Co0 are verified in terms of the high resolution Co 2p XPS spectra (Figure. 1j), wherein the fraction of Co2+ and Co3+ is higher than that of Co0+(below 5%). Therefore, the effect of Co0+ on catalytic role has been neglected. The similar multivalent doping has been found in the Co-NiO systems.[20] As a result, this composite cathode which is prepared with the Co2+(Co(NO3)2·6H2O): Mn2+ (MnSO4·H2O) mole ratio of 0.2:0.8 in the initial solution is mainly composed of Co-containing alpha-MnO2 and CC, and it can be simplified as the Co0.2Mn0.8O2/CC.

To probe the effect of the addition of Co fraction on Co-doped content and microstructure, the molar ratios of Co2+:Mn2+ in the initial solutions with a constant total concentration of two ions of 0.1:0.9 and 0.5:0.5 corresponding to Co0.1Mn0.9O2 and Co0.5Mn0.5O2 samples have been investigated. The pure MnO2 sample is introduced as a reference. The detailed Co concentration in the samples were determined using energy dispersive spectrometer (EDS) (Table S1), the elemental content of Co is increased from 0.55 at.% (Co0.1Mn0.9O2) to ~1.12 at.% (Co0.2Mn0.8O2), and it remains stable with further increasing the Co2+ concentration. The SEM images (Figure. S2a-b) show that the morphologies of Co-doped alpha-MnO2 samples remain a nanowire structure when the Co-doping fraction is below 0.2. In contrast, the radiating nanowires are severely destroyed and some plate-like precipitates are detected with the Co-doping fraction of 0.5. Note that the same alpha-MnO2 structure is identified in the
Co$_{0.5}$Mn$_{0.5}$O$_2$ sample by HRTEM (Figure. S2c-e). This similar trend has also been reported in the Al-doped MnO$_2$. The energy-dispersive spectrum (EDS) mapping was used to explore the distribution of Co, Mn and O elements in Co$_{0.2}$Mn$_{0.8}$O$_2$ nanowires (Figure S3), and the results show that Co, Mn and O elements are homogeneously distributed on the nanowires, suggesting that the Co element has uniformly doped into the MnO$_2$ nanowire, analogous to the data of EDS line scanning (Figure S3a).

2.2. Battery performance

The electrochemical properties of the Li-CO$_2$ batteries with the different cathodes are investigated. The cyclic voltammetry (CV) curves under CO$_2$ or Ar (Figure. 2a and Figure S4a) which are measured from 2 to 4.5 V vs. Li/Li$^+$ at a scan rate of 0.2 mV s$^{-1}$ reveal that there are two peaks for the pure alpha-MnO$_2$/CC cathode, which is totally different from the original CC without reactive peaks. It shows that the oxidation/reduction reactions can take place with the loading of an alpha-MnO$_2$ catalyst. Attractively, compared with those of the pure alpha-MnO$_2$/CC cathode, the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode exhibits a higher CO$_2$ reduction reaction onset potential (CO$_2$RR, ~2.69 V), a lower CO$_2$ evolution reaction onset potential (CO$_2$ER, ~3.79 V), and a higher CO$_2$RR/CO$_2$ER peak current (~1.04 mA).

Figure. 2b presents the voltage profiles of the Li-CO$_2$ battery with the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode at different current densities. The batteries can yield the capacities of 8203 and 2327 mA h g$^{-1}$ at the current densities of 100 and 500 mA g$^{-1}$ under CO$_2$, respectively. By contrast, the discharge voltages of Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode were rapidly declined to 2 V without any recognizable plateau under the atmosphere of Ar (Figure S4b), indicating that the electrochemical performance did come from the reduction of CO$_2$. The voltage profiles and long-term cycling performance of the Li-CO$_2$ batteries with the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC and MnO$_2$/CC cathodes are tested in a full discharge-charge mode at 100 mA g$^{-1}$ and 500 mA g$^{-1}$ in a range of 2-4.3 V (Figure. S5). The discharge capacity of the MnO$_2$/CC cathode is
reduced to ~250 mA h g\(^{-1}\) after merely five cycles at 100 mA g\(^{-1}\). In contrast, for the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode, a discharge capacity of 1200 mA h g\(^{-1}\) is still maintained at 100 mA g\(^{-1}\) after 200 cycles. Both capacity and cyclability are remarkably improved by using the Co-doped MnO\(_2\) cathode.

Figure. 2c shows the first discharge-charge voltage profiles of the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode at 100, 200 and 500 mA g\(^{-1}\) under a limited capacity of 1000 mA h g\(^{-1}\). The overpotential of the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode is ~0.73 V, which is about only 58\% of that of the pure MnO\(_2\)/CC. In addition, the cyclability performance of Li-CO\(_2\) batteries with different cathodes are evaluated at 100, 200 and 500 mA g\(^{-1}\) with a limited capacity of 1000 mA h g\(^{-1}\) (Fig. 2d-e and Figure. S6). The overpotential of the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode does not increase significantly even after testing 500 cycles, indicating its outstanding cycling stability. Compared with other Co-doped MnO\(_2\) samples (Figure. 1e) and the MnO\(_2\)/CC cathode (Figure. S7-8), the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode shows the largest specific capacity and the lowest overpotential (Figure. S8c).

The attractive characters of the Li-CO\(_2\) batteries lie in the long-term cyclability together with a low overpotential. The electrochemical performances of the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode were compared with those of current catalysts reported so far. As summarized in Figure. 1f, the cycling performance of Li-CO\(_2\) batteries with the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode is the best among all the Li-CO\(_2\) batteries. Simultaneously, the overpotential of the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode is the lowest (~0.73 V), which overwhelms those of other catalysts.[10, 11, 13,14, 15, 22-28]

2.3. Reaction process

Figure. 3a shows the initial galvanostatic discharge-charge curve of the Li-CO\(_2\) battery with the Co\(_{0.2}\)Mn\(_{0.8}\)O\(_2\)/CC cathode at the current density of 100 mA g\(^{-1}\). The positions A, B, C and D represent the different stages of the cell. XRD patterns (Figure. 3b) reveal that the peaks of Li\(_2\)CO\(_3\) are emerged after discharging from the position A to the position C. In contrast, the
peaks of Li$_2$CO$_3$ are gradually disappeared after charging from the position C to the position D. The process has further been confirmed by Raman spectra (Figure. 3c), in which the appearance/disappearance of carbonate stretching peaks at 1080 cm$^{-1}$ revealed the formation/decomposition of the Li$_2$CO$_3$.$^{[12]}$ This process is consistent with the reaction product of other Li-CO$_2$ batteries.$^{[10]}$ The \textit{ex-situ} SEM images (Figure. 3d-f) show the morphology variation of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode in Li–CO$_2$ batteries. After discharging to the position C, cotton-like discharge products are formed on the surface of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode, corresponding to the formation of discharge Li$_2$CO$_3$ product. In turn, the smooth nanowires are reappeared when it charges to the position D. Note that the same nanowire morphology and XRD peaks of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC electrode remain even after 50 cycles, suggesting the full decomposition of Li$_2$CO$_3$ products (Figure. S9). It demonstrates that the CC/Co$_{0.2}$Mn$_{0.8}$O$_2$ cathode has a good ability to facilitate the formation/decomposition of Li$_2$CO$_3$.

To further elucidate the reaction process of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode, \textit{in-situ} TEM has been adopted to observe the morphology and structure evolution of the Co$_{0.2}$Mn$_{0.8}$O$_2$ during the charge-discharge process in the potential range from -3.2 to +4 V. The TEM images (Figure. 4, captured from Movie 1) show that the nanowire becomes coarser, and continuously swells by applying a negative potential to the Co$_{0.2}$Mn$_{0.8}$O$_2$ nanowire against the counter electrode Li. After discharged for 162 s, the diameter increases from 44.3 to 58.1 nm. It is noteworthy that the arrow-shaped morphology in the front of the reaction side reveals that the Li ions diffuse along the surface of the nanowire and react with CO$_2$ gas. By comparison, when the positive potential is employed on the nanowire, the swell process stopped and started to shrink, and back to 47.2 nm, indicating good reversibility and cycle stability.

In addition, a large number of fine sphere-shaped particles are accumulated on the nanowire surfaces during the discharge process, and the discharge products are gradually eliminated during the charging process. The \textit{in-situ} SAED patterns (Figure. 4h–j) show that
the primitive nanowire is composed of MnO₂, and it turns to the composite of MnO₂ and Li₂CO₃ at -3.2 V, and then the nanowire changes to MnO₂ phase at +4 V. It exhibits that the cycle mechanism is related to the presence of Li₂CO₃ product, while the side reactions have been effectively eliminated. These results are also supported by the EELS analysis (Figure. 4k-l) and XPS results (Figure. S10a-c), in which the appearance/disappearance of only the Li₂CO₃ peaks not only shows no chemical structure change of the Co₀.₂Mn₀.₈O₂ nanowire during the reaction process, but also it means that the discharge product is hardly residual on the channel walls, promoting the transport of CO₂.

2.4. Catalytic mechanisms

Compared with other catalysts, the new Co₀.₂Mn₀.₈O₂/CC cathode in the Li-CO₂ batteries offers a low overpotential and long-term cycability. The mains reasons are mainly associated with three aspects: a good conductivity, a larger Brunauer–Emmett–Teller (BET) surface areas and unique Co-doping sites.

Firstly, as shown in Figure. 5a, the introduction of Co dopant can improve the conductivity of MnO₂/CC in comparison with that of the primitive MnO₂/CC. Moreover, the conductivity is positive dependent on the Co-doped concentration. Specifically, the conductivity is increasing with increasing Co-doped concentration at the initial stage, and then it reaches a stable value of ~24 S/cm². Moreover, the high conductivity is also identified by EIS tests (Figure. 5b and Figure. S10d), wherein the lower surface film resistance (Rₛ) and charge transfer resistance (Rₜ) (Table S1-S2) are achieved in the Co₀.₂Mn₀.₈O₂/CC cathode compared with the EIS values of the pure alpha-MnO₂. In addition, the overlapped EIS curve after a discharge-charge cycle indicates that the discharge products have been fully decomposed via the CO₂ evolution reaction during the charge process.

Secondly, the high rate performance and good cyclability are related to the phase morphology. Differing from the other electrodes, the Co₀.₂Mn₀.₈O₂/CC cathode not only has a higher conductivity, but also bestows the largest BET surface area (Figure. 5c-d). More importantly,
except for the nanoscale pores (3~5 nm), some large pores of 14~30 nm are existing in the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode. The high fraction of multiple sized pores is of great importance to accelerate the electrolyte diffusion and the transport of CO$_2$ gas, resulting in good capacity and rate performance.

Thirdly, to clarify the effect of Co-doped sites on the electrochemical properties of alpha-MnO$_2$, the Co-doped occupied sites, the density of states (DOS) and the electron local functions (ELF) are calculated by first principles calculations (Figure 6). On the one hand, the positive formation energy of Co-substitution sites (~3.75 eV) reveals that the Co-substitution site is instable. By comparison, the negative formation energies of the three Co-interstitial sites demonstrate that the Co atoms mainly occupy the interstitial sites, specially for the interstitial III site (~-5.17 eV, Figure. S11). This trend is consistent with the existance of the maximum value of Co-doping concentration. On the other hand, the DOS (Figure. 6d-f) mappings show that the pure alpha-MnO$_2$ is a typical oxide insulator, with a wide Fermi energy. The Co-doping can remarkably reduce the Fermi energy. Especially, the Co-interstitial site (the interstitial III) significantly induce the bandgap of alpha-MnO$_2$ to form an impurity band, strengthening the conductivity of alpha-MnO$_2$ by shortening the energy bandgap. Finally, the ELF images (Figure. 6g-h) show that the electron pair of Mn obviously increases in the Co-doped MnO$_2$. It reveals that the valence bond of Mn-O becomes weaker but the ion character of Mn-O becomes stronger, resulting in the increment of conductivity.

3. Conclusions

In summary, a new Co-interstitial alpha-MnO$_2$ nanowire catalyst has been synthesized by a simple microwave-assisted reaction. The crystal structure and reaction process were clarified by environmental spherical aberration-corrected TEM observations and theoretical calculations. A Li-CO$_2$ battery using the optimized Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode electrode offers a super-low overpotential (~0.73 V) and a long-term cyclability (over 500 cycles at a current density of 100 mA g$^{-1}$), exceeding the values of Li-CO$_2$ batteries reported so far. Depending
on experimental observations and DFT calculations, it has been confirmed that the outstanding electrochemical properties are mainly associated with the high conductivity, the large BET surface area and unique Co-interstitial doping sites. These results on Li-CO$_2$ batteries with low cost, high efficiency, high energy density and structural stability, will greatly contribute to tackle greenhouse effect, and will also provide new avenues for designing advanced metal-air batteries.

**Supporting Information**

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

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**References**

[1] M. Armand, J. M. Tarascon, Nature **2008**, 451, 652.

[2] M. S. Dresselhaus, I. L. Thomas, Nature **2001**, 414, 332.

[3] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, Nature Mater. **2011**, 11, 19.

[4] M. Leskes, N. E. Drewett, L. J. Hardwick, P. G. Bruce, G. R. Goward, C. P. Grey, Angew. Chem. Int. Ed. **2012**, 51, 8560.

[5] X. Li, S. Yang, N. Feng, P. He, H. Zhou, Chinese J. of Catal. **2016**, 37, 1016.

[6] Y. Liu, R. Wang, Y. Lyu, H. Li, L. Chen, Energy Environ. Sci. **2014**, 7, 677.

[7] B. Liu, Y. Sun, L. Liu, J. Chen, B. Yang, S. Xu, X. Yan, Energy Environ. Sci. **2019**, 12, 887.

[8] X. Zhang, Q. Zhang, Z. Zhang, Y. Chen, Z. Xie, J. Wei, Z. Zhou, Chem. Commun. **2015**, 51, 14636.

[9] Y. Qiao, J. Yi, S. Wu, Y. Liu, S. Yang, P. He, H. Zhou, Joule **2017**, 1, 359.
[10] Z. Zhang, Q. Zhang, Y. Chen, J. Bao, X. Zhou, Z. Xie, J. Wei, Z. Zhou, Angew. Chem. Int. Ed. Engl. 2015, 54, 6550.

[11] Z. Zhang, X. G. Wang, X. Zhang, Z. Xie, Y. N. Chen, L. Ma, Z. Peng, Z. Zhou, Adv Sci, 2018, 5, 1700567.

[12] L. Qie, Y. Lin, J. W. Connell, J. Xu, L. Dai, Angew. Chem. Int. Ed. 2017, 56, 6970.

[13] S. Bie, M. Du, W. He, H. Zhang, Z. Yu, J. Liu, M. Liu, W. Yan, L. Zhou, Z. Zou, ACS Appl. Mater. Inter. 2019, 11, 5146.

[14] S.-M. Xu, Z.-C. Ren, X. Liu, X. Liang, K.-X. Wang, J.-S. Chen, Energy Storage Mater. 2018, 15, 291.

[15] R. Pipes, A. Bhargav, A. Manthiram, ACS Appl. Mater. Interfaces 2018, 10, 37119.

[16] W. Ma, S. Lu, X. Lei, X. Liu, Y. Ding, J. Mater. Chem. A 2018, 6, 20829.

[17] Y. Mao, C. Tang, Z. Tang, J. Xie, Z. Chen, J. Tu, G. Cao, X. Zhao, Energy Storage Mater. 2019, 18, 405.

[18] B. Ge, Y. Wang, Y. Sun, Y. Li, J. Huang, Q. Peng, Energy Storage Mater. 2019, DOI: https://doi.org/10.1016/j.ensm.2019.02.018.

[19] D. Banerjee, H. W. Nesbitt, Geochim. Cosmochim. Acta 1999, 63, 3025.

[20] T. V. Thi, A. K. Rai, J. Gim, J. Kim, J. Power Sources 2015, 292, 23.

[21] Z. Hu, X. Xiao, C. Chen, T. Li, L. Huang, C. Zhang, J. Su, L. Miao, J. j. Jiang, Y. R. Zhang, J. Zhou, Nano Energy 2015, 11, 226.

[22] Y. Hou, J. Wang, L. Liu, Y. Liu, S. Chou, D. Shi, Huakun Liu, Y. P. Wu, W. M. Zhang, J. Chen. Adv. Fun. Mater. 2017, 27,1700564.

[23] S. Yang, Y. Qiao, P. He, Y. Liu, Z. Cheng, J.-j. Zhu, H. Zhou, Energy Environ. Sci. 2017, 10, 972.

[24] Z. Zhang, Z. Zhang, P. Liu, Y. Xie, K. Cao, Z. Zhou, J. Mater. Chem. A 2018, 6, 3218.

[25] Z. Guo, J. Li, H. Qi, X. Sun, H. Li, A. G. Tamirat, J. Liu, Y. Wang, L. Wang, Small 2018, 0, 1803246.
[26] Y. Jin, C. Hu, Q. Dai, Y. Xiao, Y. Lin, J. W. Connell, F. Chen, L. Dai, Adv. Funct. Mater. 2018, 28, 1804630.

[27] C. Wang, Q. Zhang, X. Zhang, X. G. Wang, Z. Xie, Z. Zhou, Small 2018, 14, 1800641.

[28] Z. Zhang, C. Yang, S. Wu, A. Wang, L. Zhao, D. Zhai, B. Ren, K. Cao, Z. Zhou, Adv. Energy Mater. 2019, 9, 1802805.
Figure 1. Microstructural characteristics. (a) XRD patterns of representative the CC, MnO2/CC and Co0.2Mn0.8O2/ CC. (b) SEM image of the CC. (c) SEM image of the Co0.2Mn0.8O2/ CC. (d) High-magnification SEM image of the Co0.2Mn0.8O2/ CC. (e) TEM image of the Co0.2Mn0.8O2/ CC. (f) HRTEM image of a Co0.2Mn0.8O2, nanowire, the inside is the SAED pattern of the Co0.2Mn0.8O2 nanowire. (g) Low-loss EELS mappings of the MnO2/CC (red) and the Co0.2Mn0.8O2/CC (purple). (h) XPS profile of the Co0.2Mn0.8O2. (i) and (j) Local high magnification XPS profiles of Mn 2p and Co 2p, respectively.
Figure 2. Electrochemical properties of Li-CO$_2$ batteries. (a) CV curves recorded at a scan rate of 0.2 mV s$^{-1}$ over a voltage range of 2-4.5 V vs. Li/Li$^+$ in a CO$_2$-saturated condition. (b) The first charge/discharge properties under different current densities. (c) Discharge-charge curves of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC sample under a controlled capacity of 1000 mA h g$^{-1}$ at different current densities. (d) Cycle properties of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC sample under a controlled capacity of 1000 mA h g$^{-1}$ at 100 mA g$^{-1}$. (e) Variation of cutoff voltage of the different samples under a controlled capacity of 1000 mA h g$^{-1}$ at 100 mA g$^{-1}$. (f) Comparison of cycle performance and charge/discharge voltage gap for the typical Li-CO$_2$ batteries reported so far. [10, 11, 13-15, 22-28]
Figure 3. Characteristics of the discharge-discharge products. (a) Initial cycle galvanostatic discharge/charge profiles. (b) XRD patterns of the samples corresponding to the different positions in (a). (c) Raman spectra of the different states. Typical SEM images of Co_{0.2}Mn_{0.8}O_{2}/CC cathodes with the pristine (d), the discharged state (e) and the charge state (f), respectively. The insets are the local high magnification images.
Figure 4. *In-situ* microstructural features of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC electrode. Typical morphology variation during the discharge process (a-c) and the charge process (d-f). *In-situ* SAED patterns of the primitive (h), the discharge (i) and the charge (j) Co$_{0.2}$Mn$_{0.8}$O$_2$ nanowires. (k) and (l) Low-loss and core-loss EELS mappings of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC electrode at different states.
Figure 5. Mechanisms for outstanding electrochemical properties. (a) The conductivity values of the different MnO$_2$-based electrodes. (b) EIS spectra of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC electrodes under different conditions. The inset corresponds to the fitting circuit. (c) The nitrogen adsorption-desorption isotherms of different samples. (d) The pore size distribution of different samples.
Figure 6. **Theoretical interpretation.** Optimized atomic structures: (a) the pristine $\alpha$-MnO$_2$, (b) the Co-substitutional alpha-MnO$_2$, and (c) the Co-doped alpha-MnO$_2$ (the interstitial-III site). The wathet blue, green and pink balls stand for Mn, Co and O atoms, respectively. Density of states: (d) the pristine alpha-MnO$_2$, (e) the Co-substitutional alpha-MnO$_2$, and (f) the Co-doped alpha-MnO$_2$ (the interstitial-III site). ELF images: (g) the pristine alpha-MnO$_2$ and (h) the Co-doped alpha-MnO$_2$ (the interstitial-III site).
We prepare a new Co-doped alpha-MnO$_2$ nanofiber catalyst for Li-CO$_2$ batteries, and it shows a large capacity of 8160 mA h g$^{-1}$, a low overpotential of 0.73 V and an ultrahigh cyclability (500 cycles), by improving the conductivity, enhancing the catalytic activity and prohibiting side reactions. The catalyst is highlighted by its simplicity and high-yield production of a well-defined morphology, which attributes to the industrial development of Li-CO$_2$ batteries.

**Keyword:** Catalytic Cathodes

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**A Co-Doped MnO$_2$ Catalyst for Li-CO$_2$ Batteries with Low Overpotential and Ultrahigh Cyclability**

![Graph](image-url)
Supporting Information

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Experimental sections

Preparation of Co$_x$Mn$_{1-x}$O$_2$/CC electrodes

All the reagents obtained from Aladdin (shanghai, china) were of analytical grade and used without any further purification. The Co-doped alpha-MnO$_2$ nanowires were prepared by a microwave-assisted method. A microwave system (MS, XH-8000, Beijing XiangHu Science and Technology Development Co., Ltd., China) equipped with \textit{in situ} magnetic stirring was used to heat the autoclave. MnSO$_4$·H$_2$O (0.029 g), KMnO$_4$ (0.335 g) and Co(NO$_3$)$_2$·6H$_2$O were dissolve into 20 mL of deionized water, respectively. Different molar ratios of Co(NO$_3$)$_2$·6H$_2$O: MnSO$_4$·H$_2$O were used as Co-dopant reagents. After stirring for about 30 minutes at room temperature, a piece of CC (5×5 cm$^2$) was immersed in the mixed solution and heated to 140 °C at a heating rate of 10 °C/min, and kept for 60 min with a power of 600 W. After the microwave reaction, the CC which covered with Co-doped MnO$_2$ nanowires was rinsed with deionized water. All unreacted materials were removed, and the obtained samples were dried under a vacuum at 80 °C for 24 h. The different Co$^{2+}$: Mn$^{2+}$ molar ratios of 0:1, 0.1:0.9, 0.2:0.8 and 0.5:0.5 in the initial solutions were performed, and the products were designated as MnO$_2$, Co$_{0.1}$Mn$_{0.9}$O$_2$, Co$_{0.2}$Mn$_{0.8}$O$_2$ and Co$_{0.5}$Mn$_{0.5}$O$_2$, respectively.

Material characterization

XRD patterns were collected on a Rigaku D/Max- 2500 diffractometer using a filtered Cu K$\alpha$ radiation at a sweep rate of 4 degree/min, SEM was conducted with a Hitachi S-4800. TEM images and EELS analysis were observed on a Titan ETEM G2 at 300 kV. A H7756 four-point probe was used to determine the electrical conductivity of the obtained samples. The surface areas and pore size distribution were performed on a micrometrics ASAP2020 analyzer at 196 C. XPS was conducted on a ThermoFisher with Al K$\alpha$ (1486.71 eV) X-ray radiation (15 kV and 10 mA). The binding energies obtained in the XPS analysis were corrected by referencing the C 1s peak position (284.40 eV).

Li-CO$_2$ battery assembly
The Li-CO$_2$ battery assembly was based on a CR2032 coin type battery. It was successively assembled by stacking a lithium metal anode (14 mm in diameter), a piece of glass fiber separator (16 mm in diameter) soaked with 80 μL of electrolyte, and a cathode placed on a nickel foam supporter. The Co$_x$Mn$_{1-x}$O$_2$/CC cathodes were cut into disks. A hole (4 mm in diameter) was drilled in the cathode shell so that the CO$_2$ can easily and quickly accesses the cathode. Then, the assembled batteries were placed in a 250 mL glass vessel filled with high-purity CO$_2$. The pure CO$_2$ was pumped into the glass vessel through the straight two-way piston conducted alternatively by vacuuming and ventilating three times. After incubating for 10 h, the discharge and charge cycle of the batteries were tested. 1 M LiTFSI dissolved in TEGDME solution was chosen as the electrolyte for all Li-CO$_2$ batteries. All potentials were referenced against Li/Li$^+$.  

**Electrochemical test**

The galvanostatic discharge/charge tests were collected on a LAND CT2001A battery test instrument. The specific capacity and current density were calculated according to the mass of Co$_x$Mn$_{1-x}$O$_2$ nanowires on the electrodes. The mass loading of Co$_x$Mn$_{1-x}$O$_2$ on CC was found to be 0.5-0.8 mg cm$^{-2}$. CVs were conducted on a BioLogic VMP3 electrochemical workstation in the potential window of 2.0-4.5 V (vs. Li/Li$^+$), and the scan rate was 0.2 mV s$^{-1}$. EIS curves were carried out on a BioLogic VMP3 system with the typical frequency range from 100 kHz to 10 mHz by applying the applied voltage of 5 mV.  

**First-principles calculations**

The calculations were finished with the Vienna ab initio Simulation Package (VASP) code in terms of DFT. The function and approximation have been introduced in previous results S1. The core electrons are represented by the projected enhanced wave potential. The kinetic energy cutoff above 500 eV and the K point sampling on the unit cell are 3×3×4 for 2×2×2 supercell of pristine and doping alpha-MnO$_2$. Structural optimization was performed with a force convergence criterion of 0.01 eV/A. Because Mn is a magnetic atom, the
GGA+U method is employed with U−J = 4 eV, 3 eV for Mn and Co, respectively. The lowest energy magnetic state is set based on antiferromagnetic. The optimized lattice constant of alpha-MnO$_2$ is a = b = 0.98 nm, c = 0.29 nm.

The formation energy of Co is defined as following $^S_2$:

\begin{equation}
S_1 (E_{Co}) = E_{Co} - E_{Mn} - E_{Mn}
\end{equation}
\begin{equation}
S_2 (E_{Co}) = E_{Co} - E_{Mn} - E_{Mn}
\end{equation}

where $S_1$ and $S_2$ are the formation energies of Co interstitial and substitution, respectively. $E_{Co}$ and $E_{Mn}$ are the corresponding total energies of Co interstitial and substitution, respectively. $E_{Mn}$, $E_{Co}$, and $E_{Mn}$ are the total energies of alpha-MnO$_2$, Co and Mn atoms, respectively.

S1. Peng, Q. et al. In-situ atomic-scale phase transformation of Mg under hydrogen conditions. *J. Phys. Chem. C* **122**, 19532-19539 (2018).

S2. Kuwabara, A. & Tanaka, I. First principles calculations of defect formation energies in Sr- and Mg-doped LaGaO$_3$. *J. Phys. Chem. B* **108**, 9168-9172 (2004).
Table S1. Elemental compositions of different samples dependent on EDS analysis

| Samples       | Elemental composition (at.%) |
|---------------|------------------------------|
|               | Mn  | Co  | O   | C   |
| MnO₂          | 14.85 | -   | 47.22 | 37.93 |
| Co₀.₁Mn₀.₉O₂  | 13.90 | 0.55 | 44.52 | 41.03 |
| Co₀.₂Mn₀.₈O₂  | 19.28 | 1.12 | 41.95 | 37.65 |
| Co₀.₃Mn₀.₇O₂  | 16.95 | 1.18 | 41.46 | 39.54 |
Table S2. Fitting parameters of EIS curves of the Co\textsubscript{0.2}Mn\textsubscript{0.8}O\textsubscript{2} sample in terms of fitting circuits.

| Sample       | $R_e$ (Ω) | $R_f$ (Ω) | $Q_1$ Y | $Q_2$ Y | $R_{ct}$ (Ω) | $Q_2$ n |
|--------------|-----------|-----------|---------|---------|---------------|---------|
| Pristine     | 19.72     | 46.05     | 1.2×10^{-5} | 0.71    | 40.86         | 3.7×10^{-2} | 0.61        |
| 1\textsuperscript{st} charge | 19.24     | 31.73     | 1.8×10^{-4} | 0.82    | 41.37         | 2.7×10^{-2} | 0.59        |
| 1\textsuperscript{st} discharge | 21.02     | 73.72     | 5.1×10^{-5} | 0.83    | 127.19        | 1.9×10^{-2} | 0.77        |
Table S3. Fitting parameters of EIS curves of the MnO$_2$ sample in terms of fitting circuits.

| Sample          | $R_e$ (Ω) | $R_f$ (Ω) | $Q_1$   | $R_{ct}$ (Ω) | $Q_2$  | $Y$   | n  |
|-----------------|-----------|-----------|---------|--------------|-------|-------|----|
| Pristine        | 25.61     | 62.44     | 2.1×10$^{-3}$ | 185.12       | 1.6×10$^{-5}$ | 0.83  | 0.89 |
| 1$^{st}$ charge | 38.42     | 71.16     | 1.1×10$^{-2}$ | 241.15       | 7.2×10$^{-6}$ | 0.85  | 0.84 |
| 1$^{st}$ discharge | 25.74   | 598.51    | 1.8×10$^{-3}$ | 412.34       | 4.9×10$^{-6}$ | 0.82  | 0.85 |
Figure S1. Typical XRD patterns of the different MnO$_2$ samples
Figure S2. SEM images of the MnO$_2$ (a), Co$_{0.1}$Mn$_{0.9}$O$_2$ (b), Co$_{0.5}$Mn$_{0.5}$O$_2$ (c). (d) Local high magnification image of plate-shaped Co$_{0.5}$Mn$_{0.5}$O$_2$. (e) High revolution TEM image of the plate-like alpha-MnO$_2$. 
Figure S3. EDS mapping images of Co, Mn and O elements in the Co$_{0.2}$Mn$_{0.8}$O$_2$ sample.
Figure S4. Galvanostatic discharge profiles of the Li-CO$_2$ cells with pristine Co$_{0.2}$Mn$_{0.8}$O$_2$/CC cathode at a current density of 100 mA g$^{-1}$ under both CO$_2$ and Ar.
Figure S5. Cycle properties of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC sample under a controlled current of 100 mA g$^{-1}$ (a) and 500 mA g$^{-1}$ (b), respectively. Cycle properties of the pure MnO$_2$/CC sample under a controlled current of 100 mA g$^{-1}$ (c) and 500 mA g$^{-1}$ (d).
Figure S6. Cycle performance and variation of cutoff voltage of Li-CO\textsubscript{2} batteries with the Co\textsubscript{0.2}Mn\textsubscript{0.8}O\textsubscript{2}/CC electrodes with a controlled specific capacity of 1000 mAh g\textsuperscript{-1} at 200 mA g\textsuperscript{-1} (a and b) and 500 mA g\textsuperscript{-1} (c and d).
Figure S7. Cycle performance and variation of cutoff voltage of Li-CO$_2$ batteries with the MnO$_2$/CC electrodes with a controlled specific capacity of 1000 mAh g$^{-1}$ at 200 mA g$^{-1}$ (a and b) and 500 mA g$^{-1}$ (c and d).
Figure S8. (a) The comparison of charge/discharge capacities of different samples under the same current density of 100 mA g$^{-1}$. (b) The first charge/discharge curve of different samples under a controlled capacity of 1000 mA h g$^{-1}$ at 100 mA g$^{-1}$. (c) The comparison of capacity and overpotential of different samples at the same current density of 100 mA g$^{-1}$. 
Figure S9. (a) SEM image of the initial Co$_{0.2}$Mn$_{0.8}$O$_2$/CC. (b) SEM image of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC after 50 cycles. (c) XRD patterns of the different state samples.
Figure S10. C1s XPS profiles of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC electrode (a) and the MnO$_2$/CC electrode (b) under the different states. (c) Li 1s XPS profile of the Co$_{0.2}$Mn$_{0.8}$O$_2$/CC electrode. (d) EIS spectra of the bare MnO$_2$ catalyst for Li-CO$_2$ batteries under different conditions.
Figure S11. Two occupied sites of the Co-interstitial alpha-MnO$_2$, (a) the interstitial I, (b) the interstitial II. (c) The formation energies of different occupied sites.