Singlet oxygen and dioxygen bond cleavage in the aprotic lithium-oxygen battery

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Summary

Investigation of lithium-oxygen cells on discharge using a mixture of $^{16}O^{16}O$ and $^{18}O^{18}O$ gases, showed that O-O bond cleavage occurs during disproportionation of LiO_2 to O_2 and Li_2O_2, detected by the presence of isotopic $^{16}O^{18}O$. The formation of singlet oxygen, $^1O_2$, was also monitored during disproportionation. While only 4.5 % of oxygen was found to undergo bond cleavage and scrambling of oxygen atoms, more than 40 % of the singlet oxygen produced during disproportionation comes from the scrambling pathway, making it a major source of singlet oxygen generation in lithium-oxygen batteries. Our results demonstrate that Li_2O_2 formation occurs predominantly by disproportionation and that by controlling the pathway of this step, it may be possible to suppress $^1O_2$ formation, a species that has been implicated in the degradation of lithium-oxygen batteries.

Keywords: Li-O_2 battery; isotope; oxygen scrambling; bond cleavage; singlet oxygen

Introduction

The high theoretical specific energy of the aprotic lithium-air (oxygen) battery, 3500 Wh kg^{-1}, exceeding significantly that of Li-ion batteries, has spurred investigation of the processes occurring in the battery.[1-8] The cell operates by oxidation of metallic lithium at the negative electrode and reduction of oxygen at the positive electrode to form lithium peroxide on discharge. Significant progress has been made in addressing the challenges of Li-O_2 in recent years, resulting in the demonstration of cells capable of cycling at several mA cm^{-2} with capacities of several mAh cm^{-2}.[8-15] Now the most important barrier to realisation of a Li-O_2 cell is degradation of the electrolyte, which leads to capacity fading on cycling.[10] In early studies, electrolyte degradation was attributed to reaction with species such as the superoxide O_2^-, formed as an intermediate in the conversion between O_2 and Li_2O_2.[16-18] However, recent work has identified the formation of singlet oxygen, $^1O_2$, as a major source of degradation in Li-O_2 cells, due to its reactive nature.[19-25] Understanding how $^1O_2$ is formed is essential if we are to mitigate degradation in Li-O_2 cells. [23-25] $^1O_2$ is known to form in protic systems by O-O bond cleavage, however, it was generally assumed that the reduction of O_2 to Li_2O_2 in non-aqueous Li-O_2 batteries would not form $^1O_2$, since disproportionation of the O_2^- intermediate does not require O-O bond cleavage. Disproportionation can take place by electron exchange alone: $2O_2^- \rightarrow O_2 + O_2^{2-}$, although more complex disproportionation routes have been proposed by computational methods.[26-28] Here we present the first experimental evidence for O-O bond cleavage and scrambling of oxygen during discharge in an aprotic Li-O_2 cell. We used an ether-based solvent, tetraethylene glycol dimethyl ether (tetraglyme) because ethers remain the best and the most widely studied solvents for the Li-O_2 battery, and thus our observations are specific to this electrolyte solution. We do so through monitor the oxygen-oxygen isotope composition in the presence of mixed $^{16}O^{16}O$ and $^{18}O^{18}O$ gases. We show that oxygen cleavage occurs during the disproportionation of LiO_2 to Li_2O_2 and O_2 and that disproportionation is the major pathway to Li_2O_2. Furthermore, we show that scrambling accounts for only 4.5 % of the O_2 formed during disproportionation, but accounts for 40 % of the $^1O_2$

generated. Therefore, $^1O_2$ is formed by LiO_2 disproportionation via O-O scrambling and direct electron transfer between O_2^- ions, and with a high proportion of scrambling leading to $^1O_2$ generation.

Results and discussion

The discharge reaction in an aprotic Li-O_2 battery is known to form initially lithium superoxide (1), which subsequently disproportionate to form lithium peroxide and dioxygen (2), or undergoes a second 1-electron reduction to lithium peroxide with no oxygen release (3)[16,29]:

(1) $Li^+ + O_2 + e^- \rightarrow LiO_2$

(2) $2\ LiO_2 \rightarrow Li_2O_2 + O_2$

(3) $LiO_2 + Li^+ + e^- \rightarrow Li_2O_2$

To study the possibility of oxygen-oxygen bond cleavage on discharge, the cells were discharged in a 1: 1 mixture of $^{16}O^{16}O$ and $^{18}O^{18}O$ gases, while monitoring the isotope gas composition by *in situ* differential electrochemical mass spectrometry (DEMS), Figure 1a and Figure S1. The cell assembly and experimental procedures are described in the Methods section. The results showed an overall decrease in O_2 during discharge. The integrated quantity of the total O_2 consumption (including all O_2 isotopes), shown in Figure 1 and S1, compared with the charge passed, gave an e^-/O_2 ratio of 2.04, as expected for O_2 reduction to Li_2O_2 in an ether-base electrolyte solution. Significantly, in the context of this study, the formation of $^{16}O^{18}O$ gas was observed. The isotope scrambling confirms that O-O bond cleavage occurs during discharge, producing $^{16}O^{18}O$ in the gas phase. The discharged electrode was then retrieved from the cell and the formation of predominantly Li_2O_2 particles in the electrode by electrochemical reduction of O_2 is confirmed by powder X-ray diffraction (PXRD), Fourier-transform infrared (FTIR) spectra in Figure S2 and scanning electron microscopy (SEM) images in Figure S3 of the discharged electrode. The experimental details and method of analysis are described in the Methods section. As is well known from previous studies, there is formation of some side products e.g. Li acetate.[30] However, the formation mechanisms show that this does not involve O_2 formation.[30-33] The electrode was further analysed with time-of-flight secondary ion mass spectrometry (ToF-SIMS), Figure 1b, and the signals for $^{16}O^{18}O$ and $^{18}O^{18}O$ are given in Table S1. This shows the presence of $(^{16}O^{18}O)^{2-}$ ions in the Li_2O_2 discharge product, confirming isotopic scrambling and hence O-O bond cleavage during discharge. On changing the ratio of $^{16}O^{16}O$ to $^{18}O^{18}O$ in the gas phase from 1: 1 to 1: 2, the proportion of $^{16}O^{18}O$ detected in the discharge product decreased, Figure 1b. Statistically, O-O bond cleavage and subsequent O-O bond formation is more likely to form fewer $^{16}O^{18}O$ for the same degree of bond cleavage in the 1: 2 gas mixture system. Overall, these data demonstrate that isotopic scrambling and bond cleavage occurs during the disproportionation of LiO_2 in the aprotic Li-O_2 battery on discharge.

To rule out the possibility of oxygen bond cleavage occurring during reduction (1), we investigated oxygen scrambling in the Na-O_2 battery where there is no disproportionation.[34] During discharge in a Na-O_2 battery, the major product is NaO_2, Figure S4, and thus this system provides an opportunity to analyse reaction (1) in isolation. The Na-O_2 cell assembly is described in Methods section. The cell was discharged, and the isotopic analysis was repeated in the Na-O_2 system, Figure 2a. DEMS showed no evolution of $^{16}O^{18}O$. ToF-SIMS analysis of the NaO_2 discharge product, Figure 2b, also showed no evidence of $^{16}O^{18}O$ and varying the $^{16}O^{16}O$, $^{18}O^{18}O$ isotope gas ratios had no impact on this result, all suggesting no bond cleavage and no scrambling during the reduction of oxygen to superoxide.

While NaO_2 is comparatively stable against disproportionation, the addition of Li ions to a solution containing NaO_2 can initiate the disproportionation process and formation of Li_2O_2. We note such a process (Li^+ + NaO_2) may not fully recreate the conditions for the disproportionation reaction in Li-O_2 cells.[25] However, NaO_2 formed from electrochemical discharge does offer a means of preparing stable and relatively pure superoxides for each of the specific oxygen isotopes required in our studies, allowing investigate the oxygen scrambling in a pure chemical process. When immersing the Na-O_2 discharge products, formed by discharging cells in $^{16}O^{16}O$ and $^{18}O^{18}O$ gases, in a solution composed of 0.25 M lithium bis(trifluoromethanesulfonyl)imide) (LiTFSI) in tetraglyme under Ar, a clear evolution of $^{16}O^{18}O$ is seen in the on-line mass spectrometry, Figure 3, confirming scrambling and hence O-O cleavage arising from disproportionation, the only mechanism possible when forming Li_2O_2 chemically. O-O bond cleavage will, in addition to the formation of $^{16}O^{18}O$, also form new bonds between O of the same isotope. Hence, while the identification of $^{16}O^{18}O$ proves that O-O bond cleavage occurs, to quantify the extent of such cleavage, it is necessary to take account of the formation of O_2 from O_2^- with the same isotopic oxygen atoms. For a 1: 1 mixture of $^{16}O^{16}O$ and $^{18}O^{18}O$ gases, the degree of cleavage is twice the $^{16}O^{18}O$ detected (assuming a bimolecular reaction step). These data demonstrate that 4.5 % of oxygen undergoes scrambling during disproportionation. When combined with the data from Figure 1, it proves that during discharge the second step occurs predominantly (70 %) by disproportionation (2) rather than direct reduction (3). A detailed description of calculations leading to 4.5% scrambled O_2 and 70% of Li_2O_2 formation being by disproportionation is given in Supplementary Note 1.

It is known that in a protic media, HO_2 disproportionation results in cleavage of the superoxide O-O bonds, by formation of a dimer $(HO_2)_2$ in which a new O-O bond is formed between the O atoms in HO_2, and it is these atoms that are subsequently abstracted to form $^1O_2$.[35,36] Residual amounts of water are known to promote HO_2 formation in the Li-O_2 battery,[37] and thus this could be responsible for oxygen scrambling during disproportionation. Hence, to rule out the possible water induced scrambling caused by water contamination during cell preparation and operation, we investigated the effect of water content on the evolution of $^{16}O^{18}O$ using on-line mass spectrometry. Figure S5 shows

that O_2^- remains predominantly unprotonated due to the lack of decrease in the anodic peak current to cathodic peak current ratio, which is indicative of protonation and disproportionation, until the addition of at least 1000 ppm water. Figure S6 shows that different amounts of water added to the cell (from 10 to 200 ppm) did not significantly change the amount of oxygen bond cleavage. Similar phenomenon has been reported by Schwenke et al. on the equilibrium between Li_2O_2 and water.[38] Consequently, given the water content here is < 1000 ppm, water does not appear to be a major contributor to the observed oxygen scrambling.

Given that O-O bond cleavage in the Li-O_2 system occurs during disproportionation of LiO_2 and based on the radical-radical coupling mechanism found in the protic system, we propose the following:

$$Li^{16}O^{16}O + Li^{18}O^{18}O \rightarrow Li^{18}O^{18}O^{16}O^{16}OLi \rightarrow Li^{18}O^{16}OLi + {}^{16}O^{18}O \qquad (2)$$

which involves the formation of Li_2O_4 intermediates, previously proposed by computation methods,[39] during discharge in the lithium-oxygen battery. LiO_2 has been reported to be relatively soluble in ether-based solutions and disproportionation occurs in solution.[40,41] Therefore, we anticipate the dimerization of LiO_2 equation (2) is more likely to be a liquid phase reaction. We note that higher-order clusters may also occur.

Having established that O-O bond cleavage and scrambling occurs on LiO_2 disproportionation to Li_2O_2, we then investigated the extent to which such scrambling forms reactive $^1O_2$. We did so using the $^1O_2$ trap 9,10-Diphenylanthracene (DPA), which reacts with $^1O_2$ to form 9,10-Diphenylanthracene endoperoxide (DPA-O_2) and upon heating releases molecular oxygen through a thermolysis process regenerating DPA (Scheme S1).[42] This is demonstrated in Figure S7. Adding 30 mM DPA to the electrolyte in the cell allows us to trap the $^1O_2$ generated on discharge. After purging the cell with Ar at the end of discharge, the electrolyte was heated to 90 °C, releasing the trapped $^1O_2$ and on-line mass spectrometry was used to quantify the isotopic composition, thus evaluating the link between $^1O_2$ formation and scrambling. Figure 4 shows the $^1O_2$ released from a Li-O_2 cell discharged in a 1: 1 mixture of $^{16}O^{16}O$ and $^{18}O^{18}O$. The cell generated singlet $^{16}O^{16}O$, $^{16}O^{18}O$ and $^{18}O^{18}O$ in the ratio of 1.88: 1: 1.89. The presence of singlet $^{16}O^{18}O$ proves that O-O bond cleavage and scrambling of oxygen atoms can form $^1O_2$. While it is known that degradation can occur in Li-O_2 cells, such degradation reactions are not expected to generate O_2 and $^1O_2$.[31-33] We also do not anticipate O atoms or O_3 species, as discussed in Supplementary Note 2. Statistically, the oxygen bond cleavage pathway would generate $^{16}O^{16}O$, $^{16}O^{18}O$ and $^{18}O^{18}O$ in a ratio of 1: 2: 1 (see the discussion above). The deviation from this ratio indicates additional non-scrambling pathways to $^1O_2$. Considering these data and the analysis above, it can be shown that while only 4.5 % of O_2 disproportionation undergoes O-O cleavage, it accounts for more than 40 % of the total $^1O_2$ generation, making it a significant pathway for $^1O_2$ generation in aprotic Li-O_2 batteries.

Conclusions

In summary, O-O bond cleavage and scrambling of the constituent atoms is shown to occur during disproportionation of LiO_2 to O_2 and Li_2O_2 when the aprotic Li-O_2 battery is discharged, and disproportionation is the major route to Li_2O_2. Only 4.5 % of the O_2 undergoes O-O bond cleavage during disproportionation. Given 40 % of $^1O_2$ formed on discharge contains scrambled oxygen atoms, O-O bond cleavage accounts for a disproportionately high amount of $^1O_2$ formation in Li-O_2 batteries. However, it should be noted that different solvents may impact the pathway to Li_2O_2 and thus scrambling and disproportionation. For example, the balance between electron exchanges between O^{2-} vs O-O bond cleavage, may be different for different solvents, as is the balance between disproportionation and direct O^{2-} reduction to O_2^{2-}. This hints at the possibility of suppressing singlet oxygen evolution by controlling the disproportionation route.

Experimental Procedures

Please refer to the Supplementary Information for details of the Materials and Methods.

Acknowledgements

P.G.B. is indebted to the EPSRC, including SUPERGEN programme, for financial support. L.R.J. thanks the University of Nottingham's Propulsion Futures Beacon for funding towards this research and acknowledges financial support from the EPSRC (EP/S001611/1) and the Faraday Institution (EP/S003053/1 FIRG014).

Author Contributions

S.D., S.Y., and X.G. designed experiments. S.D. and S.Y. performed electrochemical measurements, and Y.C., X.G., and C.K. performed characterization analysis. S.D., S.Y., Y.C., G.C., L.R.J., X.G. and P.G.B. interpreted the data. L.R.J. X.G. and P.G.B. wrote the paper with contributions from S.D., and S.Y.

Declaration of interests

The authors declare no competing financial interests.

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Figure 1. In situ DEMS (a) and ToF-SIMS (b) demonstrating oxygen bond cleavage during discharge in a typical Li-O_2 cell. (a) Total oxygen flux (black curve) showing O_2 ($^{16}O^{18}O$, $^{16}O^{16}O$ and $^{18}O^{18}O$ combined) consumption and $^{16}O^{18}O$ evolution (red curve) during discharge in a mixture of $^{16}O^{16}O$, $^{18}O^{18}O$ and Ar gases in a ratio of 1:1:4. (b) Relative ToF-SIMS intensity of $^{16}O^{18}O$ in the discharge product formed using two different ratios of $^{16}O^{16}O$ to $^{18}O^{18}O$ in the gas phase. A detailed description of calculation used to obtain the relative ToF-SIMS intensity is given in the Supplementary Information.

Figure 2. In situ DEMS (a) and ToF-SIMS (b) demonstrating no oxygen cleavage during discharge in a typical Na-O_2 cell. (a) Total oxygen flux (black curve) showing O_2 consumption and $^{16}O^{18}O$ evolution (red curve) during the period the cell is discharging, all in a mixture of $^{16}O^{16}O$, $^{18}O^{18}O$ and Ar gas with a ratio of 1:1:4. (b) Relative ToF-SIMS intensity of $^{16}O^{18}O$ in the Na-O_2 discharge product formed using different ratios of $^{16}O^{16}O$ to $^{18}O^{18}O$ in the gas phase.

Figure 3. O_2 evolution demonstrating oxygen bond cleavage during disproportionation of LiO_2. Total oxygen (black line) and $^{16}O^{18}O$ (red line) gas evolution, measured using on-line mass spectrometry after injecting a solution of 0.25 M LiTFSI-tetraglyme into a vial containing NaO_2, collected from Na-O_2 cells after discharge in $^{16}O^{16}O$ and $^{18}O^{18}O$, and thus containing both $Na^{16}O^{16}O$ and $Na^{18}O^{18}O$.

Figure 4. O_2 evolution demonstrating singlet oxygen generation through the O_2 scrambling pathway. $^{16}O^{16}O$, $^{18}O^{18}O$ and $^{16}O^{18}O$ gas evolution measured using on-line mass spectrometry after heating a cell that has been pre-discharged with 30 mM DPA in the electrolyte (0.25 M LiTFSI-tetraglyme).