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# Electrochemical Oxidation of Lithium Carbonate Generates Singlet Oxygen

Nika Mahne, Sara E. Renfrew, Bryan D. McCloskey, and Stefan A. Freunberger*

Abstract: *Solid alkali metal carbonates are universal passivation layer components of intercalation battery materials and common side products in metal-O_2 batteries, and are believed to form and decompose reversibly in metal-O_2/CO_2 cells. In these cathodes, Li_2CO_3 decomposes to CO_2 when exposed to potentials above 3.8 V vs. Li/Li^+. However, O_2 evolution, as would be expected according to the decomposition reaction $2\,Li_2CO_3 \rightarrow 4\,Li^+ + 4\,e^- + 2\,CO_2 + O_2$, is not detected. O atoms are thus unaccounted for, which was previously ascribed to unidentified parasitic reactions. Here, we show that highly reactive singlet oxygen ($^1O_2$) forms upon oxidizing Li_2CO_3 in an aprotic electrolyte and therefore does not evolve as O_2. These results have substantial implications for the long-term cyclability of batteries: they underpin the importance of avoiding $^1O_2$ in metal-O_2 batteries, question the possibility of a reversible metal-O_2/CO_2 battery based on a carbonate discharge product, and help explain the interfacial reactivity of transition-metal cathodes with residual Li_2CO_3.*

Energy storage in Li-based batteries is limited by the cathode, which has triggered intense research efforts to increase cathode capacity and/or voltage.[1] Candidate approaches include Li-stoichiometric[2] and Li-rich[3] transition-metal oxide (TMO) intercalation cathodes, which have higher voltage and capacity than currently used cathodes, and metal-O_2 or metal-O_2/CO_2 cathodes,[1,4] which have lower voltage but substantially higher theoretical capacity. Making high-voltage TMOs viable requires increasing the reversible potential window through understanding the high-voltage instabilities of intercalation materials and electrolytes.[1] Much recent work has revealed an intimate interdependence of electrolyte decomposition, surface species formation/decomposition, and TMO bulk and surface reconstruction.[2d,3d,5] In particular, it was recently found that the outgassing of CO_2 during the first cycle in Li-ion batteries is mostly governed by residual Li_2CO_3, which in turn affects O_2 evolution from the TMO lattice.[5b] With respect to Li-O_2 batteries, Li_2CO_3 is an unwanted parasitic product, which hampers rechargeability, accumulates on cycling, and hence causes poor energy efficiency and cycle life.[1,4a–f] The burden of Li_2CO_3 formation was seemingly made use of in rechargeable metal-O_2/CO_2 batteries based on the observation that Li_2CO_3 can be electrochemically decomposed.[4f–j,6]

Thus Li_2CO_3, be it a trace or main component, plays a central role in considerations of cyclability and stability for a large fraction of future Li battery systems, and understanding its electrochemical oxidation is paramount for further development. While it is clear that Li_2CO_3 decomposition evolves CO_2, the fate of the third O atom in CO_3^{2-} has been an enduring open question since no O_2 evolves, although this would be expected from the formal oxidation reaction:[3e,4c,f–h,j,5b]

$$2\,Li_2CO_3 \rightarrow 4\,Li^+ + 4\,e^- + 2\,CO_2 + O_2 \quad E^\circ = 3.82\ \text{V vs. Li/Li}^+ \quad (1)$$
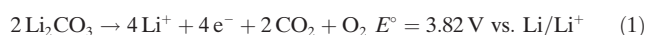
Previous explanations have proposed the formation of superoxide or "nascent oxygen", which could react with cell components in a reaction path involving carbon,[4f,6] without, however, definite proof for these mechanisms. Herein, we provide compelling evidence that the electrochemical oxidation of Li_2CO_3 forms highly reactive $^1O_2$, which, through a parasitic reaction of $^1O_2$ with battery components, explains the absence of O_2 evolution. Given its exceptional reactivity, the formation of $^1O_2$ has far-reaching implications for TMO surface reactivity and coupled parasitic reactions upon recharging metal-O_2 and metal-O_2/CO_2 batteries.

$^1O_2$ may be detected using chemical probes, which react specifically with $^1O_2$ and can be detected spectroscopically by measuring the disappearance of the probe and/or the appearance of the adduct. Reported probes include fluorophores or spin traps, which may be detected by fluorescence "switch on/off" or by EPR spectroscopy.[7] However, these probes are typically electrochemically unstable above 3.5–3.7 V vs. Li/Li$^+$ and do not allow access to the relevant Li_2CO_3 oxidation potential range above 3.8 V. Previously, we have shown that 9,10-dimethylanthracene (DMA) fulfills these requirements: it rapidly forms the endoperoxide (DMA-O_2) in the presence of $^1O_2$; both DMA and DMA-O_2 are electrochemically stable beyond 4 V (Figure S1); and DMA is also stable against superoxide, another possible reactive oxygen species. In other words, exposing DMA to superoxide

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does not form DMA-O$_2$, which otherwise would be falsely assigned to the presence of $^1O_2$.[8] To further confirm that DMA-O$_2$ forms only with $^1O_2$ but not with other possibly reactive O-containing species, we exposed the electrolyte with DMA separately to Li$_2$CO$_3$, O$_2$, CO$_2$, and Li$_2$O$_2$ and did not observe DMA-O$_2$ (Figure S2). The same holds true for DMA exposed to Li$_2$O$_2$ with CO$_2$, which forms a peroxodicarbonate, a possible intermediate of Li$_2$CO$_3$ oxidation.[9] Together, these results confirm that DMA→DMA-O$_2$ conversion is a sensitive and selective method to detect $^1O_2$ in the cell environment.

To probe whether $^1O_2$ forms upon oxidizing Li$_2$CO$_3$, we constructed electrochemical cells with Li$_2$CO$_3$-packed working electrodes as detailed in the Methods section in the Supporting Information. Li$_2$CO$_3$ was ball-milled with carbon black to ensure intimate contact between the two and the resulting powder was used to form composite electrodes using PTFE binder. To specifically probe reactions at the working electrode and to exclude unwanted reactions of the electrolyte with a Li metal anode, we used Li$_{1-x}$FePO$_4$ ($E° = 3.45$ V vs. Li/Li$^+$) as the counter and reference electrode. First, we established the onset potential of Li$_2$CO$_3$ oxidation using a potential sweep measurement in an online electrochemical mass spectrometry (OEMS) setup to follow the gases evolved. Figure 1 shows CO$_2$, O$_2$, CO, and H$_2$ evolution in comparison
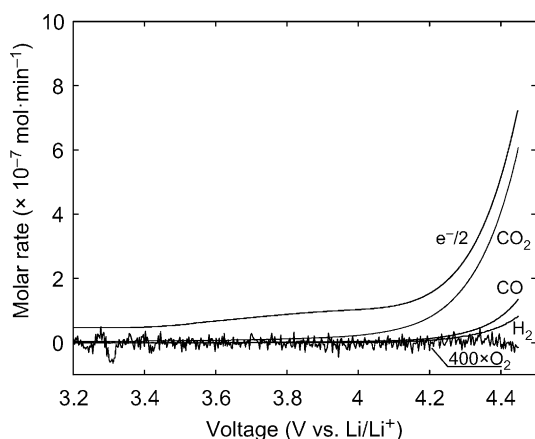

Figure 1. CO$_2$, O$_2$, CO, and H$_2$ evolution from carbon black/Li$_2$CO$_3$/PTFE (9:1:1, m:m) composite electrodes during a linear potential scan at 0.14 mVs^{-1} in 0.1 M LiTFSI in TEGDME under an Ar atmosphere.

to the electron consumption rate. CO$_2$ evolution commences at around 3.8 V, with a ratio of approximately 2e$^-$/CO$_2$ observed at higher voltages. Note that capacitive current accounts for the initial electron consumption rate above open circuit and causes the electron consumption rate to remain slightly higher than the CO$_2$ evolution rate. The onset of CO$_2$ evolution at 3.8 V is in accordance with the equilibrium potential of Reaction 1 ($E° = 3.82$ V vs. Li/Li$^+$).[4c,6] Consistent with numerous studies, O$_2$ was not detected throughout charging.[4c,g,h,5b] H$_2$ and CO evolution is observed above 4.2 V during the anodic scan of the Li$_2$CO$_3$-packed electrodes, but no gas evolution is observed below 4.5 V from blank carbon black electrodes (Figure S3). Absence of CO$_2$ when a blank

electrode is charged proves Li$_2$CO$_3$ oxidation to be the CO$_2$ source in Figure 1. The comparison of the blank and Li$_2$CO$_3$-packed electrode also indicates that the H$_2$ evolution observed (Figure 1) has to originate from a parasitic electrolyte degradation reaction induced by Li$_2$CO$_3$ oxidation, since the electrolyte otherwise appears stable at Li$_2$CO$_3$-free electrodes until at least 4.5 V.

To examine whether the highly reactive $^1O_2$ forms and could thus explain the absence of O$_2$ release, we constructed cells with the same Li$_2$CO$_3$ working electrodes and 0.1M LiTFSI in dimethoxyethane (DME) containing 30 mM DMA as the electrolyte. Cells were held at various charging potentials until a capacity of 0.064 mAh was reached. The electrolyte was then extracted and subjected to HPLC and ^1H NMR analysis (Figure 2).

HPLC analysis showed that DMA-O$_2$ formed at all charging voltages from 3.8 V onwards (Figure 2a). Blank measurements, where electrodes without Li$_2$CO$_3$ were polarized analogously, did not yield DMA-O$_2$ (Figure S4).
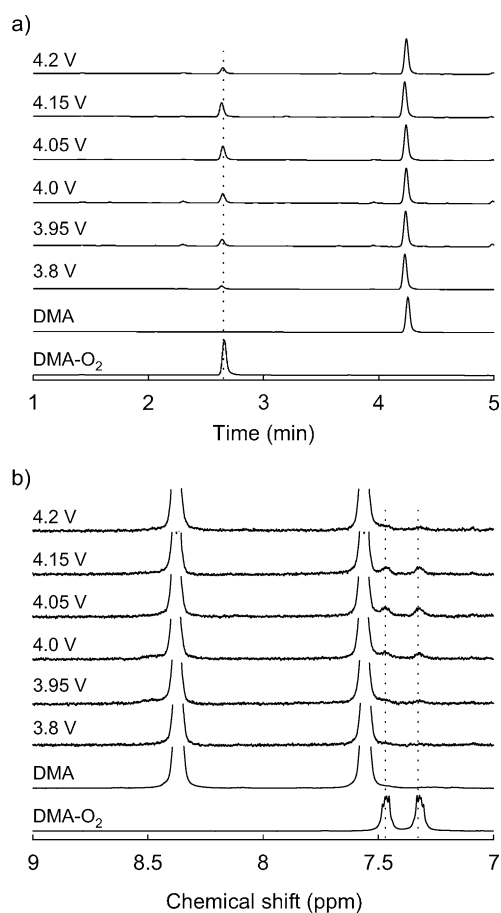

Figure 2. a) HPLC analysis of the electrolyte after polarizing carbon black/Li$_2$CO$_3$/PTFE (9:1:1 m:m) composite electrodes at the indicated potential to reach a capacity of 0.064 mAh in 0.1 M LiTFSI in DME that contained 30 mM DMA. ^1H NMR confirms DMA-O$_2$ to elute at 2.6 min (Figures S2, S5). b) ^1H NMR spectra of the same electrolyte samples. Reference measurements are shown with the starting electrolyte (labeled as DMA) and electrolyte where the DMA was fully converted into DMA-O$_2$ by in situ photogenerated $^1O_2$ (labeled as DMA-O$_2$) as described in the Supporting Information.

¹H NMR analysis of the samples confirmed the presence of DMA-O_2 at these voltages (Figure 2b, S6). The HPLC and NMR results confirm that electrochemical oxidation of Li_2CO_3 forms ¹O_2 from the onset of oxidation at 3.8 V.
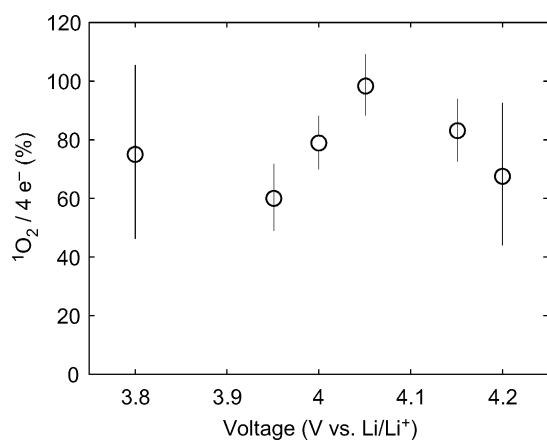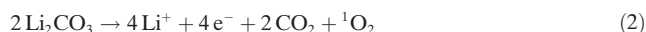
DABCO and other quenchers (e.g., LiN_3) are electrochemically oxidized at approximately 3.5–3.6 V (Figure S7).[12] Nevertheless, diffusion of fresh quencher from the separator may counterbalance quencher oxidation at the working electrode and thus may show some quenching efficiency. Figure 4 shows CO_2 and O_2 evolution during an OEMS
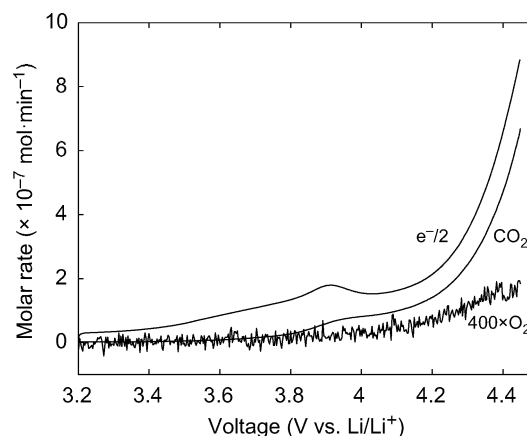

Figure 3. Amount of ¹O_2 (as quantified by HPLC as DMA-O_2) relative to the charge passed in Equation (2) at different charging potentials. Values represent lower bounds since not all ¹O_2 may react to DMA-O_2 or the electrolyte may be incompletely extracted.

Figure 4. CO_2 and O_2 evolution from Super P/Li_2CO_3/PTFE (9:1:1 m:m) composite electrodes during a linear potential scan at 0.14 mV s^{-1} in 0.1 M LiTFSI in TEGDME that contained 30 mM DABCO.

Figure 3 relates the amount of ¹O_2 formed to the charge passed in the reaction:

$$2\,Li_2CO_3 \rightarrow 4\,Li^+ + 4\,e^- + 2\,CO_2 + {}^1O_2 \qquad (2)$$

A maximum of one ¹O_2 could be produced per four electrons. ¹O_2 formed at all probed voltages to an extent well above 50% of the $4\,e^-$/¹O_2 maximum limit. The amount of ¹O_2 must, however, be inferred with caution from the measured amount of DMA-O_2 and represents a lower bound of the true value. This is because not all ¹O_2 will react with DMA, but may decay along other routes. Furthermore, the electrolyte may be incompletely extracted and thus result in an artificially low ¹O_2 value. At higher voltages (e.g., 4.2 V), DMA-O_2 could degrade to a minor extent, as shown in Figure S1 in the Supporting Information, which may explain the observed lower yield of DMA-O_2 at 4.2 V compared to 4.05 V in Figure 3. Overall, the values in Figure 3 suggest that the majority, if not all, of the "missing O_2" from the electrochemical oxidation of Li_2CO_3 forms ¹O_2 and is thus not detected in the gas phase.

The complete lack of O_2 evolution during oxidation of Li_2CO_3 (Figure 1) implies that the formed ¹O_2 reacts with cell components rather than being, even in part, deactivated to ³O_2. We therefore investigated the use of a ¹O_2 quencher, which deactivates ¹O_2 to ³O_2,[10] to possibly promote ³O_2 evolution. A variety of quenchers have been reported, including azides and aliphatic amines.[10,11] We have previously shown that 1,4-diazabicyclo[2.2.2]octane (DABCO) is effective in non-aqueous environments.[8a] For use during electrochemical oxidation of Li_2CO_3, however, the electrochemical stability of the quenchers is problematic, since

measurement similar to Figure 1, but with an electrolyte that contained 30 mM DABCO. DABCO oxidation accounts for the anodic process that onsets at around 3.6 V and peaks at 3.9 V. As before, CO_2 evolution starts at around 3.8 V and reaches a rate close to $2\,e^-$/CO_2. Intriguingly, O_2 evolution does start together with CO_2 evolution at around 3.8 V with a similarly growing rate as the voltage rises. This result further corroborates ¹O_2 formation and also shows that if a suitable quencher can be found, then Li_2CO_3 could be oxidized without the detrimental effects of ¹O_2.

Detection of ¹O_2, and ³O_2 when a quencher is present, implies that a mechanism of Li_2CO_3 oxidation involves the formation of O−O bonds. In analogy to carbonate oxidation in aqueous media,[13] it has been suggested that Li peroxodicarbonate (LiO_2COOCO_2Li) forms as an intermediate.[4h] Such an intermediate has been questioned on the basis that 1) CO_3^{2-} is poorly soluble and would thus lack mobility to combine to peroxodicarbonate and 2) the high charge density of the peroxodicarbonate anion ($^-O_2COOCO_2^-$) would not allow O−O bond formation or would lead to immediate bond cleavage.[4c,14] However, neither large carbonate mobility nor dissociation are required and a mechanism via a peroxodicarbonate intermediate can be proposed (Figure S8a) and rationalized based on previous reports.[4i,15] Formally, peroxodicarbonate can form through a $1\,e^-$ oxidation/Li^+ extraction of two Li_2CO_3 to form two $LiO_2CO^•$ moieties (**2**), which combine to LiO_2COOCO_2Li (**3**). Within the Li_2CO_3 crystal structure (Figure S8b), adjacent carbonate moieties appear to be sufficiently close to form O−O bonds once an e^- and a Li^+ is extracted in each. Mobility of the intermediates or even dissociation from the crystal lattice is thus not required. A DFT study on the oxidation of Li_2CO_3 surfaces has shown that

after first oxidation/Li^+ extraction, further Li^+ extractions are energetically most favorable at adjacent carbonate moieties, which makes their recombination likely.[15] Such recombination within the crystal lattice is also supported by DFT work on the formation of Li_2CO_3 via peroxodicarbonate, which yields adjacent carbonate moieties within the Li_2CO_3 lattice.[4i] According to the same work, the O−O bond in LiO_2COOCO_2Li is strongly stabilized by coordination with Li^+ ions in comparison to $^-O_2COOCO_2{}^-$, which is unlikely to form in a nonaqueous environment. A possible ongoing pathway to form $^1O_2$ is shown in Figure S8a. Further oxidation and decarboxylation could yield $LiCO_4$ (**4**; Figure S8a), which then in turn could yield $^1O_2$. Clarification of the exact mechanism, however, will need further computational or/and experimental work.

In conclusion, by using a selective $^1O_2$ trap and online mass spectrometry, we have shown that electrochemical oxidation of Li_2CO_3 in a nonaqueous environment yields up to stoichiometric amounts of $^1O_2$ according to the reaction $2\,Li_2CO_3 \rightarrow 4\,Li^+ + 4\,e^- + 2\,CO_2 + {}^1O_2$. This explains the absence of O_2 evolution, which has been a long-standing conundrum and a cause for much speculation regarding potential reactive oxygen species. The reaction proceeds from an onset potential of approximately 3.8 V, which is close to its thermodynamic value of 3.82 V. When a $^1O_2$ quencher is present, part of the formed $^1O_2$ could be evolved as $^3O_2$. Li_2CO_3 is a universal passivating agent in Li-ion battery cathodes and decisive in interfacial reactivity. Li_2CO_3 is also a common side product in $Li-O_2$ cathodes, as well as the targeted discharge product in $Li-O_2/CO_2$ batteries, where it then needs to be oxidized on charge to form a reversible system. Our results thus strongly suggest that Li_2CO_3 formation, even at impurity levels, will have a deleterious affect on the stability of all Li batteries where electrodes operate beyond 3.8 V vs. Li/Li^+, which includes most currently studied cathodes. Strategies to avoid $^1O_2$ formation or the presence of Li_2CO_3 during battery operation are therefore warranted.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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