Supplementary Information:

Implications of CO_2 contamination in rechargeable non-aqueous Li-O_2 batteries

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Cathode preparation

The XC72 and Ketjenblack cathodes were prepared by spray coating a slurry of XC72 or Ketjenblack (85 wt%) and PTFE (15 wt%) in a water-isopropanol (3:1 by weight) mixture. The slurry was prepared by first adding the PTFE (60% dispersion in water, Sigma Aldrich) into the water-isopropanol mixture followed by the addition of the carbon black powder. The slurry contents were then sonicated for approximately 20 minutes. The slurry was then spray coated onto a 316SS 100 mesh (TWP, Inc., Berkeley, CA) using a Badger model 350 air-sprayer. After spray coating, the XC72 or Ketjenblack coated stainless steel mesh was air dried overnight and punched into 1.1 cm^2 area cathodes. The cathodes were then dried for another 24 hours at 120° C under vacuum. After drying, the cathodes were quickly transferred into an Ar filled glove box (MBraun LABMaster SP, <1ppm O_2 and H_2O) while still hot, then washed with DME three times to remove any organic contaminants and finally dried on a hot plate (200 °C) for at least 2 hours before use in electrochemical measurements. Carbon black loadings used in this study were 1.0-1.3 mg/cm^2. P50 Avcarb carbon paper (Fuel Cell Store, www.fuelcellstore.inc) was punched into 12 mm diameter cathodes (6 mg total weight) and dried at 120 °C under vacuum for 24 hours. After drying, the cathodes were quickly transferred into an Ar filled glove box, washed with DME and dried, in a similar fashion to the carbon black cathodes. These cathodes were used to obtain the spectra reported in Figure 1b.

Cell preparation

All electrochemical cells were discharged under O_2 (Research Purity, Matheson Gas), $C^{18}O_2$ (Sigma Aldrich), or a 90:10 $^{16}O_2$:$C^{18}O_2$ mixture and charged under Ar (Research Purity, Matheson Gas) using a Biologic VSP (Knoxville, TN, USA) potentiostat at 21 °C. The 90:10 O_2:CO_2 mixture was prepared by first expanding ~150 Torr $C^{18}O_2$ into a lecture bottle which had been evacuated to <0.1 Torr prior to gas expansion (the lecture bottle originally contained ~1 bar Ar). O_2 was then expanded into the bottle to achieve a 90:10 O_2:CO_2 pressure ratio. Of course, a 90:10 ratio is much higher than the current concentration of CO_2 in air, but we selected this ratio as a standard in this study to ensure that although Li-O_2 chemistry was still the dominant electrochemistry being explored, any effects CO_2 may have on the chemistry were pronounced and simple to observe. The cells were prepared in a dry Argon glove box (<1 ppm O_2 and H_2O, MBraun USA, Inc.) by stacking a Li-metal anode (FMC Inc.), 2 Celgard 2500 separators, a cathode, and a 1 mm thick stainless steel ring to incorporate a head space above the cathode. The cell geometry is described in more detail in our previous work.[1-3] The electrolyte (1N LiTFSI in DME) used in this work was used as received from Novolyte Technologies and contained less than 10 ppm H_2O, as measured using a Karl Fisher titration (Metrohm Inc.). DME was used as a solvent because it exhibits the highest stability of solvents we have studied[4]. CO_2 solubility in diglyme, triglyme, tetraglyme, and higher order ethers has been reported by Aschenbrenner and Styring[5] and Henni et al.[6] to be approximately 6 ± 0.5 mg CO_2/g ether at 25 °C and 1 atm CO_2, regardless of the number of ether repeat units. A similar CO_2 solubility can be expected in DME. The Ostwald coefficient for O_2 solubility in DME was reported by Read to be 0.21 cm^3 O_2/cm^3 DME, which would correspond to 0.34 mg O_2/g DME at 25 °C and 1 atm O_2. Therefore, O_2 solubility is approximately 20 times less than CO_2 solubility in DME.

Differential quantitative mass spectrometery (DEMS)

The quantitative DEMS system was custom-built and described in detail in previous publications.[1-3] The DEMS system employs a modified Swagelok-cell designed to exhibit excellent hermetic integrity. The cell is discharged and charged under a static head of positive gas pressure (~1.2 bar). Gases collected at the end of the discharge under the CO_2/O_2 gas mixture were analyzed using the mass spectrometer to quantify the O_2 evolved during the reaction between Li_2O_2 and CO_2. During cell charge, Ar is pulsed into the cell head space and accumulated gases are periodically swept to the mass spectrometer chamber. The time between Ar pulses was 4 minutes for Figure 3 and S1, and 5 minutes for Figure S2. The mass spectrometer absolute sensitivity is calibrated for H_2, CO_2 and O_2 and, therefore, the absolute partial pressures of these gases are acquired. Using the volume of gas swept to the mass spectrometer per pulse allows us to accurately calculate the amount of these gases evolved between pulses.

Fourier Transform IR (FTIR) spectroscopy

The cells studied in Figure 1b were discharged for 5 mAh (P50 cathodes), after which the cell is capped, brought into the glove box and disassembled. The cathode is triply rinsed in pure DME and dried under vacuum at room temperature overnight. A small portion (~1 mg) of the cathode is scraped into a mortar, and potassium bromide is added to the carbon and ground together with a pestle. The obtained powder is pressed in an anvil to form a pellet. The anvil and pellet are placed in a sealed container and transferred to the FTIR spectrometer's (Nicolet 470, DTGS-KBr detector) nitrogen-purged chamber. The chamber is then purged for 1h with nitrogen, after which the spectrum is recorded. The results reported in Figure 1b are the spectra of a non-discharged P50 carbon paper subtracted from the spectra of discharged P50 cathodes.

Calculation of O_2 consumption during cell discharge

O_2 consumption on discharge was calculated by coupling a pressure decay measurement with a DEMS measurement. From the pressure decay measurement during a 1 mAh discharge (0.9 mA/cm^2) of a P50 cathode-based cell, 20.5 μmols of total gas were consumed during discharge. The headspace gases were analyzed after the discharge using DEMS to obtain a final CO_2:O_2 ratio, which was found to be 6.9:93.1 CO_2:O_2. From the initial and final CO_2:O_2 ratio, we calculated the moles of each gas initially and finally present in the cell headspace. These values yielded 16.6 μmol O_2 consumed and 3.9 μmol CO_2 consumed during the 1 mAh discharge.

However, as is observed in Figure 2 of the main text, CO_2 and O_2 is also consumed via a reaction with Li metal (Eqn. 2), and this reaction gives an artificially high amount of gas consumed by the active cathode chemistry. From a gas consumption measurement for a non-discharged cell under 10:90 CO_2:O_2 (i.e., gas consumed from a parasitic reaction with Li metal and no discharge), ~0.3 μmols of gas were consumed in the same amount of time (1 hour) taken to discharge the P50 cell. If we assume that equation 2 describes the active chemistry at the anode, 0.2 μmols of CO_2 and 0.1 μmols of O_2 are consumed by this reaction. Subtracting this amount of anode CO_2 and O_2 consumption from the overall consumption gives 16.5 and 3.7 μmols O_2 and CO_2, respectively, consumed by the cathode chemistry.

Li_2O_2, however, reacts chemically with CO_2 via equation 1 to evolve ½ O_2, so the total amount of O_2 consumed during the Li-O_2 *electrochemistry* (assuming Li_2O_2 formation was the dominant active electrochemistry) was actually 16.5 μmol + 3.7/2 μmol = 18.35 μmols O_2. Combining this number with total cell capacity (1 mAh) gives 2.03 e^-/O_2 during discharge, which is in agreement with our previous reports for nonaqueous Li-O_2 electrochemistry in DME-based solvents.

Calculation of CO_2 consumption for cell 3 in Figure 2

Similar to the O_2 consumption during discharge calculation, this calculation combined a pressure decay measurement with a DEMS measurement. The cell was discharged under pure $^{16}O_2$ for 1h (1 mA rate), then the headspace was purged with Ar until no O_2 was observed in the headspace (via mass spectrometry analysis). Pure $C^{18}O_2$ was then introduced and the headspace pressure was monitored for 10h. The final headspace pressure decay corresponded to a total decrease of 12.6 μmol of gas. However, at the end of the pressure decay measurement, the headspace gases were analyzed using mass spectrometry, and 3.7 μmols of $^{16}O_2$ were found to evolve from the cell, giving 16.3 μmol CO_2 consumed (i.e., 12.6 μmol + 3.7 μmol = 16.3 μmol). This O_2 evolution was not observed from cell 2 in Figure 2, which implies that the O_2 was evolved from the reaction of $C^{18}O_2$ with $Li_2{}^{16}O_2$. As a result, the O_2 was evolved proportionally to CO_2 consumption over the course of the pressure decay analysis. Therefore, the molar consumption curve of CO_2 reported in Figure 2 was simply the molar gas decrease calculated from the pressure decay measurement multiplied by 16.3/12.6 = 1.29.

600 minutes was selected as the termination of the CO_2 consumption experiments in cells 2 and 3 in Figure 2 because the reaction of Li_2O_2 with CO_2 was easily confirmed within this experimental timeframe. We presume that if given sufficient time, the reaction of Li_2O_2 with CO_2 would have proceeded to completion (i.e., all of the Li_2O_2 would have been consumed).

Mechanism for the CO_2/Li_2O_2 thermal reaction based on isotopic labeling

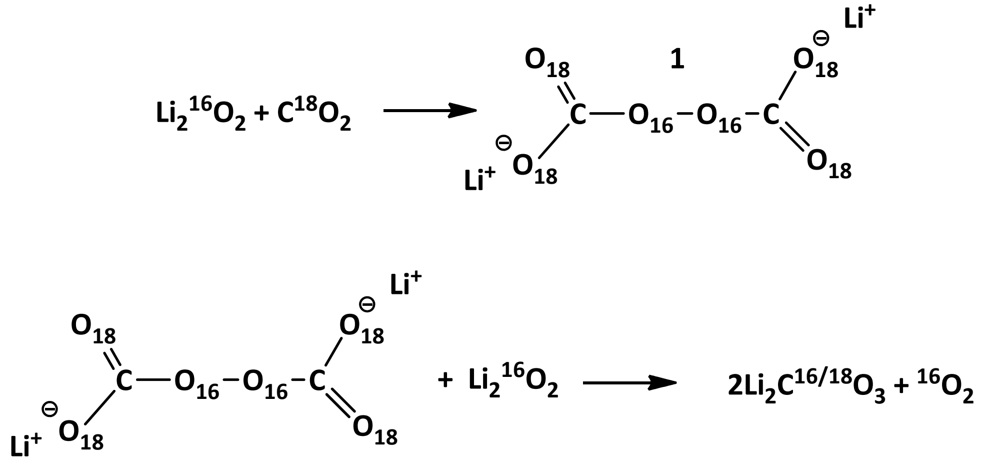
The reaction between carbon dioxide and peroxides to generate oxygen is well known ([7,8])

$Li_2O_2 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2} O_2$

In the case of cell 3 in Figure 2, where preformed Li_2O_2 was brought in contact with isotopically labeled $C^{18}O_2$, only $^{16}O_2$ is observed to evolve, as shown below:

$Li_2{}^{16}O_2 + C^{18}O_2 \longrightarrow Li_2C^{16/18}O_3 + \frac{1}{2}\,{}^{16}O_2$

This observation is consistent with the formation of a symmetrical peroxydicarbonate dianion intermediate[8]:



Thermal reversion of this adduct would be expected to regenerate $^{16}O_2$ and $C^{18}O_2$ as no O-O bond breaking is involved. In the same way, reductive electron transfer from an additional Li_2O_2 to peroxydicarbonate and cleavage to carbonate anions would yield pure $^{16}O_2$ (as seen experimentally) and the mixed $Li_2C^{16/18}O_3$ carbonate. Unfortunately, the resolution of our FTIR did not permit us to verify the presence of the isotopically mixed carbonate.

During charge of cell 3 in figure 2, $^{16}O_2$ is the only evolved oxygen isotope (Figure S2). However, if the oxidation of carbonate proceeds through the same peroxydicarbonate intermediate (1 in the above reaction scheme)[8-10], one would expect to see the appearance of mixed $^{16,18}O_2$ and $^{18}O_2$ at the end of the charging cycle (in addition to mixed CO_2), which was not the case. In fact, we can envision no possible mechanism for pure $^{16}O_2$ evolution from $Li_2C^{16/18}O_3$. It should be noted that in our previous study, no O_2 evolution was observed during charge from a cell with Li_2CO_3 artificially packed into its cathode.[1] These results strongly suggest that O_2 is only evolved from Li_2O_2 and, therefore, the reverse of equation (2) in the main text does not contribute to the charge electrochemistry. The exact mechanism of electrochemical Li_2CO_3 decomposition, including the final products formed in either solution or solid state, is unclear. Other reactions involving combined Li_2CO_3 and electrolyte decomposition at high potentials remain possibilities.

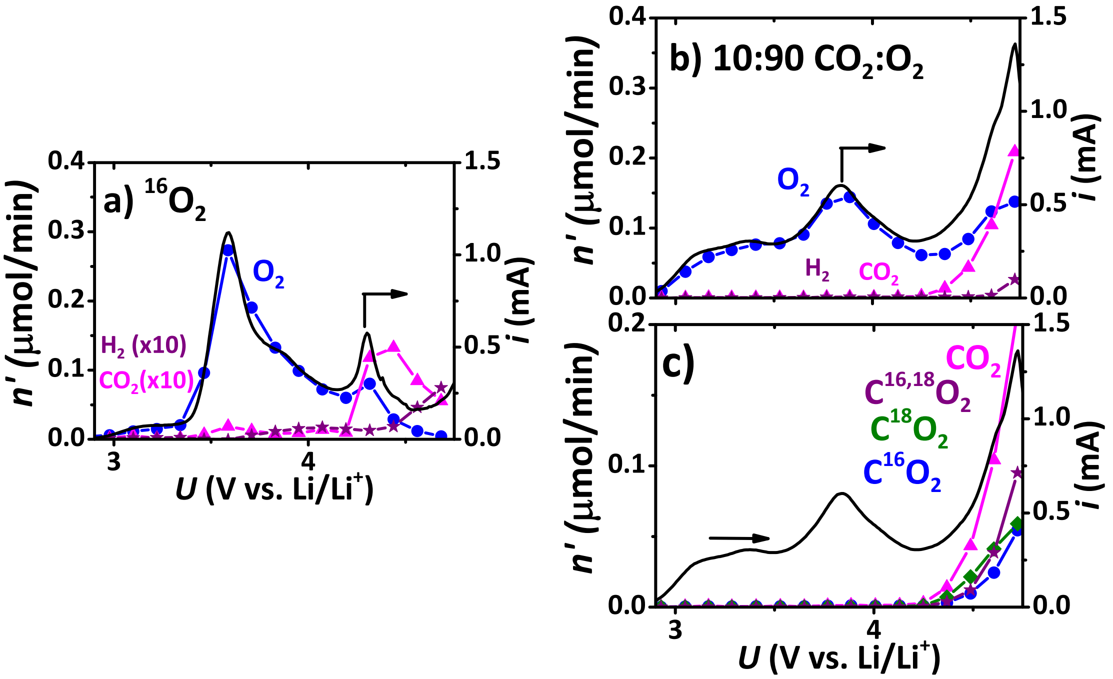


Figure S1: Oxidative potential scans (0.5 mV/s) after a galvanostatic discharge for **a)** a cell discharged under pure O_2 (discharged to 2V, 0.3 mAh), and **b)** a cell discharged under a 10:90 $C^{18}O_2$:$^{16}O_2$ mixture (discharged for 0.5 mAh). **c)** shows the different CO_2 isotopes evolved in b) ($^{16}O_2$ was the only O_2 isotope evolved in b)). XC72-based cathodes were used in these cells.

Discussion of Figure S1: Linear oxidative scans conducted at a scan rate of 0.5 mV/s show the influence on the charge overpotential due to carbonate formation from the CO_2/Li_2O_2 chemical reaction. Figure S1a presents an oxidative scan after discharge under pure $^{16}O_2$. Here the dominant peak corresponds to O_2 evolution from Li_2O_2 via a ~2 e^-/O_2 process. A small amount of CO_2 evolution is also observed during during the OER peak, but substantial CO_2 evolution is observed starting at ~4.25V. In a previous study, we ascribed this CO_2 evolution to the formation and concentration of $LiRCO_3$ (R= an alkyl constituent or lithium) in the electrodeposit during OER, followed by its decomposition at high potentials (the $LiRCO_3$ is formed at both the C/Li_2O_2 and C/electrolyte interface due to parasitic, Li_2O_2-induced reactions).[3] In contrast, CO_2 evolution contributes much more significantly to the cell charge electrochemistry in the CO_2:O_2-discharged cell (Figure S1b, c). As is observed in Figure S1c, a large amount of CO_2 evolution contains ^{18}O, which was only initially present in atmospheric CO_2 during discharge, indicating that a substantial amount of the evolved CO_2 was from Li_2CO_3 formed from the CO_2/Li_2O_2 reaction. The onset for CO_2 evolution still remains ~4.3V, regardless of whether the Li_2CO_3 originates from parasitic reactions with cell components (as is observed in the pure O_2 discharged cell), or whether it originates from a reaction between Li_2O_2 and CO_2. This implies that any cell exposure to CO_2 will result in a reduction in the cell's voltaic efficiency during cycling.

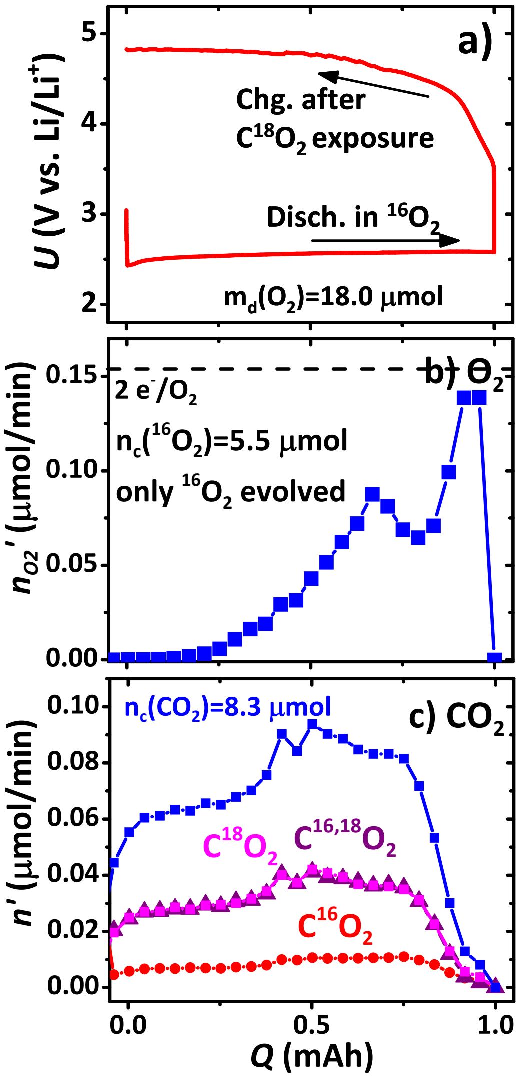


Figure S2: a) Galvanostatic discharge (0.94 mA/cm^2)-charge (0.47 mA/cm^2) profile of the '1 mAh discharge' cell studied in Figure 2 in the main text. The cell was discharged under pure $^{16}O_2$ for 1h, then the cell was purged with Ar until no O_2 was observed in the headspace (via mass spectrometry analysis). Pure $C^{18}O_2$ was then introduced and the headspace pressure was monitored for 10h. Afterwards, DEMS analysis of the headspace gases was performed at open circuit potential, the cell was purged with Ar and charged. **b)** presents O_2 evolution during charge and **c)** presents CO_2 evolution during charge. A Ketjenblack cathode was used.

References

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