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On the incompatibility of lithium $-O_2$ battery technology with CO_2 †

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When solubilized in a hexacarboxamide cryptand anion receptor, the peroxide dianion reacts rapidly with CO_2 in polar aprotic organic media to produce hydroperoxycarbonate ($HOOCO_2^-$) and peroxydicarbonate ($HOOCO_2^-$). Peroxydicarbonate is subject to thermal fragmentation into two equivalents of the highly reactive carbonate radical anion, which promotes hydrogen atom abstraction reactions responsible for the oxidative degradation of organic solvents. The activation and conversion of the peroxide dianion by CO_2 is general. Exposure of solid lithium peroxide (Li_2O_2) to CO_2 in polar aprotic organic media results in aggressive oxidation. These findings indicate that CO_2 must not be introduced in conditions relevant to typical lithium $-O_2$ cell configurations, as production of $HOOCO_2^-$ and $HOOCO_2^-$ during lithium HO_2 cell cycling will lead to cell degradation $HOOCO_2^-$ organic electrolytes and other vulnerable cell components.

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Introduction

The two-electron reduction of molecular oxygen to the peroxide dianion is an attractive cathode redox couple for developing rechargeable lithium- O_2 batteries. Lithium carbonate (Li_2CO_3) formation is deleterious to battery performance because it passivates electrodes and causes a drastic reduction in the round trip efficiency of discharge–charge cycles. Carbonate formation is typically ascribed to oxidative degradation of organic electrolytes and carbon electrodes by superoxide, and singlet oxygen. Although peroxide is often considered to be a strong oxidant in aqueous media, salts of its dianion (O_2^{2-}) are poor oxidizers in organic media due to their extremely low solubility and so, for this reason, the possible role of peroxide in furnishing carbonate is underappreciated. The presence of

carbonate-derived CO2 during the recharge cycle of lithium-O2 batteries² prompted us to consider the possibility that carbonate formation may be a consequence of peroxide combination with carbon dioxide; this would likely confer increased solubility and yield powerful oxidizers. To address this topic, we utilized an anion-receptor solubilized form of the peroxide dianion12 to elucidate the molecular level details of its reaction with carbon dioxide. As reported herein, we observed the formation of strongly oxidizing peroxy(di)-carbonate intermediates and studied their reaction with organic solvents to produce carbonate. In a complementary line of investigation, we showed that carbon dioxide activation of insoluble Li₂O₂ similarly engenders solvent oxidation with the concomitant production of carbonate. Our findings shed light on the identity and behavior of the hot oxidants generated upon the facile and quantitative combination of O22- with CO2 via direct spectroscopic detection and exploratory reaction chemistry.

Results and discussion

Reaction of O_2^{2-} with CO_2 using an anion receptor

Despite the drastic and deleterious effect that CO_2 has upon the performance of a cycling lithium–oxygen battery, our understanding of the chemical entities responsible for this effect is poor and based primarily upon computational studies or observation of terminal reaction products. To examine the effect of CO_2 on the oxidative power of peroxide, an anion receptor complex of the peroxide dianion, $[O_2 \subset mBDCA-5t-H_6]^{2-}$ (1, Fig. 1), was employed as a soluble source of peroxide dianion. The anion receptor $mBDCA-5t-H_6$ encapsulates the peroxide dianion via six $N-H\cdots O$ hydrogen bonds. Since its

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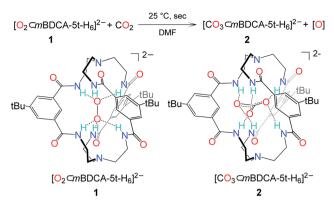


Fig. 1 The reaction scheme of peroxide cryptate 1 with CO₂ and a line drawing of $[O_2 \subset mBDCA-5t-H_6]^{2-}$ and $[CO_3 \subset mBDCA-5t-H_6]^{2-}$.

discovery, this cryptate has enabled exploration of the reactivity of the peroxide dianion with small molecules in polar organic media without the complicating influence of acidic protons. Despite being a simple molecule, the peroxide dianion has yielded rich and previously unknown chemistry, including metal-free oxidation of carbon monoxide (CO) generating carbonate, which is encapsulated by the anion receptor as $[CO_3 \subseteq mBDCA-5t-H_6]^{2-}$ (2, Fig. 1). 14

While the conversion of 1 to 2 under CO (1 atm, 40 °C) takes two hours to go to completion, exposing a dimethylformamide d_7 (DMF- d_7) solution of 1 to CO₂ (1 atm, 25 °C) resulted in the essentially instantaneous formation of carbonate cryptate $[CO_3 \subset mBDCA-5t-H_6]^{2-}$ as indicated by ¹H NMR spectroscopy. Formation of O₂ gas was not observed by gas chromatography (GC) analysis of the reactor headspace gases, 15 suggesting the possibility of oxygen incorporation into the solvent molecules. To probe the fate of the "missing oxygen atom" according to the equation at the top of Fig. 1, the reaction of CO₂ and 1 was next performed in the presence of oxygen atom acceptors. While 1 on its own is unreactive towards PPh3 and methoxythioanisole at 25 °C, exposing a mixture of 1 and an organic oxygen-atom acceptor to CO₂ (1 atm, 25 °C) resulted in the rapid formation of triphenylphosphine oxide (90%, Fig. 2) or 1-(methylsulfinyl)-4-methoxybenzene (61%, Fig. 2), respectively.

Aiming to establish the chemical identity of the oxidant(s) generated upon exposure of peroxide cryptate **1** to CO₂, we followed the reaction by variable temperature ¹³C NMR spectroscopy. A strong new signal at $\delta = 156.9$ ppm, together with one minor species resonating at $\delta = 157.4$ ppm, was observed at -50 °C (Fig. 3). We first considered peroxycarbonate ($-OOCO_2$, Fig. 3) and hydroperoxycarbonate ($HOOCO_2$, Fig. 3)

$$1 + CO_2 + X$$
 \longrightarrow $2 + XO$
 $X = PPh_3$ $XO = OPPh_3$ 90% yield

 $MeO \longrightarrow$ S $MeO \longrightarrow$ 61% yield

Fig. 2 Addition of CO_2 to 1 in the presence of an oxygen-atom acceptor.

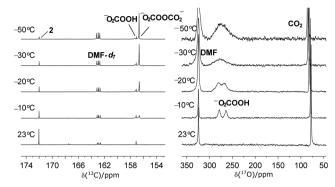


Fig. 3 Variable temperature 13 C NMR (left) and 17 O NMR (right) analysis of the reaction between 13 CO $_2$ and 1.

as candidates to correspond to the observed 13 C NMR signals, since hydroperoxycarbonate is known to be active for sulfide oxidation. 16,17 The salt [PPN][HOO 13 CO $_2$] (PPN = bis(triphenylphosphine)iminium), which was generated *in situ* from H $_2$ O $_2$ and bicarbonate [PPN][H 13 CO $_3$] ($\delta = 160.0$ ppm), $^{18-20}$ showed a single 13 C resonance at $\delta = 157.5$ ppm, confirming the identity of the minor intermediate as HOOCO $_2$.

Moreover, ¹³C Gauge-Independent Atomic Orbital (GIAO) NMR calculations of the chemical shifts of potential candidates were performed.¹⁵ From a range of potential chemical species (Fig. 4), symmetric peroxydicarbonate (${}^{-}O_{2}COOCO_{2}^{-}$) emerged as the most plausible assignment for the major product at $\delta =$ 156.9 ppm, having the best match between the observed and calculated ¹³C NMR chemical shift.¹⁵ In an effort to independently generate "O2COOCO2", an experiment was carried out in which excess ¹³CO₂ was added to a frozen mixture of potassium tert-butoxide and bis(trimethylsilyl) peroxide giving rise to a single new ¹³C NMR resonance at $\delta = 155.5$ ppm (-40 °C), tentatively supporting our identification of the major 1 + CO₂ product as symmetric peroxydicarbonate. Differences in the medium and reaction conditions may account for the observed chemical shift difference (155.5 ppm here versus 156.9 ppm, above). Similarly, superoxide (O2 •) has been documented to absorb two equivalents of CO2, generating unsymmetrical peroxydicarbonate (Fig. 4) as a precipitate.21 In our hands, the low

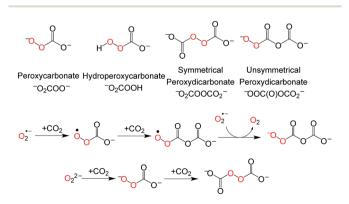


Fig. 4 Possible intermediates during the conversion of $\bf 1$ and CO_2 to $\bf 2$ (top) and formation of symmetric and unsymmetric peroxydicarbonate (bottom).

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solubility of this unsymmetrical peroxydicarbonate material precluded its characterization by solution ¹³C NMR studies under conditions we employed successfully for in situ characterization of "O2COOCO2" and HOOCO2". This establishes that different oxidants are generated upon addition of CO₂ to superoxide as compared with the peroxide dianion (Fig. 4).

Further support for the formation of HOOCO₂ and O₂-COOCO₂ upon interaction of CO₂ with peroxide sources was provided by variable temperature ¹⁷O NMR spectroscopy. Due to the fast relaxation times of ¹⁷O nuclei, observation of the ¹⁷O resonance for mid-size molecules such as 1-17O2 and 2-CO17O2 was expected to be challenging in solution.²² Indeed, ¹⁷O NMR measurements of independently prepared peroxide cryptate $1^{-17}O_2$ and carbonate cryptate $2\text{-CO}^{17}O_2$ (70%, $^{17}O\text{-enriched}$) showed no resonances between $\delta = -1100$ and +1800 ppm (H₂O used as a reference, $\delta = 0$ ppm) in DMF. However, solidstate ¹⁷O NMR measurements for 1-¹⁷O₂ and 2-CO¹⁷O₂ were successful, as reported previously in the case of 2-CO¹⁷O₂, 14 and in the present work for 1-17O2, providing the benchmark 17O NMR chemical shifts (δ = 260 ppm for 1- 17 O₂ and 170 ppm for 2-CO¹⁷O₂) (Fig. 5, Table 1). As seen in Fig. 3, 70% ¹⁷O-enriched samples of HOOCO2⁻ and ⁻O2COOCO2⁻ generated in DMF solution at -78 °C from the reaction of $1^{-17}O_2$ and $^{13}CO_2$ resulted in a broad ¹⁷O NMR resonance at $\delta = 275.3$ ppm, assigned as overlapping signals of HOOCO2- and O2- $COOCO_2^-$. Upon gradual warming of the sample to -10 °C, the intensity of the signal decayed; the signal ultimately resolved into two peaks with equal intensities at $\delta = 278.7$ and 264.0 ppm, distinct from those observed for 1-17O2 and 2-CO¹⁷O₂. The two peaks observed are attributed to HOOCO₂

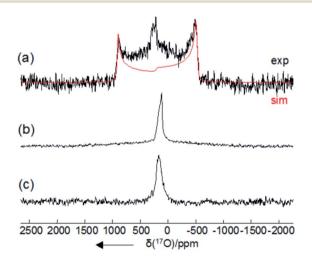


Fig. 5 Experimental (black trace) and simulated (red trace) solid-state 17 O NMR spectra of (a) 1- 17 O₂, (b) 2-CO 17 O₂, and (c) product resulting from the treatment of solid 1-17O₂ with CO₂. All solid-state ¹⁷O NMR experiments were performed on a Bruker Avance-600 (14.1 T) spectrometer under static conditions. A Hahn echo sequence was used for recording the static spectra to eliminate the acoustic ringing from the probe. A 4 mm Bruker MAS probe was used without sample spinning. The effective 90° pulse was of a duration of 1.7 μ s. High power ¹H decoupling (70 kHz) was applied in all static experiments. A liquid H₂O sample was used for both RF power calibration and ¹⁷O chemical shift referencing ($\delta = 0$ ppm).

which contains two chemically inequivalent ¹⁷O atoms (δ = 278.7 ppm for HOOCO₂ and 264.0 ppm for HOOCO₂, in contrast to the situation for ${}^{-}O_2COOCO_2{}^{-}$ in which the peroxy oxygen atoms are related by symmetry. The appearance of the relatively sharp ¹⁷O NMR signals assigned to HOOCO₂ coupled with the concurrent observation of monodeprotonated cryptand $([mBDCA-5t-H_5]^{-})^{14}$ by ¹H NMR spectroscopy strongly suggests that HOOCO₂ is not strongly sequestered inside the anion receptor. The observed ¹⁷O NMR chemical shifts are in accordance with expectations arising from 17O NMR absolute shielding calculations and compare well with data for benchmark organic compounds containing the peroxy functional group.23

The mechanism of CO₂/peroxide driven oxidation

Having thereby established the identity of the active oxidants generated from the combination of O_2^{2-} and CO_2 as $HOOCO_2^{-}$ and $^-\mathrm{O_2COOCO_2}^-$, we next turned our attention to the mechanism of CO₂/peroxide driven oxidation. The reaction of ¹⁸Olabeled 1 and CO2 was performed in the presence of an oxidizable substrate. Exposure of a mixture of 1-18O2 and PPh3 to CO₂ furnished ¹⁸OPPh₃ as the oxidized product based on GCMS analysis.¹⁵ The obtained ¹⁸O isotope labeling data precluded the possibility of O-O bond cleavage prior to the oxygen atom transfer (OAT) reaction, as such a process would yield isotopic scrambling and result in a mixture of ¹⁶OPPh₃ and ¹⁸OPPh₃. Therefore, H¹⁸O₂CO₂ – with its peroxy unit intact as it was derived from the peroxide dianion - is implicated as the active species for the OAT conversion of PPh3 to OPPh3 (Fig. 6, OAT pathway). In contrast, addition of CO₂ to a solution of 1-18O2 in the presence of the hydrogen atom donor 9,10-dihydroanthracene (DHA) led to a statistical mixture of anthraquinone products with 16O and 18O incorporation.15 The observed isotope scrambling was likely due to a sequence of H-atom abstraction/radical recombination reactions. By analogy to the behavior of organic peroxydicarbonates,26 symmetrical peroxydicarbonate would be expected to undergo O-O bond homolysis generating two equivalents of the reactive carbonate radical CO₃ ·- (Fig. 6, hydrogen atom transfer (HAT) pathway).²⁷ Quantum chemical calculations indicate that homolytic cleavage of the O-O bond in "O2COOCO2" is only mildly endergonic (reaction free energy +14 kcal mol⁻¹). This species thus has an unusually weak O-O bond.

Homolytic cleavage of the O-O bond and generation of CO₃. appears to be favorable for two reasons: (i) repulsion of the negative charge due to poor solvation in organic solvents resulting in coulombic explosion28 and (ii) resonance stabilization of the unpaired electron of the carbonate radical anion over the carbonate π system. Carbonate radicals have been generated previously via laser photolysis of aqueous persulfate in the presence of bicarbonate.29 Carbonate radicals have been implicated in guanine oxidation²⁷ and are also believed to be formed upon treatment of peroxynitrite (ONOO-) with CO2, and in that case generate nitrogen dioxide as a byproduct. 27,30,31 Furthermore, in the manganese-catalyzed oxidation of amino acids by H2O2, the formation of reactive oxygen species only

Table 1 Experimental solid-state ¹⁷O NMR and ADF computational results on [K₂(DMF)₃][¹⁷O₂⊂mBDCA-5t-H₆]. [K₂(DMF)₃][C¹⁷O₃⊂mBDCA-5t-H₆], and related compounds

Compound		$\delta_{ m iso}{}^a/ m ppm$	$\delta_{11}/{ m ppm}$	δ_{22} /ppm	δ_{33} /ppm	$C_{ m Q}/{ m MHz}$	$\eta_{ m Q}/{ m MHz}$
1	Exp	260	335	335	110	-16.6	0.0
	ADF	308	388	388	148	-17.5	0.000
2	Exp	170	266	194	50	7.5	0.7
	ADF	223	335	222	112	7.03	0.95
O_2^{2-}	ADF	221	398	398	-13.3	-18.66	0.000
H_2O_2	Exp^b	180	_	_	_	-16.31	0.687
	ADF	182	383	211	-48	-16.81	0.969
$\mathrm{Li}_2\mathrm{O}_2$	Exp^c	227	352	352	-23	-18.66	0.00

^a The uncertainties in the experimental data are: $\delta_{\rm iso} \pm 2$ ppm; $\delta_{ii} \pm 10$ ppm; $C_{\rm Q} \pm 0.2$ MHz; $\eta_{\rm Q} \pm 0.1$. ^b See ref. 24. ^c See ref. 25.

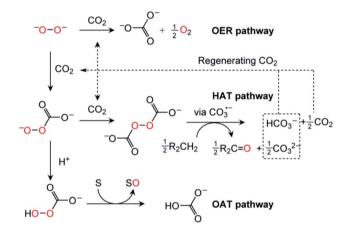


Fig. 6 Proposed mechanistic pathways for CO₂-mediated solvent decomposition in lithium-O₂ batteries. OER is an "oxygen evolving reaction", HAT is a "hydrogen atom transfer" oxidative process involving hydrogen atom abstraction by carbonate radical anion, and OAT is "oxygen atom transfer" to a substrate, S.

occurred when HCO₃ buffer was used. 32,33 Carbonate radicals generated in lithium-oxygen batteries can then engage in HAT reactions with solvents containing weak C-H bonds, driven by the high O-H bond strength (BDE \cong 107 kcal mol⁻¹) of the bicarbonate that is formed.27 Accordingly, we suggest that for stability under lithium-O2 cell cycling conditions, an organic solvent/electrolyte should have no C-H bonds of BDE \cong 107 kcal mol⁻¹ or less.

To experimentally confirm the generation of CO₃, 1 was treated with CO2 in the presence of the spin trap 5-tertbutoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO), and the reaction was monitored by EPR spectroscopy.34 Upon addition of the CO2, signals for the hydroxyl adduct [BMPO-OH] together with small quantities (ca. 5%) of an unidentified spintrap adduct suspected to be [BMPO-OCO₂]' were observed within seconds (Fig. 7). Formation of [BMPO-OH] is proposed to occur via a rapid reaction between the chemically generated CO₃ and BMPO, initially yielding [BMPO-OCO₂], followed by decarboxylation and protonation. The proton source under these conditions could be the anion receptor mBDCA-5t-H₆ (Fig. 7C). This sequence is directly along the lines proposed for the related spin trap DMPO under exposure to carbonate radicals.35,36 On longer timescales, [BMPO-OH] was further oxidized to [BMPO-O] and other unidentified decomposition products.34

Activation of solid Li₂O₂ with CO₂ in aprotic organic media

To examine the effect of CO₂ on the oxidative power of Li₂O₂ under conditions relevant to the charging of lithium-air cells, commercially available solid Li2O2 was exposed to CO2 (1 atm, 25 °C, 48 h) in 1,2-dimethoxyethane (DME). In contrast to the results from the control experiments carried out similarly but in the absence of CO₂, substantial amounts of methyl methoxyacetate were identified among the products of DME oxidation (Fig. 8). Approximately 51% of the Li₂O₂ was consumed, and quantitative conversion of the consumed Li2O2 to Li2CO3 (based upon lithium) was observed by 13C NMR spectroscopy and total inorganic carbonate (TIC) analysis.15 The consumed peroxide must generate an oxidizing equivalent; 74% was identified as

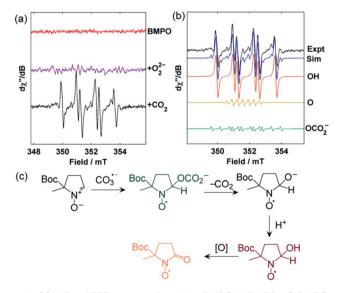


Fig. 7 (a) X-Band EPR spectra of: pristine BMPO in DMF (red), BMPO + 1 without adding CO₂ in DMF (purple), and exposure of BMPO + 1 to CO_2 in DMF (black). (b) Simulation of the EPR spectra of BMPO + 1 + CO₂ in DMF by linear combination of the contribution from: [BMPO-OCO₂]*- (green), [BMPO-OH]* (red), and [BMPO-O]* (yellow). (c) Formation of [BMPO-Ol* from [BMPO-OH]* and an oxidant "[O]".

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$$\begin{array}{c} \text{MeO} \\ \text{OMe} \\ \text{Li}_2\text{O}_2(s) + \text{CO}_2 \\ \text{excess} \\ \end{array} \begin{array}{c} \text{Li}_2\text{CO}_3(s) + [\text{O}] \\ \end{array} \begin{array}{c} \text{15\%} \\ \text{+ H}_2\text{O} \\ \end{array} \begin{array}{c} \text{+ H}_2\text{O} \\ \end{array}$$

Fig. 8 CO_2 -mediated oxidation of organic solvents by Li_2O_2 . Addition of excess CO_2 to solid Li_2O_2 in the organic solvent 1,2-dimethoxyethane (DME) generates an oxidizing equivalent "O", which converts to O_2 (74%) and methyl methoxyacetate (15%) with the remainder unidentified. A similar reaction performed in dimethylsulfoxide (DMSO) generated dimethylsulfone (DMSO₂) in a 90% yield.

evolved O2 and 15% as methyl methoxyacetate (Fig. 8), with the remainder unidentified. We also introduced solid Li₂O₂ into neat DMSO under a CO₂ atmosphere (1 atm, 25 °C, 48 h), given the reported use of DMSO in lithium-O₂ cells.³⁷ More than 90% of the Li₂O₂ consumed participated in the conversion of DMSO to DMSO₂ (Fig. 8). Viewed in the context of cycling lithium-O₂ cells, the rate of CO₂-induced solvent decomposition in bona fide lithium-air cells is perhaps lower than that observed in the current study due to the difference in CO2 partial pressures. Nonetheless, considering the low cycling rate and long cycling time of a typical lithium-air battery,38 our findings highlight that extensive oxidative degradation of the electrolyte in a cell will occur during cell cycling even when a small amount of CO2 is introduced or otherwise generated in the system. 39 During cell cycling, CO2 is generated at the surface of lithium peroxideimpregnated carbon electrodes,39 leading us to speculate that the proposed chemistry (Fig. 8) should be expected to occur on a polarized electrode/electrolyte interface as well. It should be noted that while commercial Li₂O₂ was used in the present study, it is conceivable that the varied morphologies of electrochemically generated Li₂O₂ may react with CO₂ at different rates. Due to the preponderance of conditions which result in varied Li₂O₂ crystallinity, size and surface structure, 40,41 commercial Li2O2 was chosen as an ideal benchmark reactant with CO_2 .

A recent publication reported that when present in a charging lithium–air cell (>3.5 V vs. Li⁺/Li), the secondary amine 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TEMP) was converted to the oxyl amine radical 4-oxo-TEMPO, as confirmed by EPR spectroscopy. 4-oxo-TEMP has been used in the past as a trap for singlet oxygen, leading the authors to propose that singlet oxygen was responsible for the observed conversion. An alternative explanation for the production of 4-oxo-TEMPO involves the oxidants being generated by activating Li₂O₂ with CO₂, considering that the onset potential of CO₂ formation in a typical lithium–air cell is also 3.5 V. Accordingly, we found that exposing Li₂O₂ to CO₂ (1 atm, 25 °C, 24 h) in the same solvent and electrolyte as described in the literature, but without the application of an electrode potential, also resulted

in the formation of 4-oxo-TEMPO. Of the oxidizing equivalents generated during the transformation of ${\rm Li_2O_2}$ to ${\rm Li_2CO_3}$, ca. 15% were incorporated into the 4-oxo-TEMPO reaction product based on EPR spin quantification. These experiments suggest that the oxidation of 4-oxo-TEMP is most likely due to ${\rm CO_2}/{\rm peroxide}$ -derived oxidants as opposed to singlet oxygen formation or at the very least that 4-oxo-TEMP is not a selective probe for singlet oxygen in Li-O₂ cells under conditions of ${\rm CO_2}$ availability.

Conclusions

While previous studies on lithium-O2 batteries have attributed the low cycling number and capacity fading to singlet oxygen¹⁰ and superoxide, 4-7 it is now clear that CO2/peroxide-derived oxidants are responsible for carbonate formation by way of the active oxidants $HOOCO_2^-$ and $CO_3^{\bullet-}$ via $^-O_2COOCO_2^-$. Since prototypical lithium-air cells (ether electrolyte, carbon cathode) lose 5-7% of their capacity to parasitic CO₂ formation per complete cycle³⁹ and have a typical cycling number of ca. 50, the resulting CO₂/peroxide dianion-derived oxidants were expected to cause organic electrolyte degradation. This oxidative degradation may occur both during discharge through reaction of the peroxide dianion with CO₂ and during recharge through electrochemical oxidation of carbonate initially generating the carbonate radical (CO3'-). It has been established that recharging a lithium-O₂ battery regenerates CO₂ from Li₂CO₃, however identification of the mechanism and product(s) of electrochemical Li₂CO₃ degradation have been unclear.² Our studies provide evidence for a mechanistic pathway by which carbonate radical anions, when generated, engage in C-H abstraction from the solvent (C-H bond \cong 107 kcal mol⁻¹, or less)27 and lead to solvent degradation and reformation of CO2 (Fig. 6). The regenerated CO₂ sets in motion a decomposition cycle, therefore if even a small percentage of the total Li₂O₂ is converted to CO2, extensive oxidative degradation of the electrolyte in a cell will occur over the course of many cycles. If CO₂ cannot be excluded from these systems then it is critical that the electrolyte and other cell components are invulnerable to reactive CO₂/peroxide-derived oxidants if the full potential of rechargeable lithium-O2 battery systems is to be realized.

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