The Stabilization Effect of CO₂ Chemistries in Li-O₂/CO₂ Batteries
Kai Chen, Gang Huang, Jin-Ling Ma, Dong-Yue Yang, Xiao-Yang Yang, Yue Yu, and Xin-Bo Zhang

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 Li-O₂/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 CO₂. 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 Li-O₂/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 Li-O₂ 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 Li-O₂ 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. However, many challenges are waiting to be resolved before Li-air batteries can be applicable. A Li-air battery usually composes 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. 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. 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. As a result, most significant improvements have been achieved in pure oxygen to avoid these issues, applying these kinds of Li-O₂ 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 Li₂O₂. This results 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. 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, and 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. Since the product in our Li-O₂/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 Li-O₂/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
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 Li₂CO₃ appear in the discharged cathode and these peaks almost vanish after subsequent recharge, implying the formed Li₂CO₃ 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 Li₂CO₃ 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 Li₂CO₃ during the cycling process of the Li-O₂/CO₂ 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-O₂/CO₂ battery permits reversible formation and decomposition of Li₂CO₃.

It is widely accepted that the discharge reaction proceeds according to Eq. 1 in Li-O₂ batteries.

\[ 2Li + O_2 \rightarrow Li_2O_2 \]  (1)

While in the Li-O₂/CO₂ battery, since the gas atmosphere has been changed to O₂/CO₂ (1:1), the fundamental reaction mechanisms are still unclear. To elucidate this, operating pressure test has been conducted (Figure S7). As a comparison, the pressure change during cycling of Li-O₂ battery has also been given. From Figure 1F we can see that the Li-O₂ battery follows the 2.07 e/O₂ coefficient during discharge, in line with the theoretical value of 2 e/O₂ in Eq. 1. With the introduction of CO₂ 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-O₂/CO₂ (1:1) battery (Figure 1G). Considering that Li₂CO₃ is the exclusive discharge product as above proved, the overall discharge reaction formula in Li-O₂/CO₂ (1:1) battery is as follows (Eq. 2), whose theoretical value is 1.33 e/gas.

\[ 2Li + 1/2O_2 + CO_2 \rightarrow Li_2CO_3 \]  (2)

It is obvious that the pressure cannot recover to the initial states in both Li-O₂ and Li-O₂/CO₂ 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, O₂⁻, O₂, etc. \[\text{[8]}\]

In the first charge, 6.02 e/gas and 3.17 e/gas are achieved respectively in the Li-O₂ and Li-O₂/CO₂ batteries, indicating more parasitic reactions happen in the Li-O₂ battery than in the Li-O₂/CO₂ battery. The differential electrochemical mass spectra (DEMS) during charge of Li-O₂/CO₂ battery was then tested. The generation of O₂, CO and CO₂ as well as some fragments resulted from electrolyte decomposition can be clearly observed from Figure S8, confirming the occurrence of side reactions.

In Li-O₂ batteries, the Li anodes are easy to be corroded by H₂O, generating porous LiOH layer, \[\text{[9]}\] which allows H₂O 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-O₂/CO₂ 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-O₂ and Li-O₂/CO₂ batteries. To clarify the origin of this phenomenon, the cycled Li anode in Li-O₂/CO₂ battery has been systematically characterized. Figures 2B and 2C give the C 1s and Li 1s XPS spectra of the cycled Li anode. The strong C 1s and Li 1s peaks of Li₂CO₃ at 289.6 and 55.1 eV can be clearly observed, \[\text{[10]}\] confirming the formation of Li₂CO₃ on the Li anode surface. The other C 1s peaks show the CH₃COO 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. \[\text{[9]}\] Moreover, the Raman spectrum of the cycled Li anode also reveals a Li₂CO₃ peak at 1,084 cm⁻¹ (Figure 2D), which is consistent with the XPS results.

The SEM image in Figure 2E displays that nanosheet-like, dense Li₂CO₃ covers the surface of the cycled Li anode, which can be further confirmed by the zoom-out SEM images in Figures S9A and 9B. However, the cycled Li anode in Li-O₂ battery exhibits a porous surface composed of LiOH (Figures S9C and 9D). The surface morphology of the Li anode after cycling in Li-O₂/CO₂ battery is similar with the paper reported by Asadi Mohammad et al. \[\text{[11]}\] Nevertheless, the Li anode protection induced by our design is much easier without the need of pre-cycling the Li anode in another system and tedious battery assembly and disassembly processes.

The Li anode protection effects induced by different systems are further compared in Figure 2F by exposing the original Li plate and the Li plates cycled in Li-O₂/CO₂ and Li-O₂ batteries to open air. It can be observed that, even after 60 min, the Li₂CO₃ protected Li plate still not totally darken and the central part remains stable, demonstrating the superior stability of the Li plate cycled in Li-O₂/CO₂ battery than that cycled in Li-O₂ battery. Moreover, the anode protection effect in our system can be reinforced with the increase of cycle number, because the protective Li₂CO₃ will continuously form on the Li anode surface (Figure 2G and Figure S10). By comparing the Li anodes after cycling in Li-O₂ and Li-O₂/CO₂ batteries for 120 h, Figure S11 demonstrates the vital role of the CO₂ for protecting the Li anode.
Note that the Li$_2$CO$_3$ 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 Li$_2$CO$_3$ film (Table 1). The first route is the direct reaction between Li and CO$_2$ to form C and Li$_2$CO$_3$. 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 O$_2$ or H$_2$O participates in the reactions. This can be identified by whether cycling is requested for the formation of Li$_2$CO$_3$ layer, because H$_2$O mainly comes from electrolyte decomposition during cycling. A contrast experiment was conducted by using two Li$_2$O$_2$/CO$_2$ 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 O$_2$ running in the Li$_2$O$_2$ batteries with pre-cycled Li anode in Li$_2$O$_2$/CO$_2$ battery and unycled Li anode. The pre-cycled Li anode ran in Li$_2$O$_2$/CO$_2$ battery for 80 h and the unycled Li anode was rested at the same situation for 80 h.

The above experiments indicate that cycling is indispensable for the formation of Li$_2$CO$_3$ protection film, in other words, the H$_2$O generated by the decomposition of the electrolyte during cycling is critical for the formation of Li$_2$CO$_3$ protection film. Therefore, route II can be excluded. The H$_2$O in the cycled battery will react with Li anode to form LiOH and H$_2$, followed by the reaction between LiOH and CO$_2$. Since the reactions in route III is very fast, CO$_2$ can capture LiOH once it forms. On the basis of above analysis, we speculate that route III is the most reasonable mechanism for the Li$_2$CO$_3$ formation on the Li anode. Furthermore, to directly visualize the CO$_2$ 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 O$_2$ and O$_2$/CO$_2$ and exposed them to air. As indicated in Figure S14, the Li plate can be stabilized more than 10 days with the help of CO$_2$.

Super oxide radical, a strong nucleophilic reagent, has been widely proved to be the main origin of side reactions in Li$_2$O$_2$ batteries, including electrolyte decomposition and cathode oxidation.[2b, 2c, 11] Therefore, capturing superoxide is very meaningful to stabilize the battery system. Back to 1984, Julian L. R. confirmed that O$_2$ was prone to bind CO$_2$ through reactions in Eqs. 3 and 4 [12], which was further supported by the theoretical calculation conducted by Lim H. K.[20] So we can reasonably speculate that CO$_2$ can capture O$_2$ to reduce the disproportionation reaction in Li$_2$O$_2$/CO$_2$ battery, thus parasitic reactions can be greatly alleviated (Figure 3A).

**Table 1. Proposed routes for the formation of Li$_2$CO$_3$ on Li anode.**

<table>
<thead>
<tr>
<th>Routes</th>
<th>Reactions</th>
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<tbody>
<tr>
<td>I</td>
<td>4Li + 3CO$_2$ $\rightarrow$ 2Li$_2$CO$_3$ + C</td>
</tr>
<tr>
<td>II</td>
<td>2Li + 3O$_2$ + CO$_2$ $\rightarrow$ Li$_2$CO$_3$</td>
</tr>
<tr>
<td>III</td>
<td>Li$_2$O + H$_2$O $\rightarrow$ LiOH (sol) + ½ H$_2$ (g)</td>
</tr>
<tr>
<td></td>
<td>2LiOH(sol) + CO$_2$(sol) $\rightarrow$ Li$_2$CO$_3$(s) + H$_2$O(l)</td>
</tr>
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</table>

Total: 2Li + 3H$_2$O(sol) + CO$_2$(sol) $\rightarrow$ Li$_2$CO$_3$(s) + 3H$_2$(g)
induced stabilization effect. The above evidences demonstrate that the introduction of CO$_2$ into the reaction gas can effectively alleviate the electrolyte decomposition.

Figure 3. Schematic and confirmation of CO$_2$-endowed cathode and electrolyte stabilization in Li-O$_2$/CO$_2$ batteries. (A) The proposed reaction route of capturing O$_2$ by CO$_2$. (B, C) The RRDE experiments in O$_2$ and O$_2$/CO$_2$ with 0.1 M LiCF$_3$SO$_3$/TEGDME electrolyte. (D, E) $^1$H and $^13$C NMR spectra of the cycled electrolytes dissolved in D$_2$O.

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 10$^{th}$ discharge and charge, no obvious peaks corresponding to Li$_2$CO$_3$ and other species can be detected for CNT and Pd/CNT cathodes, probably due to the limited cycling capacity and good charge efficiency in this short cycle number. However, after 50 cycles, Li$_2$CO$_3$ peak at 880 cm$^{-1}$ is clearly seen for CNT cathode, indicating the remnant of undecomposed Li$_2$CO$_3$ discharge product. In addition, C-O stretching vibrations related peaks around 940-1230 cm$^{-1}$ and HCOO$^-$ 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. In contrast to CNT cathode, there are no peaks at 940-1230 cm$^{-1}$ or 785 cm$^{-1}$ associated with the 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 Li$_2$CO$_3$ peak at 880 cm$^{-1}$ appears at the 50$^{th}$ 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 10$^{th}$ discharge, the surfaces of the CNT and Pd/CNT cathodes are covered by amorphous Li$_2$CO$_3$ (Figures 4C and 4G). Then, most of the Li$_2$CO$_3$ product decomposes after 10$^{th}$ 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 Li$_2$CO$_3$ to extend the battery life, while the CNT cathode cannot recover after 50$^{th}$ charge (Figures 4E and 4F). The above results show minimal side products (HCOO$^-$ and CH$_3$COOLi originating from cathode and electrolyte decomposition in the Li-O$_2$/CO$_2$ battery with Pd/CNT cathode, which is superior to Li-O$_2$ batteries with severe side products just after 20 cycles, proving the participation of CO$_2$ 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-O$_2$/CO$_2$ batteries, their electrochemical performances need to be amply studied. Figure S19 has proven that O$_2$ is indispensable in the feeding gas to ensure a high capacity and CO$_2$ 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-O$_2$/CO$_2$ batteries in a fixed voltage window of 2.0-4.5 V. In the 1$^{st}$ 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 5$^{th}$ cycle, the capacity of Pd/CNT based battery fades to 2726 mAh g$^{-1}$, but still nearly twice 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 Li$_2$CO$_3$ 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 S5B). 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 Li-O₂/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 at 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 LiC₂F₆SO₂/TEGDME electrolyte, an electrolyte with low-donor-number (DN) TEGDME as solvent. To prove the universality of CO₂ induced electrochemical performance improvement, Li-O₂/CO₂ batteries with high-DN DMSO based electrolyte have been investigated (see details in Figures S24-S27). As expected, the introduction of CO₂ into the reaction gas not only promotes the lifetime but also elevates the energy efficiency of DMSO-based Li-O₂ batteries. The reason for the Li-O₂/CO₂ battery failure after 715 cycles has been investigated in detail (Figures S28-S30) and it is found that the failed cathode is the origin of the battery failure rather than the Li metal anode. Now that the Li-O₂/CO₂ battery can sustain such a long life, the Li anode stability after hundreds of cycles has been checked. Figure S31 demonstrates that the Li loss is only 6.23% after 500 cycles in the Li-O₂/CO₂ battery, making the Li plate can live more than 8000 cycles if the cathode is changed every 500 cycles. In sharp contrast, the Li plate in the Li-O₂ battery shows a high loss of 25.77% after just 50 times cycling and only 194 cycles can be achieved theoretically. The huge difference in Li loss between these two batteries can be explained by the anode stability revealed by Figure S32.

Above results have shown great success of introducing CO₂ into the Li-O₂ battery system. In view that high activity and instability of metal anodes is a common issue in metal-O₂ batteries, we hypothesize that this concept is applicable in other metal-O₂ battery systems, like Na-O₂ and K-O₂ batteries. Figures S33-S35 give the cycling performance of Na/K-O₂ batteries with/without introduction of CO₂. The Na-O₂/CO₂ battery can sustain 129 stable cycles, twice that of Na-O₂ battery (62 cycles). More importantly, the K-O₂/CO₂ battery achieves a life of 294 cycles, far exceeding the 5 cycles of K-O₂ battery. The successful adoption of O₂/CO₂ in these two battery systems has proven the versatility of CO₂ usage in metal-air batteries.

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 H₂O and intermediates. Moreover, the existence of CO₂ can also capture O₂, 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 CO₂ endows. Due to the synergistic optimizations brought by catalytic Pd/CNT cathode and CO₂, 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 CO₂ 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

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

The application of Li-O_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_2, H_2O, etc) will make the situation even worse. Carbon dioxide in air is previously considered detrimental to Li-O_2 batteries because of the Li_2CO_3 formation. However, here we found that CO_2 could make Li-O_2 battery more stable due to new chemistries CO_2 brings. On the anode side, CO_2 can facilitate the formation of a protective and self-healing Li_2CO_3 film, which can expel the H_2O and aggressive intermediates during cycling. As to cathode and electrolyte, they are also well protected since O_2 intermediate is captured by CO_2 to reduce the nucleophilicity and prevent the formation of ^1O_2. As a result, the CO_2 can suppress the side reactions and promote the stability of the Li-O_2 batteries to achieve excellent performance. After applying this concept in Na-O_2 and K-O_2 batteries, we confirm this idea can potentially make practical metal-air batteries more viable.