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Realizing stable carbonate electrolytes in Li–O_2/CO_2 batteries

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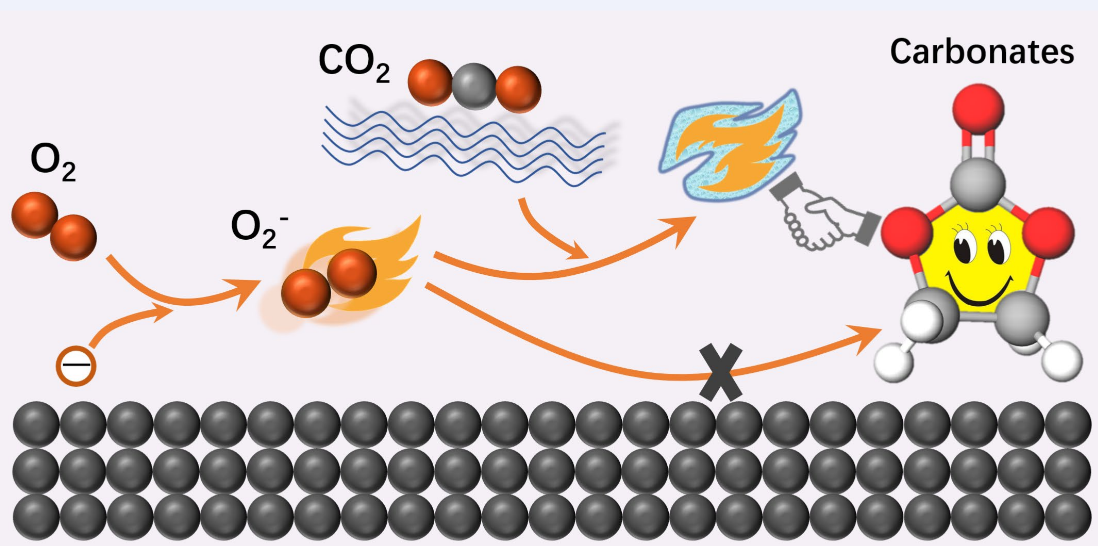
Comprehensive Summary

The increasing demand for high-energy storage systems has propelled the development of Li-air batteries and Li-O_2/CO_2 batteries to elucidate the mechanism and extend battery life. However, the high charge voltage of Li_2CO_3 accelerates the decomposition of traditional sulfone and ether electrolytes, thus adopting high-voltage electrolytes in Li-O_2/CO_2 batteries is vital to achieve a stable battery system. Herein, we adopt a commercial carbonate electrolyte to prove its excellent suitability in Li-O_2/CO_2 batteries. The generated superoxide can be captured by CO_2 to form less aggressive intermediates, stabilizing the carbonate electrolyte without reactive oxygen species induced decomposition. In addition, this electrolyte permits the Li metal plating/stripping with a significantly improved reversibility, enabling the possibility of using ultra-thin Li anode. Benefiting from the good rechargeability of Li_2CO_3, less cathode passivation, and stabilized Li anode in carbonate electrolyte, the Li-O_2/CO_2 battery demonstrates a long cycling lifetime of 167 cycles at 0.1 mA cm^{-2} and 0.25 mAh cm^{-2}. This work paves a new avenue for optimizing carbonate-based electrolytes for Li-O_2 and Li-O_2/CO_2 batteries.



Keywords

Li-O_2/CO_2 batteries | Carbonate electrolytes | High-voltage electrolytes | Superoxide capture | Anode stabilization

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Background and Originality Content

The increasing demand for batteries with high energy density has promoted the development of new energy storage systems beyond Li-ion batteries. Lithium-oxygen (Li-O_2) batteries are a promising candidate due to their ultrahigh theoretical energy density (3450 Wh/kg). In the past decade, Li-O_2 batteries have achieved tremendous progresses in both mechanism deciphering and prototype application.[1-4] However, most of the studies were conducted in pure oxygen environment, even though the final goal is to use Li-O_2 batteries in ambient environment. The complex air components including CO_2 and H_2O may greatly influence the reaction mechanism and battery performance.[5-7] Therefore, the roles of CO_2 in Li-air batteries should be thoroughly understood, which has resulted the investigations of Li-O_2/CO_2 batteries.[8-10]

For a long time, CO_2 is considered as a negative factor in Li-O_2/CO_2 batteries due to the high charge voltage induced by the wide-bandgap insulator lithium carbonate.[7,11-14] However, some recent reports have claimed that the CO_2 could bring some advantages, like forming protective layer on Li anode and capturing O_2^- to alleviate side reactions.[9,15] Nevertheless, the high decomposition potential of Li_2CO_3 is still difficult to be resolved effectively. It has been reported that this high overpotential could be reduced by adopting suitable catalysts, like Pd/CNT[9], Ru/GNS,[16] Ru/NiO@Ni/CNT,[17] Ru/N-doped CNT[5], and $NiCo_2O_4$ hollow microspheres.[18] Unfortunately, at the late stage of the battery charging, the voltage would still climb to 4.5 V. Besides, the catalytic cathodes could also facilitate the oxidation of electrolytes at high voltages. Yu Qiao et al[8] tailored the electrolyte composition to generate $[Li(DMSO)_3]^+$ – $[TFSI^-]$ contact ion pairs to realize a Li_2CO_3-free Li-O_2/CO_2 battery by stabilizing peroxodicarbonate ($C_2O_6^{2-}$). The charge voltage was limited to around 3.5 V for the only first 20 cycles with a capacity of ~750 mAh/g. Prolonging cycling or increasing cycling capacity may induce the formation of Li_2CO_3, thus high charge voltage and electrolyte decomposition is inevitable. Therefore, adopting electrolytes with high-voltage resistance to avoid side reactions on the cathode side is important but has not been achieved currently.

Up to now, the electrolytes for Li-O_2/CO_2 batteries are inherited from Li-O_2 batteries. That is to say, tetraethyleneglycol dimethyl ether (TEGDME)- and dimethyl sulfoxide (DMSO)-based electrolytes are the mainstream in Li-O_2/CO_2 batteries. Despite TEGDME and DMSO are relatively stable toward O_2^- (a critical intermediate in Li-O_2 batteries), they are prone to decompose at above 4.5 V, which is easily achieved during the charge process in Li-O_2/CO_2 batteries. The consequent side products derived from electrolyte decomposition could block the active sites and passivate the cathode to cause short life. Different from TEGDME and DMSO-based electrolytes, carbonate electrolytes possess a wider electrochemical window (oxidation potential up to 5.0 V vs Li^+/Li), thus they are promising in Li-O_2/CO_2 batteries. Interestingly, carbonate electrolytes were widely used in Li-O_2 batteries at the infant stage in years of 2000-2010, which was inspired by their application in Li-ion batteries.[19-23] However, in early 2010s, many reports have found that carbonate electrolytes are not stable and the discharge products in Li-O_2 batteries usually include Li_2CO_3 as a side product.[24-27] This culprit was identified to be the incompatibility between O_2^- and carbonates.[24] Later, many works started to adopt DMSO- and TEGDME-based electrolytes. However, the real chemical stability of DMSO and TEGDME toward Li has been questioned, while carbonate electrolytes are more stable toward Li.[28,29] As to Li-O_2/CO_2 batteries, the formed O_2^- can be captured by CO_2 to alleviate its aggressivity, thus carbonate electrolytes may be rejuvenated to endure the high charge voltage to enable a stable and long-life Li-O_2/CO_2 battery.

Herein, we checked the applicability of carbonate electrolytes in Li-O_2/CO_2 batteries and selected commercial electrolyte LB001 [1 M $LiPF_6$ in EC/DMC (1:1 vol)] for deep investigation. We found the carbonate electrolytes were stable at >5.0 V and compatible with the electrodes (cathode and anode) and intermediates of Li-O_2/CO_2 batteries. Theoretical calculation has confirmed that the formed O_2^- is more prone to bind CO_2 rather than the carbonate molecules, thus stabilizing the electrolyte. At the anode side, the oxygen and CO_2 saturated LB001 electrolyte could empower significantly improved Li plating/stripping CEs (up to ~92%), much

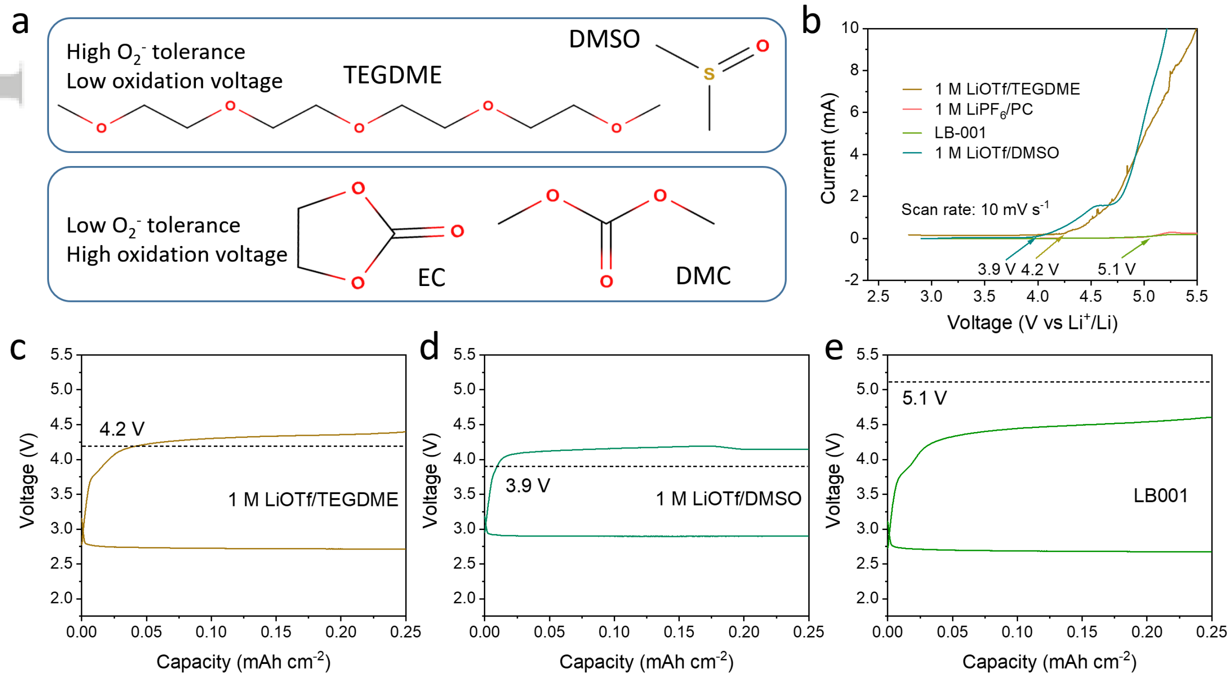

Figure 1 The properties of solvents for electrolytes in Li-O_2/CO_2 batteries. (a) The structures of TEGDME, DMSO, EC, and DMC, and their tolerance toward O_2^-. (b) High voltage stabilities of the electrolytes of 1 M LiOTf/TEGDME, 1 M $LiPF_6$/PC, LB001, and 1 M LiOTf/DMSO. (c-e) Discharge-charge profiles of the Li-O_2/CO_2 batteries with super P cathodes and different electrolytes at 0.1 mA cm^{-2}.

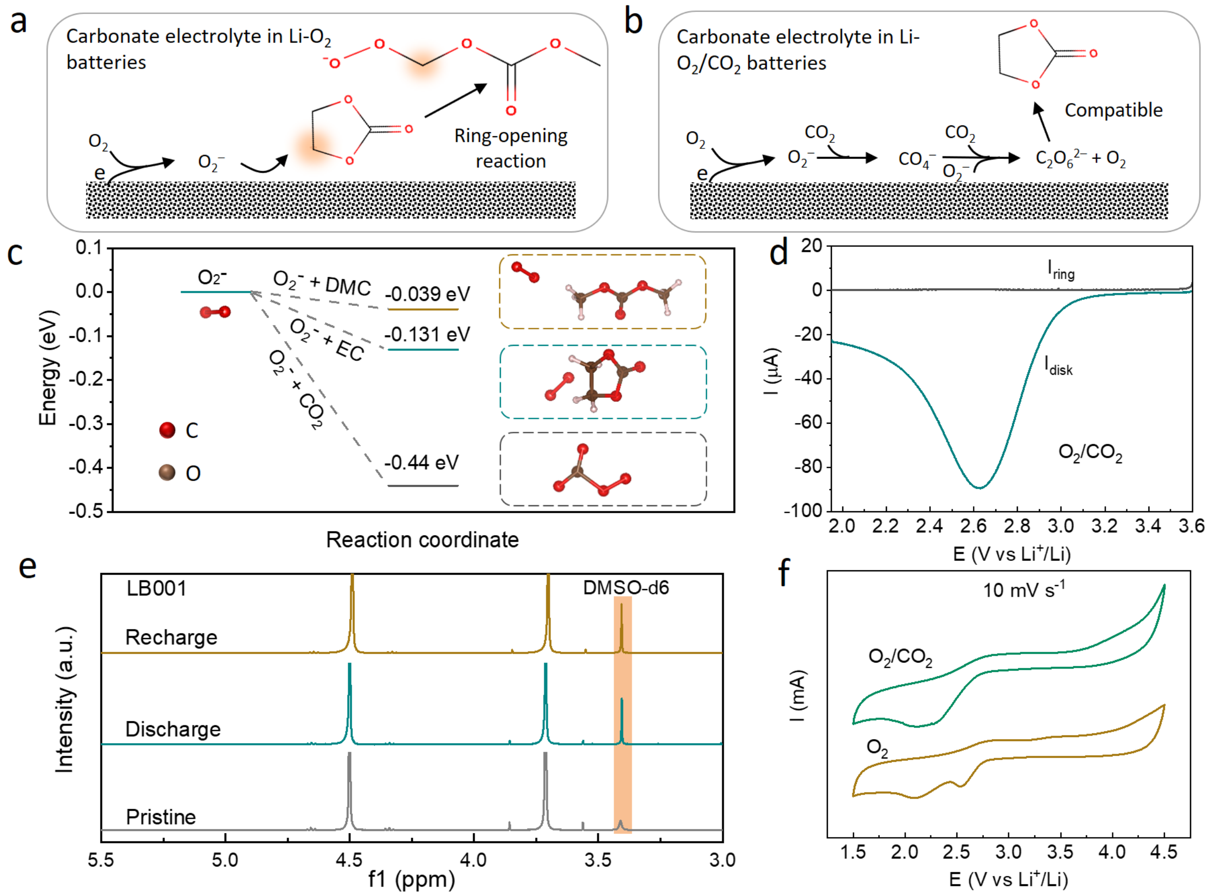

Figure 2 The stability of LB001 electrolyte in Li–O_2/CO_2 batteries. (a) The decomposition of EC after the attack of O_2^-. (b) The compatibility of CO_2–captured O_2^- with EC. (c) Binding energies of O_2^- with DMC, EC, and CO_2 molecules. (d) RRDE result in LB001 electrolyte with O_2 and CO_2 participation. (e) NMR tests of pristine LB001 electrolyte and the electrolytes after discharge and recharge. (f) Cyclic voltammetries of Li-O_2 battery and Li-O_2/CO_2 battery in the range of 1.5-4.5 V at a scan rate of 10 mV s^{-1}.

higher than those of the DMSO- and TEGDME-based electrolytes with CEs lower than 25%, ranking LB001 the best electrolyte ever reported for Li-O_2/CO_2 batteries. Furthermore, the formed Li_2CO_3 discharge product of Li-O_2/CO_2 batteries with LB001 is rechargeable. Profiting from these advantageous effects of LB001, the Li-O_2/CO_2 battery runs stably for 167 cycles at a current density of 0.1 mA cm^{-2} and a fixed capacity of 0.25 mAh cm^{-2}, while the batteries with TEGDME- and DMSO-based electrolytes could only operate 65 cycles and 99 cycles, respectively. We anticipate this work will expand the electrolyte candidates in Li-O_2/CO_2 batteries and inspire further performance improvements by designing advanced carbonate-based electrolytes.

Results and Discussion

Figure 1a shows the molecular structures of TEGDME, DMSO, EC, and DMC. Among them, TEGDME and DMSO have high O_2^- tolerance and solubility, while for EC, ring-opening reaction will happen due to the attack of O_2^-. The stability between Li metal and LB001 was then checked (Figure S1). After immersing a Li plate in LB001 for 10 days, the plate still exhibits metallic luster, indicating their compatibility to some extent. The linear sweep voltammetries compare the high-voltage resistance of different electrolytes (Figure 1b). It is clear that the carbonate-based electrolytes, including 1 M $LiPF_6$/propylene carbonate (PC) and LB001, are stable below 5.1 V, while 1 M LiOTf/DMSO and 1 M LiOTf/TEGDME start to decompose at 3.9 V and 4.2 V, respectively. Even at >5.1 V, the decomposition of the carbonate electrolytes is still very limited. This means that during cycling of Li-O_2/CO_2 batteries, serious parasitic reactions may be involved along with the decomposition of DMSO and TEGDME when the charge voltage surpasses their upper limits. To check whether this will occur, the discharge-charge profiles of Li-O_2/CO_2 batteries with 1 M LiOTf/TEGDME, 1 M LiOTf/DMSO, and LB001 were tested (Figure 1c-e). It can be seen that the charge voltages for the TEGDME- and DMSO-based batteries are 4.3 V and 4.2 V, higher than their corresponding voltage range. By contrast, the charge voltage for the battery with LB001 is only around 4.5 V, within the stability window of LB001. Therefore, the side reactions in Li-O_2/CO_2 batteries with LB001 electrolyte can be greatly suppressed due to its high-voltage resistance. For 1 M $LiPF_6$/PC, the situation is similar to LB001, the charge voltage is ~4.5 V (Figure S2). Considering the high viscosity of 1 M $LiPF_6$/PC, we selected LB001 for further detailed investigation.

Another threat to the electrolyte stability is the O_2^- formed during battery cycling. For Li-O_2 batteries, the formed O_2^- can attack EC molecule through ring-opening reaction (Figure 2a). With the existence of CO_2, the O_2^- could be quickly consumed by CO_2 to form $C_2O_6^{2-}$ (Figure 2b), an important intermediate in Li-O_2/CO_2 batteries. This intermediate is mild compared with O_2^-, thus improving the compatibility with EC. Density functional theory was utilized to compare the binding energies between O_2^- and DMC, EC, and CO_2 (Figure 2c). The adsorption energy for DMC is only -0.039 eV, indicating DMC is barely bonded with O_2^-, avoiding the O_2^- attack. For EC, the adsorption energy is –0.131 eV, much lower than the CO_2-induced –0.44 eV with the change of bond angle of CO_2 due to the binding of O_2^-. That is to say, the formed O_2^- binds with CO_2 preferentially, and accordingly eliminates the formation of $^1O_2$

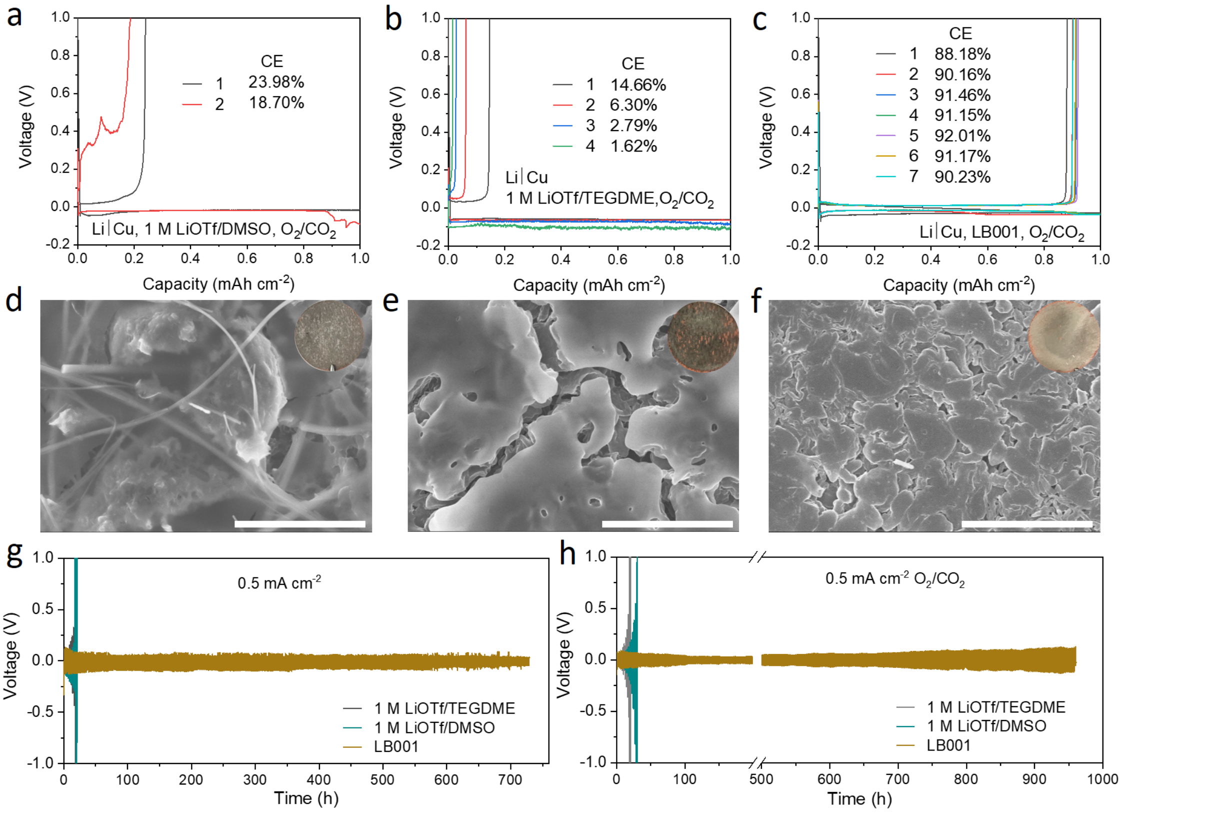

Figure 3 The performance of Li||Cu batteries and Li||Li batteries. (a-c) Coulombic efficiencies of Li||Cu batteries using 1 M LiOTf/DMSO (a), 1 M LiOTf/TEGDME (b), and LB001 (c) electrolytes at 0.2 mA cm^{-2} with a fixed plating capacity of 1.0 mAh cm^{-2} and a cut-off charge voltage of 1.0 V. (d-e) The morphologies of Cu surfaces after plating 1 mAh cm^{-2} of Li at 0.2 mA cm^{-2} using 1 M LiOTf/DMSO (d), 1 M LiOTf/TEGDME (e), and LB001 (f) electrolytes saturated with O_2/CO_2. Scale bar, 10 µm. (g,h) Cycling performance of Li||Li symmetrical batteries at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} with bare electrolytes (g) and O_2/CO_2-saturated electrolytes (h).

from the disproportionation of superoxide. To confirm the O_2^- cleavage by CO_2, rotating ring-disk electrode (RRDE) experiment was conducted (Figure 2d). Oxygen was reduced to O_2^- on the disk electrode and then it was transferred to the ring electrode to be oxidized to generate oxidation current. However, with CO_2 participation, no oxidation current can be detected on the ring electrode, implying that the O_2^- could be quickly consumed by CO_2. Since the absence of ring current may also be caused by the electrolyte induced O_2^- depletion,[24,30] the stability of LB001 electrolyte was then tested after discharge and charge by nuclear magnetic resonance (NMR). The NMR signals of pristine, discharged, and charged electrolytes are identical, again confirming the preferential binding of O_2^- by CO_2 and the good compatibility of LB001 in Li-O_2/CO_2 batteries (Figure 2e). The O_2^- capturing can also be reflected on the cyclic voltammetry of Li-O_2/CO_2 batteries (Figure 2f). Compared with the two reduction peaks at 2.54 V and 2.10 V in Li-O_2 batteries, which can be attributed to O_2 reduction to O_2^- and further reduction of O_2^- to O_2^{2-}, only one reduction peak at 2.58 V appears in Li–O_2/CO_2 batteries. This can be explained as the captured O_2^- and following intermediate cannot be reduced further, which is consistent with many mechanistic investigations that have proved the reduction reactions only consist of O_2 reduction to O_2^- through one-electron transfer.[12,31] In addition, if the electrolyte molecules are reactive toward O_2^-, the formed discharge product would be amorphous along with complex side products,[24,32,33] while our discharge product is crystalline and pure phase, which will be shown and discussed later. In sum, we have confirmed that the reduced oxide species can be captured by CO_2 thus the carbonate electrolyte is stable in this environment and a long-life Li-O_2/CO_2 battery could be expected.

Next, we focused on the electrochemical stability of LB001 toward the Li anode and the Li reversibility during cycling in Li-O_2/CO_2 batteries. To explore the advantages of LB001 over DMSO- and TEGDME-based electrolytes, the Li plating/stripping CEs were determined by constructing Li||Cu cells with these electrolytes. The batteries were discharged at 0.2 mA cm^{-2} to 1.0 mAh cm^{-2} and then charged to 1.0 V. Firstly, the electrolytes without O_2/CO_2 were evaluated. In Figure S3a, the initial CE for 1 M LiOTf/DMSO is only 20.76%, then increases to above 30% in the following cycles. This reveals that DMSO may bring poor CEs in Li metal batteries. The results for 1 M LiOTf/TEGDME are even worse (Figure S3b). The CEs for the first four cycles are 13.94%, 9.53%, 5.17%, and 3.09%. Unexpectedly, the cell with LB001 shows an initial CE of 90.92%, and the following CEs increase and a highest CE of 96.32% could be reached (Figure S3c). This makes the LB001 based Li||Cu cell exhibit an average CE of 93.18% for the first 50 cycles (Figure S4). To check the morphologies of the deposited Li on Cu foil, the Cu electrodes plated by 1 mAh cm^{-2} Li were observed by the scanning electron microscope (SEM) (Figure S5). As can be shown in Figure S5a, there is only a small amount of Li depositing on the Cu electrode in the DMSO-based electrolyte, and most of Li is attached to the glass fibers, thus the amount of stripped Li is very limited due to the poor conductivity of glass fiber. As to the deposited Li in 1 M LiOTf/TEGDME, it can be directly visualized by the digital picture of the Cu electrode (Figure S5b). However, from the SEM image, cracked Li layer is observed on the surface. Under the surface, the Li deposition is mossy. This will induce serious side reactions during the following cycles. Being consistent with the high CEs in LB001, the deposited Li on the Cu electrode shows metallic luster and smooth surfaces (Figure S5c). These

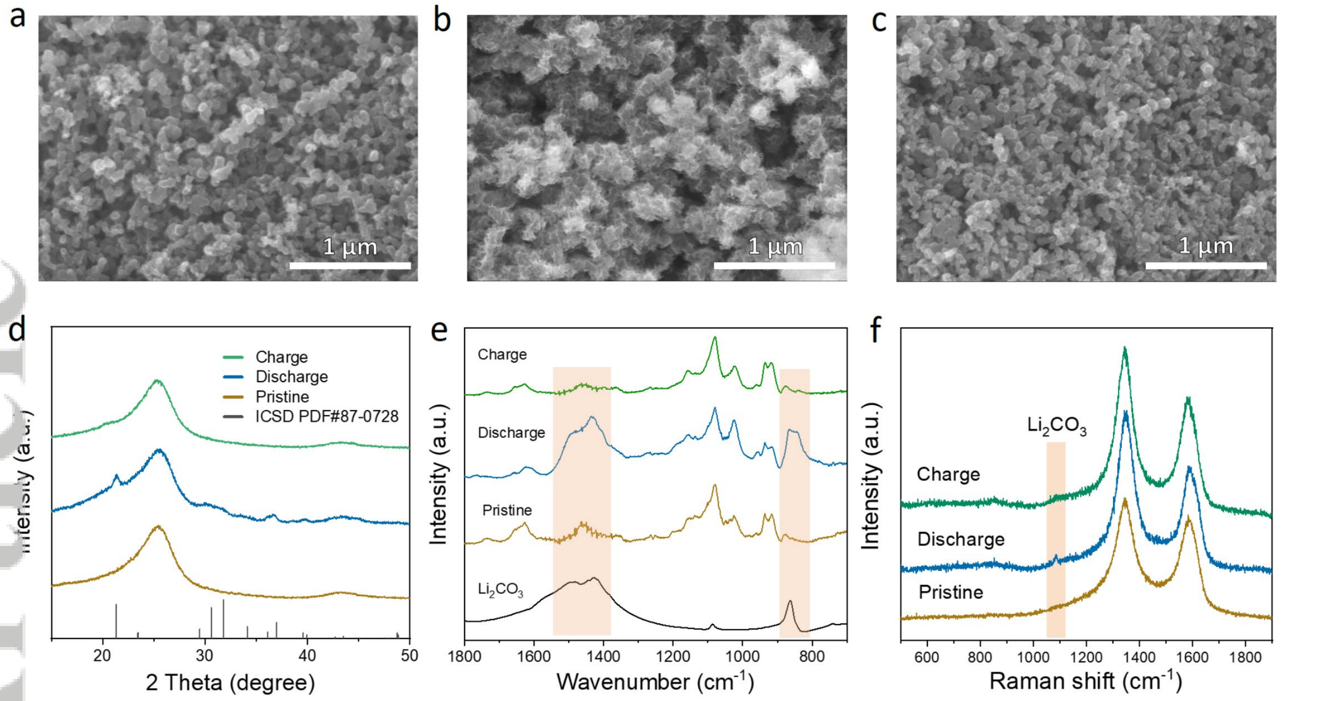

Figure 4 The rechargeabiliy of Li-O_2/CO_2 batteries with LB001 electrolytes and super P cathodes. SEM images of the pristine (a), discharged, (b) and recharged (c) cathodes, scale bar, 1 μm. (d) XRD patterns, (e) FTIR and (f) Raman spectra of the pristine, discharged, and recharged cathodes.

electrochemical tests and morphological characterizations have proved LB001 possesses dramatic advantages over DMSO and TEGDME-based electrolyte in Li-metal batteries.

To mimic the Li plating and stripping in Li-O_2/CO_2 batteries, these electrolytes were saturated by O_2 and CO_2 before cell assembly. The reversibility of Li in these electrolytes were again tested in Li||Cu cells. In O_2/CO_2-saturated DMSO electrolyte, the initial CE is 3.98%, then it drops to 18.70% in the second cycle (Figure 3a), much lower than the one without O_2 and CO_2. For TEGDME, the participation of O_2 and CO_2 also renders poor CEs. The initial CE of 14.66% decreases to 1.62% after only four cycles (Figure 3b). Even though the introduction of O_2 and CO_2 negatively influences the CEs in DMSO and TEGDME-based cells to a large extent, the effect in LB001 is minimal. The initial CE for O_2/CO_2-saturated LB001 is 88.18% and the CEs are higher than 90% in the following six cycles (Figure 3c). Furthermore, an average CE of 87.32% could be realized in the first 50 cycles (Figure S6). The high CEs of the O_2/CO_2 saturated LB001 can also be reflected in the morphologies of the deposited Li. In O_2/CO_2-saturated DMSO and TEGDME electrolytes, the Li morphologies are similar to the results in bare electrolytes, with mossy Li or obvious Li dendrites (Figure 3d,e). For the LB001 electrolyte, uniform Li deposition and metallic luster can be observed (Figure 3f). Generally, the CEs decrease after the involvement of O_2/CO_2, which may be caused by the reactivity between O_2/CO_2 and fresh Li. Nevertheless, the results presented here delivers the positive aspects of adopting LB001 in Li-O_2/CO_2 batteries. The DMSO- and TEGDME-based electrolytes display poor Li reversibility whether with the existence of O_2/CO_2 or not, which has long been neglected in the reported Li-O_2 and Li-O_2/CO_2 batteries because much excessive Li at the anode side could cover the Li inefficiency. Developing electrolytes with high Li efficiency is paramount in the future to reduce the amount of Li used in batteries. Here, the good Li reversibility brought by LB001 would make this possible, then less excessive Li could be used in Li-O_2/CO_2 batteries in the future.

Symmetrical Li||Li batteries were then tested in these electrolytes with and without O_2/CO_2 participation. When cycling the batteries at 0.1 mA cm^{-2} without O_2/CO_2, LB001 enables the battery to cycle for more than 640 hours, while the batteries with the other two electrolytes experience obvious voltage increase after 200 hours and 270 hours (Figure S7). When the current density is increased to 0.5 mA cm^{-2}, the cycling performance of the batteries with DMSO and TEGDME electrolytes deteriorates to 20 hours (Figure 3g). Especially, the instability of DMSO in the symmetrical cell can be visualized from the separator color change and the swell of the coin cell (Figure S8). However, a long life of 720 hours can still be sustained for LB001 (Figure 3g). When O_2/CO_2 is involved, the protection effects from the CO_2 are beneficial for extending the battery life, and the life of the Li||Li battery with LB001 is prolonged to 960 hours (Figure 3h). Unfortunately, the battery performance of the symmetrical batteries with the other two electrolytes only shows puny improvement (Figure 3h). Since high overpotentials of Li stripping and plating will be reflected on the Li-O_2/CO_2 batteries to generate low discharge voltage and high charge voltage to trigger serious side reactions, the stabilization of Li anode by LB001 is more likely to contribute to a long-life Li-O_2/CO_2 battery.

To prove the viability of LB001 in Li-O_2/CO_2 batteries, super P were used as cathodes to assemble batteries for investigation. The surface of pristine super P particles is smooth (Figure 4a). After discharge, nanosheet-like product forms on the particle (Figure 4b, Figure S9) and the product can be removed after subsequent recharge (Figure 4c) to recover the clear surface. The morphologies of discharge products in the Li-O_2/CO_2 batteries with TEGDME and DMSO electrolytes were also characterized. The product in TEGDME-based battery shows similar sheet-like product (Figure S10a,b), while rhombic particle piles are detected for the DMSO electrolyte (Figure S10c,d). The similarity and difference in discharge product can be attributed to the different donor numbers of electrolyte solvents (DMSO: 29.8, TEGDME: 16.6, EC: 16.4, DMC: 17.2), which could influence the discharge pathways of batteries.[12,34-36] To identify the composition of discharge product and the rechargeability of the battery system, X-ray diffraction (XRD), Raman scattering, and Fourier transform infrared spectroscopy (FTIR) were utilized to characterize the cathodes at different states. From the XRD patterns (Figure 4d) we can see that clear peaks at 21.34°, 30.60°, 31.80°, 36.09°, and 36.96° correspond well with the standard Li_2CO_3 crystalline (ICSD PDF#87-

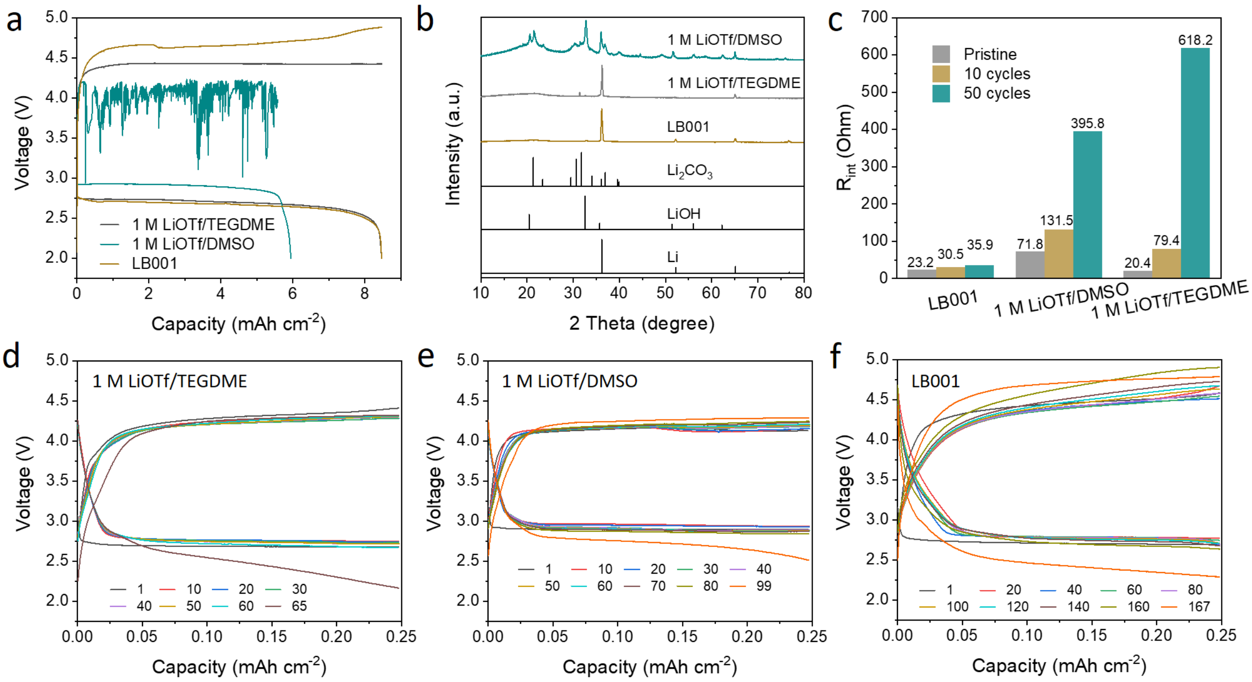

Figure 5 Battery performance of Li-O_2/CO_2 batteries with different electrolytes. (a) Full discharge-charge profiles of the Li-O_2/CO_2 batteries with 1 M LiOTf/TEGDME, 1 M LiOTf/DMSO, and LB001. (b) XRD patterns of the Li anodes after cycling for 50 cycles in Li-O_2/CO_2 batteries. (c) Interfacial impedances of the Li-O_2/CO_2 batteries at pristine state, after 10 and 50 cycles. (d-f) Cycling performance of the Li-O_2/CO_2 batteries with 1 M LiOTf/TEGDME (d), 1 M LiOTf/ DMSO (e), and LB001 (f) electrolytes at 0.1 mA cm^{-2} with a fixed capacity of 0.25 mAh cm^{-2}.

0728) for the discharged cathode and these peaks disappear after charge. Similar phenomenon is also observed in the FTIR and Raman results. The evident FTIR signals at 862, 1428, and 1491 cm^{-1} (Figure 4e) and the Raman peak at 1080 cm^{-1} (Figure 4f) are attributed to Li_2CO_3, and the charge process repristinates the spectroscopies, which is consistent with the SEM results. These evidences have unambiguously confirmed the rechargeability of the Li-O_2/CO_2 batteries with LB001 as electrolyte.

After confirming the LB001 does not change the electrochemistry of Li-O_2/CO_2 batteries with the highly reversible Li_2CO_3 formation and decomposition, the battery performance was then evaluated. In Figure 5a, the batteries with 1 M LiOTf/TEGDME and LB001 electrolytes exhibit similar capacity (~8.5 mAh cm^{-2}) after discharging to 2.0 V. However, the DMSO-based battery just delivers 5.6 mAh cm^{-2} capacity and experiences drastic voltage fluctuation during the charge process, indicating serious high voltage induced electrolyte decomposition. Then, the batteries were cycled at 0.1 mA cm^{-2} with a fixed capacity of 0.25 mAh cm^{-2}. After 50 cycles, the anode and cathode were characterized by SEM and XRD. Figure S11a,b manifests the cycled Li is severely corroded and pulverized with the 1 M LiOTf/DMSO electrolyte, which may be caused by the intrinsic instability between Li and DMSO. By contrast, the Li anodes cycled in LB001 and 1 M LiOTf/TEGDME electrolytes are relatively more stable with well remained metallic luster, and only non-uniform thin layers can be observed (Figure S11c,d). The anodes were then tested by XRD to identify the compositions of the cycled Li anodes. Strong peaks of LiOH and Li_2CO_3 appear on the Li anode cycled in LiOTf/DMSO (Figure 5b), which is consistent with the large amount of corroded Li in Figure S11a,b. Within expectation, the Li anode in LB001 shows no signals of Li_2CO_3 or LiOH, and only a tiny peak from Li_2CO_3 can be seen for the Li anode cycled in LiOTf/TEGDME. The cathodes after cycling were also visualized by SEM to check whether there is any undecomposed product accumulation. As shown in Figure S12a,b, only a thin passivation layer can be observed on the super P cathode in the LB001-based battery, which may be caused by the high charge efficiency enabled by the absence of electrolyte decomposition. We note that the decomposition voltage of LB001 is higher than those of DMSO and TEGDME (Figure 1c-e), this may facilitate the complete decomposition of Li_2CO_3 and make the realization of longer cycling life become possible. However, for the cathodes cycled in DMSO- and TEGDME-based electrolytes, the accumulated products are distinct on the super P particles (Figure S12c-f), which blocks the electron and Li^+ transfer at the cathode/electrolyte interface to limit the cycling performance.

The accumulation of undecomposed product on the cathode could also be reflected by the increase of cell impedance. Electrochemical impedance spectroscopy (EIS) was performed to examine the impedance changes during cycling (Figure 5c and Figure S13). After resting for 3 hours, the pristine spectroscopies were acquired. The batteries with DMSO electrolyte shows higher interfacial impedance (R_{int}, 71.8 Ω) than those of LB001 (23.2 Ω) and TEGDME (20.4 Ω). Considering both anode/electrolyte and cathode/electrolyte interfaces contribute to R_{int}, the high pristine R_{int} of the battery with DMSO may arise from the instability of Li and DMSO. After 10 cycles, the R_{int} of LB001 just increases to 30.5 Ω, much lower when compared with LiOTf/DSMO (131.5 Ω) and LiOTf/TEGDME (79.4 Ω). Beyond expectation, even after 50 cycles, the R_{int} of LB001 (35.9 Ω) experiences little change, different from the significant R_{int} increase for the batteries with LiOTf/DSMO (395.8 Ω) and LiOTf/TEGDME (618.2 Ω) electrolytes. Figure S11 and Figure 5b have shown that the anodes are stable in LB001 and LiOTf/TEGDME, thus the impedance difference between LB001 and LiOTf/TEGDME mainly comes from the cathode/electrolyte interface, which is well consistent with the serious product accumulation in LiOTf/TEGDME (Figure S12e,f). As to the battery with LiOTf/DMSO, the impedance boom is resulted from the Li anode corrosion and cathode passivation (Figure S11a,b and Figure S12c,d). These results have proved that LB001 can play a positive role in anode protection and cathode-side product decomposition in Li-O_2/CO_2 batteries, and accordingly reflected in batteries is to improve the cycling performance. In Figure 5d,e, the Li-O_2/CO_2 batteries with LiOTf/TEGDME and LiOTf/DMSO could only run 65 and 99 cycles, respectively at 0.1 mA cm^{-2} with a fixed capacity of 0.25 mAh cm^{-2}. While for the battery with LB001, it exhibits a long-term cycling lifetime of 167 cycles due to the stabilized anode and excellent cathode rechargeability enabled by the LB001. At the same cycling condition, 1 M $LiPF_6$/PC could even enable a higher battery cycling performance of 202 cycles (Figure S14). Therefore, carbonate electrolytes can be a favorable electrolyte candidate in Li-O_2/CO_2 batteries.

Conclusions

In conclusion, to resolve the decomposition of electrolytes in Li-O_2/CO_2 batteries, we have demonstrated that high-voltage resistant carbonate electrolytes (e.g. LB001) could be good choices. The generated O_2^- can be captured by CO_2 to alleviate its aggressivity, thus the carbonate electrolyte is stable with the intermediates in Li-O_2/CO_2 batteries. At the Li anode side, carbonate electrolytes are intrinsically stable with Li and enable excellent Li reversibility with high CEs in Li||Cu batteries, while traditional DMSO- and TEGDME-based electrolytes exhibit poor CEs. Moreover, the high-voltage stability of carbonate electrolyte makes the Li_2CO_3 discharge product can be effectively decomposed during charge, reducing the cathode passivation to a great extent. As a consequence, the Li-O_2/CO_2 battery with LB001 can steadily run for 167 cycles, much higher than the 65 and 99 cycles of the batteries with TEGDME- and DMSO-based electrolytes. This work has proposed that the outdated carbonate electrolytes in Li-O_2 batteries can be appropriate candidates for Li-O_2/CO_2 batteries. We anticipate this work will inspire more efforts to look for high-voltage and stable electrolytes for Li-O_2 and Li-O_2/CO_2 batteries.

Experimental

Materials. The carbonate electrolytes including LB001 [1 M $LiPF_6$ in EC:DMC (1:1 vol)] and 1 M $LiPF_6$/PC were bought from DoDoChem. These electrolytes were directly used without further treatments. Electrolytes of 1 M $LiCF_3SO_3$ in DMSO or TEGDME were prepared in our lab. $LiCF_3SO_3$ and TEGDME were purchased from Alladin. Before usage, the Li salt was vacuum dried to remove residue water at 130 °C overnight while TEGDME was dried using molecular sieves to make the water content low than 30 ppm. Super-dry DMSO was purchased form J&K Scientific, which was directly used without pre-treatment. Super-dry n-hexane brought from J&K Scientific was used to wash the cathodes and anodes before characterizations.

Cathode preparation. Super P and PVDF were mixed in NMP in a mass ratio of 9:1 to form a slurry. After adequate grinding in a mortar, the slurry was then sprayed on both sides of the carbon paper followed by drying in a vacuum oven at 80 °C overnight. The total mass loading the cathode was 7.0 mg cm^{-2}. The prepared carbon paper was then cut into pieces of 1 cm × 1 cm.

Assembly of Li-O_2/CO_2 batteries. The batteries were assembled based on ECC-Air cells (EL-cell GmbH, Germany) which consist gas inlets and outlets for gas flowing to ensure pure gas environment and prevent gas leakage. The structure of this kind of battery can be seen in our previous work.[9] The battery assembly was conducted in a glove box with O_2 <0.1ppm and H_2O <0.1 ppm. During battery assembly, a lithium plate (14 mm in diameter and 400 nm in thickness) was placed on the bottom, and then a glass fiber separator (18 mm in diameter) and super P cathode (1 cm^2) were consequently stacked on the Li anode. The used electrolyte amount was 150 µL. Finally, other battery components were configured to seal the battery. After assembly, the batteries were tested in a thermotank (25 °C). Before galvanostatic cycling or other electrochemical tests, the batteries were tested for 3 hours in flowing gas to obtain a steady environment.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2021xxxxx.

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Entry for the Table of Contents

Realizing stable carbonate electrolytes in Li–O_2/CO_2 batteries

Kai Chen, Jia-Yi Du, Jin Wang, Dong-Yue Yang, Jiang-Wei Chu, Hao Chen, Hao-Ran Zhang, Gang Huang*, and Xin-Bo Zhang*

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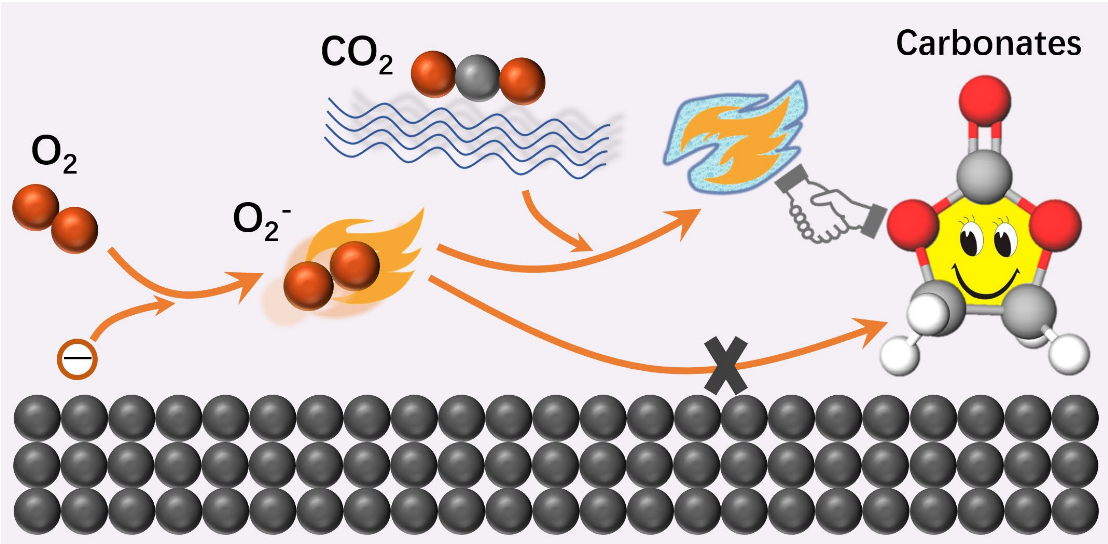

Carbonate electrolytes are not stable in Li-O_2 batteries due to the attack of O_2^-. However, in Li-O_2/CO_2 batteries the generated O_2^- can be captured by CO_2 to stabilized carbonate electrolytes. Thanks to the high-voltage resistance and good Li reversibility, they are excellent electrolytes for long-life Li-O_2/CO_2 batteries.

