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To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202006303

Link to VoR: https://doi.org/10.1002/anie.202006303
The Stabilization Effect of CO₂ Chemistries in Li-O₂/CO₂ Batteries

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During discharge, O₂ from air can react with Li⁺ to form Li₂O₂, air electrode, a nonaqueous electrolyte and a Li plate as anode. A Li-air battery usually comprises of a porous carbon material as cathode and thus the making “onboard” pure oxygen supply system is an ideal candidate for next-generation energy supplier.¹ However, large number of available choices, the ultrahigh theoretical specific energy, however, even in pure oxygen (O₂), the vulnerability of conventional organic electrolytes and carbon cathodes towards reaction intermediates, especially O₂⁻, and the corrosive oxidation and crack/pulverization of Li metal anode lead to poor cycling stability of the Li-air battery. Even worse, the water and/or CO₂ in air are reported to bring more serious parasitic reactions and security issues. Therefore, most significant improvements are achieved in pure O₂, and thus the making “onboard” pure oxygen supply system is inevitable for practical Li-air battery, which not only reduces the energy density of the overall system, but also makes the system complex and expensive to produce and maintain. Therefore, realizing the ultimate goal of applying such systems in open-air environment is a demanding requirement. Here, contrary to previous assertions, we found that CO₂ could improve the stability of both anode and electrolyte, and a high-performance rechargeable Li₂O₂/CO₂ battery is then developed. The introduced CO₂ can not only facilitate the in situ formation of a passivated protective Li₂CO₃ film on Li anode, but also restrain side reactions involving electrolyte and cathode by capturing O₂. Moreover, the Pd/CNT catalyst in cathode can extend the battery lifespan by effectively tuning the product morphology and catalyzing the decomposition of Li₂CO₃. By simultaneously addressing the bottleneck problems of poor rechargeability, instability of carbon cathode, liquid electrolyte and Li anode, the designed Li₂O₂/CO₂ battery achieves a full discharge capacity of 6,628 mAh g⁻¹ and a long life of 715 cycles, which is even better than those of pure Li₂O₂ batteries. When extending the concept to other important metal-air systems including Na-O₂/CO₂ and K-O₂/CO₂ batteries, the electrochemical performances are also greatly improved compared with those of Na/K-O₂ batteries, proving the general effectiveness of the strategy. We believe the findings here present an important step towards Li-air batteries from Li₂O₂ batteries as well as other metal-air systems.

Abstract: The lithium (Li)-air battery possesses ultrahigh theoretical specific energy, however, even in pure oxygen (O₂), the vulnerability of conventional organic electrolytes and carbon cathodes towards reaction intermediates, especially O₂⁻, and corrosive oxidation and crack/pulverization of Li metal anode lead to poor cycling stability of the Li-air battery. Even worse, the water and/or CO₂ in air are reported to bring more serious parasitic reactions and security issues. Therefore, most significant improvements are achieved in pure O₂, and thus the making “onboard” pure oxygen supply system is inevitable for practical Li-air battery, which not only reduces the energy density of the overall system, but also makes the system complex and expensive to produce and maintain. Therefore, realizing the ultimate goal of applying such systems in open-air environment is a demanding requirement. Here, contrary to previous assertions, we found that CO₂ could improve the stability of both anode and electrolyte, and a high-performance rechargeable Li₂O₂/CO₂ battery is then developed. The introduced CO₂ can not only facilitate the in situ formation of a passivated protective Li₂CO₃ film on Li anode, but also restrain side reactions involving electrolyte and cathode by capturing O₂. Moreover, the Pd/CNT catalyst in cathode can extend the battery lifespan by effectively tuning the product morphology and catalyzing the decomposition of Li₂CO₃. By simultaneously addressing the bottleneck problems of poor rechargeability, instability of carbon cathode, liquid electrolyte and Li anode, the designed Li₂O₂/CO₂ battery achieves a full discharge capacity of 6,628 mAh g⁻¹ and a long life of 715 cycles, which is even better than those of pure Li₂O₂ batteries. When extending the concept to other important metal-air systems including Na-O₂/CO₂ and K-O₂/CO₂ batteries, the electrochemical performances are also greatly improved compared with those of Na/K-O₂ batteries, proving the general effectiveness of the strategy. We believe the findings here present an important step towards Li-air batteries from Li₂O₂ batteries as well as other metal-air systems.

Introduction

Pursuing energy storage systems with higher energy densities has never stopped since last century, and this trend has been accelerated by the fast development of clean energy utilization and electronic devices and vehicles in recent years. Among the large number of available choices, the ultrahigh theoretical specific energy density (~3500 Wh/kg) of Li-air battery makes it an ideal candidate for next-generation energy supplier.¹ However, many challenges are waiting to be resolved before Li-air batteries can be applicable. A Li-air battery usually comprises of a porous carbon material as air electrode, a nonaqueous electrolyte and a Li plate as anode. During discharge, O₂ from air can react with Li⁺ to form Li₂O₂, which subsequently decomposes during recharge.¹b,¹d Despite the overall reaction is simple, even in pure oxygen (O₂), the vulnerability of conventional organic electrolytes and carbon cathodes towards reaction intermediates, especially O₂⁻, and the corrosive oxidation and crack/pulverization of Li metal anode render the system complicated and severely limit the cycling stability of the Li-air battery.² Currently, no method can solve these problems simultaneously. The situation is even worse when operating the system in air, since the H₂O and/or CO₂ in air are reported to bring more serious parasitic reactions and security issues.³ As a result, most significant improvements have been achieved in pure oxygen to avoid these issues,⁴ applying these kinds of Li₂O₂ batteries in practical condition will reduce the overall energy density and increase the cost because of the O₂ supply systems. Therefore, realizing the ultimate goal of applying such system in open-air environment is a demanding requirement.

Many groups noticed that CO₂ could deteriorate the battery performances, and they claimed that CO₂ participated in the discharge process in a complexed way to form Li₂CO₃, which was more difficult to be decomposed than Li₅O₁₀.⁵b-⁵d However, in high charge overpotentials, low coulombic efficiencies (CEs) and short battery lifespan. Therefore, researchers suggest that CO₂ should be completely removed from the Li-air batteries to make the reactions easier.⁵a-c, ⁵a, ⁶-⁹ Based on these results, the impact of CO₂ seems to be fully understood and subsequently, the investigations on CO₂ in Li-O₂ batteries have not received much attention. However, CO₂ is an indispensable component in air, we cannot bypass this obstacle on the way towards Li-air battery, thus devoting efforts to unveiling the true role of CO₂ is critical.

Contrary to previous assertions, here we found that CO₂ could improve the stability of the battery components, including cathode, electrolyte and Li anode. It is well known that the side product, Li₂CO₃ in Li-O₂ batteries is stable with electrolytes and cathodes while the discharge product of Li₂O₂ is not.⁷ Since the product in our Li₂O₂/CO₂ battery is solely Li₂CO₃, the battery stability can be boosted. Furthermore, CO₂ can promote the formation of Li₂CO₃ on the Li surface to protect it from H₂O and other offensive intermediates. The mechanism of Li₂CO₃ formation is then discussed in detail. After in-depth research in the stability of cathode and electrolyte by NMR and FTIR, it has also been confirmed that CO₂ can capture O₂⁻ to reduce its nucleophilicity. Therefore, the introduction of CO₂ into the O₂ reaction gas stabilizes the whole battery system, and thus a high performance Li₂O₂/CO₂ battery has been obtained. In addition, we have added CO₂ in Na (K)-O₂ batteries and the performances have been greatly improved as well.

Results and Discussion

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A prototype ECC-AIR Li-O2/CO2 battery was assembled based on Pd/CNT cathode with flowing O2/CO2 (1:1) at 1 atm. The composition and structure information of the synthesized Pd/CNT can be found in Figures S1-S3 and the structure of ECC-AIR type cell is shown in Figure S4. Compared with CNT cathode, an obvious decrease in charge overpotential can be observed for the Pd/CNT cathode (Figure S5), revealing its effectiveness in promoting the decomposition of the discharge product. The evolution of Pd/CNT cathode after discharge and charge has been recorded by FTIR and Raman spectra. In the FTIR spectra (Figure 1A), typical peaks at 1437 cm\(^{-1}\) and 878 cm\(^{-1}\) corresponding to Li\(_2\)CO\(_3\) appear in the discharged cathode and these peaks almost vanish after subsequent recharging, implying the formed Li\(_2\)CO\(_3\) discharge product can be reversibly decomposed during the charge process. Similar results can also be observed in the Raman spectra with the emergence and disappearance of the Li\(_2\)CO\(_3\) peak at 1084 cm\(^{-1}\) in the discharged and recharged cathodes (Figure 1B). SEM characterization was then conducted to further confirm the formation and decomposition of Li\(_2\)CO\(_3\) during the cycling process of the Li-O\(_2\)/CO\(_2\) batteries (Figures 1C-1E). A more detailed evolution of the discharge product can be seen in Figure S6. All these results affirm that the designed Li-O\(_2\)/CO\(_2\) battery permits reversible formation and decomposition of Li\(_2\)CO\(_3\).

It is widely accepted that the discharge reaction proceeds according to Eq. 1 in Li-O\(_2\) batteries.

\[
2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 \quad (1)
\]

While in the Li-O\(_2\)/CO\(_2\) battery, since the gas atmosphere has been changed to O\(_2\)/CO\(_2\) (1:1), the fundamental reaction mechanisms are still unclear. To elucidate this, operando pressure test has been conducted (Figure S7). As a comparison, the pressure change during cycling of Li-O\(_2\) battery has also been given. From Figure 1F we can see that the Li-O\(_2\) battery follows the 2.07 e/O\(_2\) coefficient during discharge, in line with the theoretical value of 2 e/O\(_2\) in Eq. 1. With the introduction of CO\(_2\) into the reaction gas, the number of electrons transferred per gas molecule changes to 1.30 (1.30 e/gas) during discharge of the Li-O\(_2\)/CO\(_2\) (1:1) battery (Figure 1G). Considering that Li\(_2\)CO\(_3\) is the exclusive discharge product as above proved, the overall discharge reaction formula in Li-O\(_2\)/CO\(_2\) battery is as follows (Eq. 2), whose theoretical value is 1.33 e/gas.

\[
2\text{Li} + \frac{1}{2}\text{O}_2 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 \quad (2)
\]

It is obvious that the pressure cannot recover to the initial states in both Li-O\(_2\) and Li-O\(_2\)/CO\(_2\) batteries after recharging the same capacity, probably due to the existence of side reactions. The side reactions are resulted from the electrolyte decomposition and/or carbon degradation induced by the intermediates, O\(_2\), O\(_2^*\), etc. [9] In the first charge, 6.02 e/gas and 3.17 e/gas are achieved respectively in the Li-O\(_2\) and Li-O\(_2\)/CO\(_2\) batteries, indicating more parasitic reactions happen in the Li-O\(_2\) battery than in the Li-O\(_2\)/CO\(_2\) battery. The differential electrochemical mass spectra (DEMS) during charge of Li-O\(_2\)/CO\(_2\) battery was then tested. The generation of O\(_2\), CO and CO\(_2\) as well as some fragments resulted from electrolyte decomposition can be clearly observed from Figure S8, confirming the occurrence of side reactions.

In Li-O\(_2\) batteries, the Li anodes are easy to be corroded by H\(_2\)O, generating porous LiOH layer, [24] which allows H\(_2\)O to continuously diffuse across, and thus constantly consuming the remaining Li anode and finally leading to the exhaustion of the Li anode and death of the batteries. When disassembling the cycled Li-O\(_2\)/CO\(_2\) battery, we found that the Li anode was very stable in this system without corrosion. Figure 2A vividly shows the difference of the Li anodes after cycling in Li-O\(_2\) and Li-O\(_2\)/CO\(_2\) batteries. To clarify the origin of this phenomenon, the cycled Li anode in Li-O\(_2\)/CO\(_2\) battery has been systematically characterized.

Figures 2B and 2C give the C 1s XPS results of the cycled Li anode. The other C 1s peaks show the CH\(_3\)OCO\(_2\)Li at 287.9 eV and C-C bond at 284.8 eV, which may arise from the SEI film formed on the Li surface. [9] Moreover, the Raman spectrum of the cycled Li anode also reveals a Li\(_2\)CO\(_3\) peak at 1084 cm\(^{-1}\) (Figure 2D), which is consistent with the XPS results.
O2/CO2 battery can generate Li2CO3 protection layer, the Li anode (see Figure S11A). Even though pre-cycling of Li anode in Li-O2 battery is similar to the Li anode in Li-O2 without resting in O2/CO2 compared with the resting Li anode (Figure 2G), which is cycling for another 100 h, the pre-cycled Li anode is less corroded 80 h while the other one cycling for 80 h. Subsequently, the gas indicating that the presence of CO2 is indispensable for the formation of Li2CO3 layer, because H2O mainly comes from electrolyte decomposition during cycling. A contrast experiment was conducted by using two Li2O2/CO2 batteries: one resting for 80 h while the other one cycling for 80 h. Subsequently, the gas environment of the batteries was changed to pure O2. After cycling for another 100 h, the pre-cycled Li anode is less corroded compared with the resting Li anode (Figure 2G), which is completely dark without observable protection effect, and is very similar to the Li anode in LiO2 battery without resting in O2/CO2 (see Figure S11A). Even though pre-cycling of Li anode in LiO2/CO2 battery can generate Li2CO3 protection layer, the Li anode can still be corroded during cycling in LiO2 battery by the penetration of H2O across the Li2CO3 film in the long run, indicating that the presence of CO2 is indispensable for the formation of Li2CO3 protection film, in other words, the H2O generated by the decomposition of the electrolyte during cycling is critical for the formation of Li2CO3 protection film. Therefore, route II can be excluded. The H2O in the cycled battery will react with Li anode to form LiOH and H2, followed by the reaction between LiOH and CO2. Since the reactions in route III is very fast, CO2 can capture LiOH once it forms.10 On the basis of above analysis, we speculate that route III is the most reasonable mechanism for the Li2CO3 formation on the Li anode. Furthermore, to directly visualize the CO2 induced protective effect on Li anode, a simulation experiment has been designed, please see the results and discussions in Figure S13. In addition, we also immersed Li plates in the electrolytes pre-saturated with O2 and O2/CO2 and exposed them to air. As indicated in Figure S14, the Li plate can be stabilized more than 10 days with the help of CO2.

Super oxide radical, a strong nucleophilic reagent, has been widely proved to be the main origin of side reactions in Li-O2 batteries, including electrolyte decomposition and cathode oxidation.92, 106, 107 Therefore, capturing superoxide is very meaningful to stabilize the battery system. Back to 1984, Julian L. R. confirmed that O2- was prone to bind CO2 through reactions in Eqs. 3 and 4, which was further supported by the theoretical calculation conducted by Lim H. K.107 So we can reasonably speculate that CO2 can capture O2- to reduce the disproportionation reaction in Li2O2/CO2 battery, thus parasitic reactions can be greatly alleviated (Figure 3A). Furthermore, since singlet oxygen, another cause for parasitic reactions in Li-O2 batteries, forms by disproportionation of superoxide (O2-) (Eq. 5),92, 106, 107 if O2- is captured, its disproportionation no longer happens, further reducing the side reactions.

\[
\begin{align*}
\text{O}_2^- + \text{CO}_2 & \rightarrow \text{CO}_2^- + \text{O}_2 \quad (3) \\
\text{CO}_2^- + \text{O}_2^- + \text{CO}_2 & \rightarrow \text{C}_2\text{O}_6^{2-} + \text{O}_2 \quad (4) \\
\text{O}_2^- + \text{O}_2^- & \rightarrow \text{O}_2 + (1-x)\text{O}_2 \\
\end{align*}
\]

The above speculation can be confirmed by comparing the ring current of the rotating ring-disk electrode (RRDE) in O2 and O2/CO2 atmospheres. In the RRDE experiment, O2 is first reduced to O2- at the disk, followed by the detection and oxidation at the ring. If the O2- is captured by CO2, it cannot be oxidized anymore, thus there is almost no ring current can be detected. Figures 3B and 3C compare the ring currents in the O2 and O2/CO2 systems. It is clear that the \(I_{\text{ring}}\) decreases sharply to nearly zero after involving CO2, showing that CO2 can indeed capture O2- (Figures 3B and 3C and Figure S15), in good consistency with previous reports.92, 107 The stability of different electrolytes towards O2 and CO2 captured O2- are compared and discussed in detail in Figure S16. The evolution of TEGDME electrolytes after cycling was checked by \(^{1}H\) and \(^{13}C\) nuclear magnetic resonance (NMR) spectra (Figures 3D and 3E). After discharge for 10 h, the electrolytes in both systems are decomposed with the appearance of new chemical shifts at 36 ppm in \(^{13}C\) spectra and 2.6 ppm in \(^{1}H\) spectra. As expected, the impurity peak intensities of Li2O2/CO2 battery are much lower than those of Li-O2 battery. Furthermore, after 20 cycles, the differences are more obvious with almost no impurities can be seen for Li2O2/CO2 battery while peaks for the side products appear significantly in Li-O2 battery. Even using commercial electrolyte, the Li2O2/CO2 battery still outlives the Li-O2 battery (180 vs. 109 cycles, Figure S17) because of less electrolyte decomposition with the help of CO2.

### Table 1. Proposed routes for the formation of Li2CO3 on Li anode.

<table>
<thead>
<tr>
<th>Routes</th>
<th>Reactions</th>
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<tbody>
<tr>
<td>I</td>
<td>(4\text{Li} + 3\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C})</td>
</tr>
<tr>
<td>II</td>
<td>(2\text{Li} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3)</td>
</tr>
</tbody>
</table>
| III    | \[
\begin{align*}
\text{LiOH} + \text{H}_2\text{O} & \rightarrow \text{LiOH} + \text{H}_2 \quad (5) \\
2\text{LiOH} + \text{CO}_2 & \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} \\
\text{Total:} & \quad 2\text{Li} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 | \text{H}_2\text{O} \\
\end{align*}
\] |

### Figure 2. Characterizations of the Li anode after cycling in LiO2/CO2 batteries. (A) Schematics of the Li anode in LiO2 battery and the Li2CO3 protection effect on the Li anode in LiO2/CO2 battery. (B-E) XPS spectra of C 1s and Li 1s, Raman spectrum and SEM image of the Li anode after cycling in LiO2/CO2 battery. (F) Li anode stability towards air after cycling in LiO2/CO2 and LiO2 batteries for 80 h. The time on the picture means the exposure time in air (relative humidity: 40%). (G) The optical pictures of Li anodes after 100 h running in the LiO2 batteries with pre-cycled Li anode in LiO2/CO2 battery and uncycled Li anode. The pre-cycled Li anode ran in LiO2/CO2 battery for 80 h and the uncycled Li anode was rested at the same situation for 80 h.

Note that the Li2CO3 layer is very useful for protecting the Li anode, we need to elucidate its formation mechanism. There are three possible routes for the formation of Li2CO3 film (Table 1). The first route is the direct reaction between Li and CO2 to form C and Li2CO3. According to the Raman result in Figure 2D, no peaks for C are detected, so route I can be ruled out. The difference between routes II and III is whether O2 or H2O participates in the reactions. This can be identified by whether cycling is requested for the formation of Li2CO3 layer, because H2O mainly comes from electrolyte decomposition during cycling. A contrast experiment was conducted by using two Li2O2/CO2 batteries: one resting for 80 h while the other one cycling for 80 h. Subsequently, the gas environment of the batteries was changed to pure O2. After cycling for another 100 h, the pre-cycled Li anode is less corroded compared with the resting Li anode (Figure 2G), which is completely dark without observable protection effect, and is very similar to the Li anode in LiO2 battery without resting in O2/CO2 (see Figure S11A). Even though pre-cycling of Li anode in LiO2/CO2 battery can generate Li2CO3 protection layer, the Li anode can still be corroded during cycling in LiO2 battery by the penetration of H2O across the Li2CO3 film in the long run, indicating that the presence of CO2 is indispensable for the formation of Li2CO3 layer. Another comparison by resting the Li anodes in LiO2/CO2 and LiO2 batteries further confirms that the Li2CO3 protection film cannot be formed by simply stirring Li anode in LiO2/CO2 battery (Figure S12). These experiments indicate that cycling is indispensable for the formation of Li2CO3 protection film, in other words, the H2O generated by the decomposition of the electrolyte during cycling is critical for the formation of Li2CO3 protection film. Therefore, route II can be excluded. The H2O in the cycled battery will react with Li anode to form LiOH and H2, followed by the reaction between LiOH and CO2. Since the reactions in route III is very fast, CO2 can capture LiOH once it forms.10 On the basis of above analysis, we speculate that route III is the most reasonable mechanism for the Li2CO3 formation on the Li anode. Furthermore, to directly visualize the CO2 induced protective effect on Li anode, a simulation experiment has been designed, please see the results and discussions in Figure S13. In addition, we also immersed Li plates in the electrolytes pre-saturated with O2 and O2/CO2 and exposed them to air. As indicated in Figure S14, the Li plate can be stabilized more than 10 days with the help of CO2.

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\end{align*}
\]
induced stabilization effect. The above evidences demonstrate that the introduction of CO₂ into the reaction gas can effectively alleviate the electrolyte decomposition.

To confirm whether the side reactions can be attenuated at the cathode, the composition and morphology evolutions of the CNT and Pd/CNT cathodes at the end of discharge and charge states after multiple cycles were checked by FTIR and SEM. As indicated in the FTIR spectra in Figures 4A and 4B, after 10th discharge and charge, no obvious peaks corresponding to Li₂CO₃ product. In addition, C-O stretching vibrations related peaks around 940-1230 cm⁻¹ and HCOOLi peak at 785 cm⁻¹ also emerge, revealing the instability of CNT cathode and the electrolyte decomposition induced by high charge voltage or attacks from intermediate species during cycling.[15] In contrast to CNT cathode, there are no peaks at 940-1230 cm⁻¹ or 785 cm⁻¹ associated with decomposition of CNT or electrolyte can be observed for Pd/CNT cathodes, probably due to the limited cycling capacity and good charge efficiency in this short cycle number. However, after 50 cycles, Li₂CO₃ peak at 880 cm⁻¹ is clearly seen for CNT cathode, indicating the remnant of undecomposed Li₂CO₃ discharge product. In addition, C-O stretching vibrations related peaks around 940-1230 cm⁻¹ and HCOOLi peak at 785 cm⁻¹ also emerge, revealing the instability of CNT cathode and the electrolyte decomposition induced by high charge voltage or attacks from intermediate species during cycling.[15] In contrast to CNT cathode, there are no peaks at 940-1230 cm⁻¹ or 785 cm⁻¹ associated with decomposition of CNT or electrolyte can be observed for Pd/CNT cathode after 50 cycles, manifesting its high stability to withstand the rigorous cycling conditions. Although Li₂CO₃ peak at 880 cm⁻¹ appears at the 50th discharge, its intensity decreases after charge, disclosing the good catalytic effect of Pd/CNT. Similar results are also confirmed by Raman spectra in Figure S18. The discrepancy between CNT and Pd/CNT cathodes can be further clarified by SEM. After 10th discharge, the surfaces of the CNT and Pd/CNT cathodes are covered by amorphous Li₂CO₃ (Figures 4C and 4G). Then, most of the Li₂CO₃ product decomposes after 10th charge, leaving uncovered CNT and Pd/CNT cathodes (Figures 4D and 4H). Even after 50 cycles, the morphology of the Pd/CNT cathode can almost recover to the initial state (Figures 4I and 4J), revealing that Pd/CNT can effectively facilitate the decomposition of the Li₂CO₃ to extend the battery life, while the CNT cathode cannot recover after 50th charge (Figures 4E and 4F). The above results show minimal side products (HCOOLi and CH₃COOLi) originating from cathode and electrolyte decomposition in the Li-O₂/CO₂ battery with Pd/CNT cathode, which is superior to Li-O₂ batteries with severe side products just after 20 cycles,[15] proving the participation of CO₂ can truly stabilize the Pd/CNT cathode and reduce parasitic reactions.

Considering the high catalytic effect and stability of Pd/CNT cathodes, stabilized electrolytes and Li anodes in the Li-O₂/CO₂ batteries, their electrochemical performances need to be amply studied. Figure S19 has proven that O₂ is indispensable in the feeding gas to ensure a high capacity and CO₂ plays a positive role to further increase the capacity. Figure 5A compares the full discharge and charge performances of the CNT and Pd/CNT based Li-O₂/CO₂ batteries in a fixed voltage window of 2.0-4.5 V. In the 1st cycle, the Pd/CNT based battery achieves a high discharge capacity of 6628 mAh g⁻¹, much higher than the 4384 mAh g⁻¹ capacity of CNT based battery delivered. At 5th cycle, the capacity of Pd/CNT based battery fades to 2726 mAh g⁻¹, but still nearly two times the capacity of CNT based battery (1562 mAh g⁻¹). Moreover, at a limited cycling capacity of 1000 mAh g⁻¹, the battery with Pd/CNT cathode exhibits a lower voltage gap than the battery with CNT cathode: 1.68 V vs. 1.88 V (Figure S5). The 0.2 V difference, in the long run, can keep the decomposition of Li₂CO₃ at a lower charge potential to reduce electrolyte decomposition (Figure S20). After this, electrochemical impedance spectroscopy (EIS) analysis has been conducted to check the interfacial stabilities of the batteries at different stages (Figure 5B). Except for the initial stage, the interfacial impedance of the battery with Pd/CNT cathode is always lower than that of battery with CNT cathode, indicating more stable electrode/electrolyte interphases are formed in the Pd/CNT based battery.
Figures 5C and 5D give the cycling performance of Pd/CNT based Li-O2/CO2 batteries with fixed capacities of 500 and 1000 mAh g\(^{-1}\), respectively. Accordingly, long cycling life of 715 and 255 cycles can be achieved for the batteries. As a comparison, the cycling performance of CNT based Li-O2/CO2 battery with a fixed capacity of 1000 mAh g\(^{-1}\) is shown in Figure S21A, which can only realize 56 cycles. For Li-O2 battery with Pd/CNT cathode, it only runs for 94 cycles (Figure S21B), much shorter than the 255 cycles of Li-O2/CO2 battery. In addition, the terminal potential of charges experiences no obvious increase even changing the discharge product from Li2O2 in Li-O2 battery to Li2CO3 in Li-O2/CO2 battery (Figure S21C). Excellent rate capability can also be realized in the Pd/CNT based Li-O2/CO2 batteries (Figure S22). These inspiring cycling and rate performances have never been achieved by previous Li-O2 (O2) or Li2O2/CO2 batteries (see Table S1). Thanks to the synergistic effects of the Pd/CNT cathode and CO2 enabled benefits on the whole battery, the cycling life of the designed Li-O2/CO2 battery even exceeds those of advanced Li-O2 battery systems.\(^{[16]}\) Although the charge overpotential of the Pd/CNT based Li-O2/CO2 battery is higher than some reported Li-O2 batteries, its ultra-long lifetime can offset this disadvantage, because the price of consuming extra energy for charging the battery is much cheaper than the cost of manufacturing six new Li-O2 batteries if we suppose a Li-O2 battery can run for 100 cycles at the same condition. If intermittent energy (wind or solar energy) is employed, the cost can be further reduced. The cycling performances of Li-O2 and Li-O2/CO2 batteries with higher capacities have also been compared in Figure S23. The performances of Li-O2/CO2 batteries again markedly exceed those of Li-O2 batteries.

The above investigations are based on LiCF\(_3\)SO\(_3\)/TEGDME electrolyte, an electrolyte with low-donor-number (DN) TEGDME as solvent. To prove the universality of CO\(_2\) induced electrochemical performance improvement, Li-O2/CO2 batteries with high-DN DMSQ based electrolyte have been investigated (see details in Figures S24–S27). As expected, the introduction of CO\(_2\) into the feeding gas can induce a passivated Li2CO3 film formed on the Li anode surface during cycling, which can protect the Li anode from attacking by H\(_2\)O and intermediates. Moreover, the existence of CO\(_2\) can also capture O\(_2\)- to reduce side reactions related to electrolyte and cathode. Even though Li-O2/CO2 batteries have been reported previously, no researchers noticed the gas mixtures’ protection effect on Li anode and stabilization role on electrolyte and cathode. We first propose and prove these new functions that CO\(_2\) endows. Due to the synergistic optimizations brought by catalytic Pd/CNT cathode and CO\(_2\), the Li-O2/CO2 battery achieves high performances with a full discharge capacity of 6628 mAh g\(^{-1}\) and a long life of 715 cycles. Instead of deteriorating the Li-O2 batteries as people considered before, here CO\(_2\) plays a positive role that promotes the battery performance and lifetime. Such a good performance has surpassed most of the state-of-the-art Li-O2 batteries. Besides, the strategy we adopt here is applicable in other battery systems, like Na- and K-O2/CO2 batteries. We believe that this work deepens our understanding towards Li-O2/CO2 and Li-O2 batteries, and makes an important attempt to prompt the applications of Li-O2 batteries in open-air environments.

**Conclusion**

In summary, we have demonstrated a high-capacity and long-life rechargeable Li-O2/CO2 (1:1) battery by using Pd/CNT as cathode. Thanks to the high catalytic Pd/CNT cathode, the Li2CO3 discharge product can be efficiently decomposed. The introduction of CO2 into the feeding gas can induce a passivated Li2CO3 film formed on the Li anode surface during cycling, which can protect the Li anode from attacking by H\(_2\)O and intermediates. Moreover, the existence of CO\(_2\) can also capture O\(_2\)- to reduce side reactions related to electrolyte and cathode. We first propose and prove these new functions that CO\(_2\) endows. Due to the synergistic optimizations brought by catalytic Pd/CNT cathode and CO\(_2\), the Li-O2/CO2 battery achieves high performances with a full discharge capacity of 6628 mAh g\(^{-1}\) and a long life of 715 cycles. Instead of deteriorating the Li-O2 batteries as people considered before, here CO\(_2\) plays a positive role that promotes the battery performance and lifetime. Such a good performance has surpassed most of the state-of-the-art Li-O2 batteries. Besides, the strategy we adopt here is applicable in other battery systems, like Na- and K-O2/CO2 batteries. We believe that this work deepens our understanding towards Li-O2/CO2 and Li-O2 batteries, and makes an important attempt to prompt the applications of Li-O2 batteries in open-air environments.

**Acknowledgements**

The authors thank the National Key R&D Program of China (2017YFA0206700), the National Natural Science Foundation of China (21725103), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21010210) and the K. C. Wong Education Foundation (GJTD-2018-09).

**Keywords:** stabilization • Li-oxygen battery • carbon dioxide • side reaction prevention • superoxide capture

RESEARCH ARTICLE


The application of Li-O\textsubscript{2} batteries is hindered by the anode corrosion and side reactions involving electrolyte and cathode. When they are operated in open air, the complex gas components (CO\textsubscript{2}, H\textsubscript{2}O, etc.) will make the situation even worse. Carbon dioxide in air is previously considered detrimental to Li-O\textsubscript{2} batteries because of the Li\textsubscript{2}CO\textsubscript{3} formation. However, here we found that CO\textsubscript{2} could make Li-O\textsubscript{2} battery more stable due to new chemistries CO\textsubscript{2} brings. On the anode side, CO\textsubscript{2} can facilitate the formation of a protective and self-healing Li\textsubscript{2}CO\textsubscript{3} film, which can expel the H\textsubscript{2}O and aggressive intermediates during cycling. As to cathode and electrolyte, they are also well protected since O\textsubscript{2} intermediate is captured by CO\textsubscript{2} to reduce the nucleophilicity and prevent the formation of \textsuperscript{1}\text{O}_{2}. As a result, the CO\textsubscript{2} can suppress the side reactions and promote the stability of the Li-O\textsubscript{2} batteries to achieve excellent performance. After applying this concept in Na-O\textsubscript{2} and K-O\textsubscript{2} batteries, we confirm this idea can potentially make practical metal-air batteries more viable.