

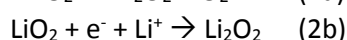
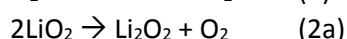
A Rechargeable Lithium-O₂ Battery with Dual Mediators Stabilising the Carbon CathodeXiangwen Gao^{1‡}, Yuhui Chen^{1‡}, Lee R. Johnson¹, Zarko Jovanov¹ and Peter G. Bruce^{1*}¹ Departments of Materials and Chemistry, Parks Road, University of Oxford, OX1 3PH, UK

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ABSTRACT

At the cathode of a Li-O₂ battery, O₂ is reduced to Li₂O₂ on discharge, the process being reversed on charge. Li₂O₂ is an insulating and insoluble solid, leading ultimately to low rates, low capacities and early cell death if formed on the electrode surface, problems overcome by forming/decomposing Li₂O₂ from solution. A Li-O₂ cell is described that decouples completely the electrochemistry at the cathode surface from Li₂O₂ formation/decomposition. Mediators on discharge (2,5-Di-tert-butyl-1,4-benzoquinone [DBBQ]) and charge (2,2,6,6-tetramethyl-1-piperidinyloxy [TEMPO]) transfer electrons between the cathode surface and Li₂O₂. The cell cycles with a capacity of 2 mAh cm⁻²_{areal} at 1 mA cm⁻²_{areal} with low polarisation on charge/discharge, indicating that dual mediators combined with a true gas diffusion electrode could deliver 40 mAh cm⁻²_{areal} at rates >> 1 mA cm⁻²_{areal}. Arguably, the most important advantage of dual mediators is they avoid instability at the carbon cathode. Carbon is the most attractive material for the porous cathode in Li-O₂ cells, but is too reactive degrading to Li₂CO₃. By forming/decomposing Li₂O₂ in solution and not in intimate contact with the carbon, by avoiding high charge potentials and because only mediators transfer electrons at the carbon surface, carbon instability is avoided (< 0.008 % carbon decomposition per cycle compared with 0.12 % without mediators), addressing one of the biggest barriers to the progress of Li-O₂ cells.

The Li-O₂ battery possess the highest theoretical specific energy of any battery, 3500 Wh kg⁻¹. If it could be realised in practice it would transform energy storage¹⁻¹⁵. A typical Li-O₂ battery is composed of a lithium anode separated by a non-aqueous electrolyte from a porous carbon cathode, at which O₂ is reduced to Li₂O₂ on discharge, the process being reversed on charge. Reduction of O₂ to Li₂O₂ at the cathode of a Li-O₂ cell on discharge normally proceeds via the intermediate LiO₂:



An interesting recent report described arresting discharge at step 1, LiO₂, thus improving cycleability, although at the expense of specific energy (1 e⁻/O₂ for LiO₂ instead of 2 e⁻/O₂ for Li₂O₂)¹⁶. Here we focus on Li₂O₂.

On discharging a Li-O₂ cell, O₂ reduction to Li₂O₂ that grows on the carbon cathode surface leads to passivating films, resulting in early cell death (low capacity) and low rates^{2,4}. If Li₂O₂ grows from solution, high capacities (Supplementary Fig. S1) and rates are possible, but oxidation is hindered, requiring mediators on charge^{8,10,17-27}. Growing Li₂O₂ from solution on discharge rather than on the cathode surface, can be achieved by using electrolyte solutions or additives that dissolve the intermediate LiO₂^{2,28,29}. However, LiO₂ is reactive (a strong nucleophile) towards electrolyte solutions and electrodes, and polar solvents that dissolve LiO₂ are known to readily decompose^{3,30,31}. As a result, low polarity, low donor number, solvents are preferred. Reduction mediators can be used to promote solution growth in such low donor number solvents on discharge^{20,32-34}. It has been shown that the use

of 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) as a reduction mediator in Li-O₂ cells results in reduction of O₂ to Li₂O₂ following a different path that avoids LiO₂³². This permits solution growth of Li₂O₂ from low polarity electrolyte solvents, such as ethers, which are more stable but are unable to dissolve LiO₂ and therefore unable to promote directly the solution reaction^{1,29}.

Here we describe the cycling of a Li-O₂ cell with mediators on discharge and charge, in a low donor number, ether, solvent that does not dissolve LiO₂. We note that this differs from a recently published Li-O₂ battery, which operates in a flow cell configuration using mediators to form and decompose Li₂O₂ in tanks outside the cell³⁵. On discharge, DBBQ is reduced at the cathode surface and transfers electrons to O₂ in solution, reducing it to form Li₂O₂. On charge, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), is oxidised at the cathode surface and transfers electron-holes to Li₂O₂ oxidising it in solution to O₂. Note that the observed potentials of redox mediators are affected by the electrolyte solution composition and by the ratio of the reduced and oxidised forms present. Mediators must operate in the correct voltage range for O₂ reduction to Li₂O₂ and vice versa²¹. By decoupling completely, the growth/decomposition of Li₂O₂ (the energy storage reaction) from the electrochemistry at the cathode surface, we obtain cycling with capacities of 2 mAh cm⁻²_{areal} at a rate of 1 mA cm⁻²_{areal} and discharge/charge potentials of 2.7 and 3.6 V, respectively. The capacity was limited to 2 mAh cm⁻²_{areal} at 1 mA cm⁻²_{areal} because the O₂ entered the porous cathode only from the electrode/gas interface, resulting in clogging of the pores at the interface, poor mass transport and limited utilisation of the porous cathode. The results indicate that by combining dual mediators (to promote solution formation/decomposition of Li₂O₂) with a true gas diffusion electrode (which could deliver O₂ throughout the electrode akin to a fuel cell cathode) would give capacities of 40 mAh cm⁻²_{areal}, and at rates >> 1 mA cm⁻²_{areal}. This is the value modelling studies have shown is necessary for a Li-O₂ cell to achieve 500-600 Wh kg⁻¹^{6,15}.

Electrolyte and carbon cathode stability are important challenges for Li-O₂ cells. Very recently, a paper using LiBr as a charge mediator demonstrated improved electrolyte stability and this was ascribed by the authors to the avoidance of forming reactive Li_{2-x}O₂ on charge²⁷. Concerning carbon instability, there have been extensive efforts to modify carbons, their surfaces or apply coatings, which have resulted in improved resistance to decomposition^{36,37}. The present work addresses the stability of the carbon electrode by decoupling the electrochemistry from the Li₂O₂ formation/decomposition on discharge and charge, intimate contact and hence reactivity between Li₂O₂ and the carbon surface is minimised, charging voltages are well below 4 V at which carbon is known to decompose significantly to Li₂CO₃, and the surface electrochemistry involves only electron transfer between mediating molecules, which is less affected by Li₂CO₃. As a result, the use of dual mediators avoids the instability of carbon electrodes, previously dismissed as being too unstable in Li-O₂ cells. Carbon is by far the most attractive material from which to form porous cathodes, hence demonstrating that it is significantly more stable with mediators addresses one of the major barriers to progress of the Li-O₂ battery. It should be noted that the stability of Li₂O₂ in contact with the electrolyte solution remains one of the key challenges still to be addressed in Li-air.

The dual mediator cell

Plots of the voltage versus capacity on discharge and charge for cells with and without dual mediators at a porous, gas diffusion layer (GDL), carbon cathode, are shown in Fig. 1. Experimental details, including construction of the cells, preparation of the electrode and electrolyte solutions, and the methods used for characterisation are all described in the Supplementary Information. As in previous studies of Li-O₂ cells, LiFePO₄ was used as the anode instead of Li to avoid unwanted reactions involving the latter^{32,38}. We note that the potential of the LiFePO₄ anode, 3.45 V vs Li⁺/Li, would not result in a practical cell voltage. Without the dual mediators, the cell in Fig. 1 dies quickly, with a

capacity of only $0.1 \text{ mAh cm}^{-2}_{\text{areal}}$, on the 1st discharge. Charging requires 4.5 V. Within 5 cycles the capacity is reduced to only $0.02 \text{ mAh cm}^{-2}_{\text{areal}}$, Fig. 1(b). These results are consistent with previous studies in ethers^{31,32}. In contrast, with the reduction and oxidation mediators, at a current density of $1 \text{ mA cm}^{-2}_{\text{areal}}$, a capacity of $2 \text{ mAh cm}^{-2}_{\text{areal}}$, can be sustained, 20 x greater on cycle 1 and 100 x greater on cycle 5 than without mediators. The charging voltage is also much lower at $\sim 3.6 \text{ V}$.

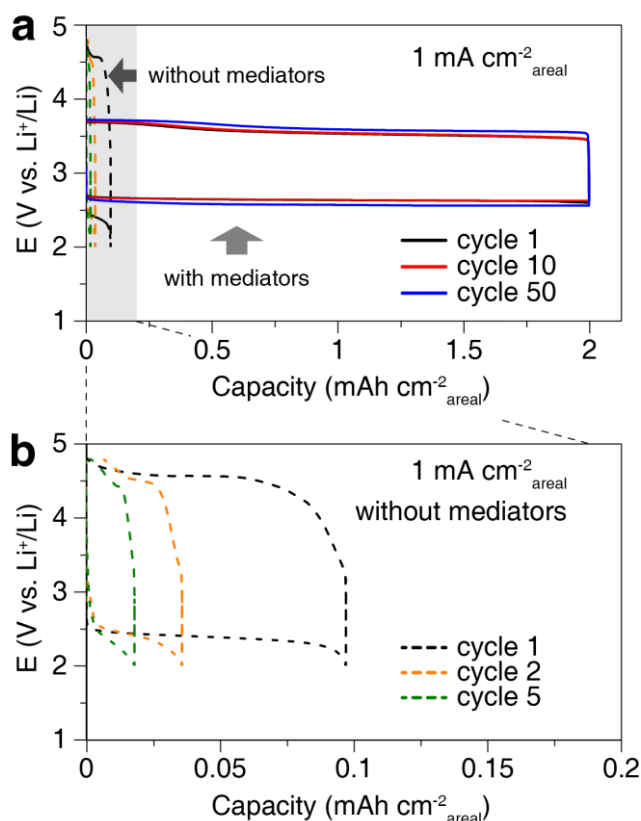


Figure 1 | Discharge-charge curves of GDL based porous carbon electrodes with and without mediators. (a) cycled in 0.3 M LiClO₄ in DME with 25 mM DBBQ-25 mM TEMPO (solid lines) and without DBBQ-TEMPO (dash lines) under 1 atm O₂ at an areal current density of $1 \text{ mA cm}^{-2}_{\text{areal}}$. (b) Enlarged section of the discharge-charge curves recorded without DBBQ-TEMPO in (a).

The charging voltage is set by the TEMPO mediated oxidation and is slightly lower than that in previous studies using TEMPO^{21,39,40}. The higher voltage in previous studies may arise from Li₂O₂ film growth on the electrode surface inhibiting mediator access and hence oxidation, whereas in the present work Li₂O₂ grows from solution. There is a slight increase in the charging voltage towards the end of charge, which is discussed later. SEM images of the electrodes are shown in Fig. 2 and infrared spectrometry (FTIR) results in Fig. 3. They demonstrate the formation of Li₂O₂ particles on the 1st discharge and their complete removal on charge.

The capacity in Fig. 1(a) was deliberately limited to $2 \text{ mAh cm}^{-2}_{\text{areal}}$, at $1 \text{ mA cm}^{-2}_{\text{areal}}$ because of pore clogging at the gas/electrode interface beyond this capacity, which results in polarisation, then Li₂O₂ film formation and further polarisation, as discussed below. The so-called GDL electrode is not a true gas diffusion electrode, as used in a fuel cell, in which O₂ is delivered to the electrolyte/electrode interface along gas channels. It is simply a porous carbon cathode flooded with the electrolyte solution and exposed to the O₂ atmosphere only on the side opposite to the electrolyte separator, as shown in Supplementary Fig. S2. As a result, Li₂O₂ particles form preferentially at the electrode/gas interface (where O₂ is readily available). SEM images collected from a cell in which discharge was extended beyond $2 \text{ mAh cm}^{-2}_{\text{areal}}$, Supplementary Fig. S3(a), indicates that the pores become clogged near the

electrode/gas interface, Supplementary Fig. S3(c) and (d), impeding mass transport, and this is associated with the gentle decrease in discharge voltage and increase in charge voltage above $2 \text{ mAh cm}^{-2}_{\text{areal}}$. Extending the depth of discharge further sees the gentle voltage decrease continue. As the voltage continues to decrease, it reaches a potential where Li_2O_2 film formation commences and the voltage now drops rapidly to the end of discharge. This rapid downturn is consistent with previous studies, in the absence of a mediator, that assign the end of discharge to Li_2O_2 film formation^{41,42}. In practice, as the voltage decreases only gently when pore blocking commences, it is difficult to use a voltage cut-off for cycling. Hence discharge was arrested at $2 \text{ mAh cm}^{-2}_{\text{areal}}$.

To explore the rate capability, cells were operated at three different current densities up to $2 \text{ mA cm}^{-2}_{\text{areal}}$, Supplementary Fig. S4(a). At the highest current density the discharge voltage is lower and the onset of voltage downturn is significantly earlier. This is consistent with the rate performance being limited by O_2 mass transport, resulting in even more of the Li_2O_2 deposition occurring at the gas/electrode interface and earlier pore clogging. We note that the high charge potential at $2 \text{ mA cm}^{-2}_{\text{areal}}$ is due to the formation of a Li_2O_2 film during the downturn on discharge, blocking the electrode. We also examined the effect of reducing the mediator concentration to 12.5 mM and 6.25 mM and this had no significant effect on the performance between 25 mM and 12.5 mM, Supplementary Fig. S4(b), supporting the conclusion that the rate capability is limited by O_2 rather than mediators mass transport at those concentrations. When the mediator concentration was reduced to 6.25 mM, the discharge capacity dropped dramatically, suggesting that mediator mass transport became the limiting factor rather than the O_2 mass transport. The diffusion coefficients of O_2 , DBBQ and TEMPO were measured by CV, as described in the Supplementary Information, and are $4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $8.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. Although the mediators are slower their concentration is approximately three times higher than O_2 . Furthermore, the mediators are regenerated so rate limitations cannot be assumed based on a simple comparison of diffusion coefficients.

The results in Fig. 1 represent utilisation of only c.a. 4 % of the total electrode pore volume due to these mass transport limitations. A true gas diffusion electrode would alleviate this problem, delivering O_2 evenly throughout the electrode, accessing a much higher proportion of the electrode volume and increasing significantly the capacity to store charge and at higher rates. Assuming 80 % of the porosity could be filled with Li_2O_2 (leaving 20 % of the porosity for the electrolyte)⁹, an encouragingly large capacity of $40 \text{ mAh cm}^{-2}_{\text{areal}}$ could be achieved and at significantly higher rates. This exceeds the range of 5 to 30 mAh cm^{-2} estimated to be necessary for a practical Li- O_2 cell to achieve up to 500-600 Wh kg^{-1} ^{6,15}. In short, the use of dual mediators mitigates limitations imposed by the formation/decomposition of Li_2O_2 on the electrode surface, as shown in the comparison between Fig. 1(a) and (b). The hurdle to achieving yet higher capacities at higher rates becomes one of designing a suitable gas diffusion electrode to alleviate O_2 mass transport limitations. Of course, stable electrolyte solutions are also required for reversible, extended cycling.

Product analysis

As shown previously, FTIR is very sensitive to the products of any side reactions^{31,43}. There is evidence of some lithium acetate and carbonate at the end of the 1st discharge, Fig. 3, consistent with previous reports for Li- O_2 cells with ether based electrolytes at the end of discharge and the Li_2O_2 yield at the end of discharge of 88 %, discussed later^{14,30,31}. The yield on discharge is close to that reported in literature⁴⁴ as the major side-reaction is still due to the decomposition of electrolyte and a more stable solvent is required to overcome this problem. $\text{CH}_3\text{CO}_2\text{Li}$ is oxidised on charge, confirmed by the FTIR spectra shown in Fig. 3⁴³. Li_2CO_3 cannot be effectively oxidised at 3.6 V thus it accumulates during cycling^{45,46}. Its persistence on extended cycling is seen in FTIR spectra, Fig. 3 and SEM images for cycle 10 and 50, Fig. 2(e) and (g), where Li_2CO_3 is apparent as fine particles at the end of charge. The slight

increase in voltage seen for all cycles towards the end of charge is discussed in the following section. The increase in voltage seen on cycle 50 across the whole of the charge is in accord with the accumulating Li_2CO_3 , Fig. 3. Therefore, it is the building up of Li_2CO_3 on cycling and its accumulation on the electrode surfaces after 50 cycles that resulted in stopping cycling at cycle 50. As we discuss in the next section, the use of mediators suppresses carbon decomposition to Li_2CO_3 so the majority of the Li_2CO_3 that accumulated and limited cycling is due to electrolyte solution decomposition.

The consumption and evolution of O_2 was investigated operando by monitoring the gas pressure change in the head space above the cell during discharge and charge^{46,47}, the results are shown in Supplementary Fig. S5. The experiment is described in the Methods Section. The pressure drop on discharge, due to O_2 consumption, corresponds to $2.03 \text{ e}^-/\text{O}_2$, consistent with formation of Li_2O_2 . DEMS was also carried out during discharge and charge and the ratio of O_2 evolved on charge to O_2 consumed on discharge is 86 %, Supplementary Fig. S6, consistent with the yield of Li_2O_2 , which was 88 % on the 1st discharge. The latter was calculated by titrating the amount of Li_2O_2 formed using UV-vis spectrometry with addition of TiOSO_4 solution⁴⁸. Given the $2.03 \text{ e}^-/\text{O}_2$ ratio on discharge,

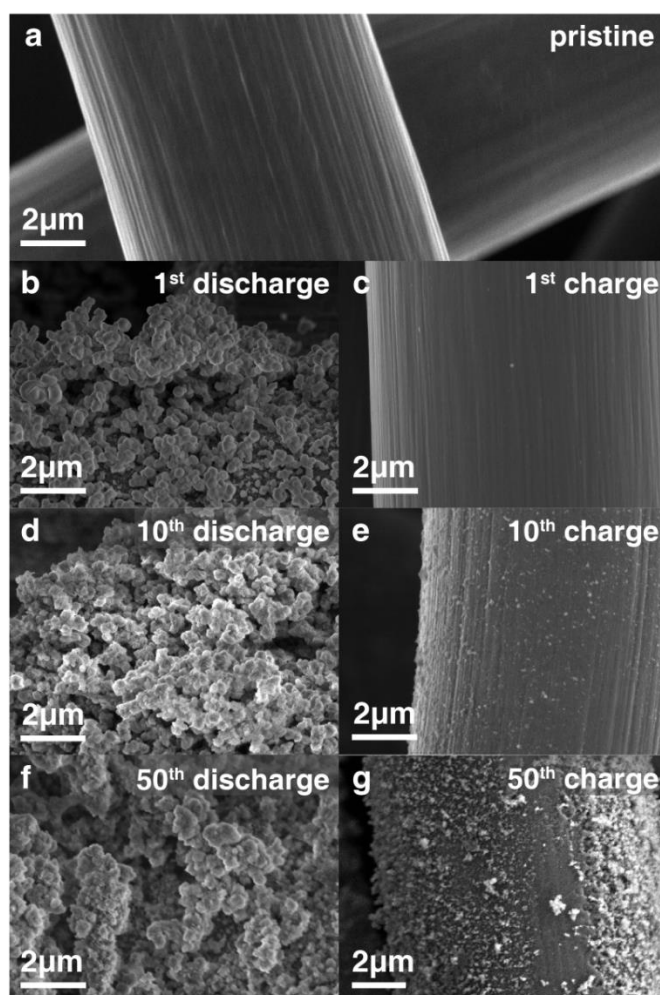


Figure 2 | SEM images of the GDL based porous carbon electrodes after cycling in a dual-mediator $\text{Li}-\text{O}_2$ cell. (a) Pristine cathode. After cycling in 25 mM DBBQ-25 mM TEMPO-0.3 M LiClO_4 in DME under 1 atm O_2 : cathodes at end of (b) 1st discharge, (c) 1st charge, (d) 10th discharge, (e) 10th charge, (f) 50th discharge and (g) 50th charge.

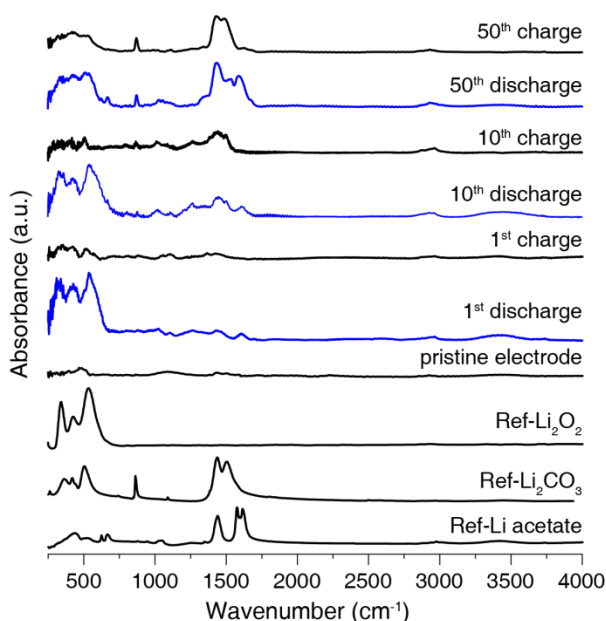


Figure 3 | FTIR spectra of GDL based porous carbon electrodes after cycling in a dual-mediator Li-O₂ cell. Discharged and charged in 25 mM DBBQ-25 mM TEMPO-0.3 M LiClO₄ in DME under 1 atm O₂.

this suggests the CH₃CO₂Li and Li₂CO₃ by-products, identified by FTIR, form by reaction with Li₂O₂ rather than any intermediate in the O₂ reduction reaction. The curve on charge tracks that on discharge over most of its length, indicating that the reduction reaction is reversed on charge, Supplementary Fig. S5(b). At the later stage of charge, all Li₂O₂ is consumed, TEMPO⁺ has nothing to oxidise and hence the pressure ceases to increase. This is consistent with the chemical yield of 88 % and indicates the point at which all the Li₂O₂ has been oxidised and the last ~10% of charge capacity is due to TEMPO oxidation alone, resulting in an increasing ratio of [TEMPO⁺]/[TEMPO] and hence increasing voltage⁴⁰. This is the origin of the slight increase in voltage towards the end of charge on each cycle. The complete oxidation of Li₂O₂ was confirmed by titration at the end of charge, in agreement with its absence from the FTIR data, Fig. 3. Yields after the 10th and 50th discharge of 84 % and 75 % indicate that the side reactions increase with cycling, likely due to increasing decomposition products in the electrolyte solution reacting with the Li₂O₂.

Carbon cathode and electrolyte solution stability

Carbon cathodes have been shown to be unsuitable for Li-O₂ cells, decomposing to form Li₂CO₃, with deleterious consequences for the performance, such as a large charging voltage, low rate and severe capacity fading, as illustrated in Fig. 1(b)^{3,12,38}. However, this is not the case for the cells with dual mediators, comparing Fig. 1 (a) and (b). To investigate the effect of dual mediators on carbon stability, Li-O₂ cells were constructed using ¹³C-carbon to form a porous positive electrode, and then subjected to cycling with and without dual mediators under the same conditions, as described in the Supplementary Information. The ¹³C-carbon permits identification of decomposition products arising from the carbon electrode. The electrodes were extracted from the cell and treated with acid to decompose any Li₂¹³CO₃ to ¹³CO₂, which was detected by mass spectrometry. The details are given in the Supplementary Information and the results are shown in Fig. 4. They demonstrate that with mediators, the carbon decomposition is much suppressed. Less than 0.008 % of the carbon electrode decomposed each cycle, compared with 0.12 % for the same electrode in the absence of mediators; the latter result is very similar to previous studies³. Previous studies in fuel cells have shown that

carbon can be decomposed above 4 V vs Li^+/Li . However, studies in $\text{Li}-\text{O}_2$ cells have shown that carbon decomposition begins at 3.5 V and becomes significant on charging at c.a. 3.6 V, when the carbon is also in contact with Li_2O_2 ³⁸. The much lower carbon decomposition and the much reduced effect on the performance of the $\text{Li}-\text{O}_2$ cell in the presence of dual mediators, as seen in Fig. 1, may be attributed to Li_2O_2 oxidation not taking place at the carbon electrode surface and the charging potential, and hence oxidation, occurring all at ~ 3.6 V (i.e. no rise in charging potential and therefore no increase, in decomposition)^{3,38}. Also, the electron transfer reactions of the molecular mediators at the electrode are less affected by the presence of Li_2CO_3 . This last factor is evident from the fact that the cell with dual mediators continues to cycle with amounts of Li_2CO_3 that have negative effects on non-mediated $\text{Li}-\text{O}_2$ cells, compare cycle 19 with, and cycle 3 without mediators in Fig. 4.

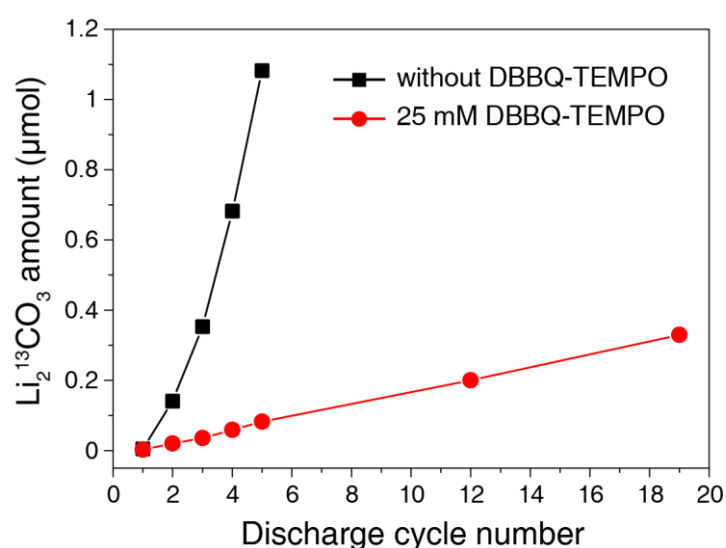


Figure 4 | Amounts of $\text{Li}_2^{13}\text{CO}_3$ in the ^{13}C -carbon cathodes at the end of discharge on each cycle. Determined by subjecting the electrodes to acid to liberate $^{13}\text{CO}_2$ from the $\text{Li}_2^{13}\text{CO}_3$. The electrolyte solution was 0.3 M LiClO_4 in DME without (black) and with (red) 25 mM DBBQ- 25 mM TEMPO mediators under 1 atm O_2 .

Considering the implications for the GDL electrodes used here, McCloskey *et al* have demonstrated that carbon decomposition is expected to be insensitive to the type of carbon, also both GDL and ^{13}C carbons were heated in 5 % H_2 in Ar prior to use to promote similar surface chemistries³. As the carbon corrosion occurs on the surface and if it scales with surface area then the GDL based porous carbon electrode would exhibit a 0.1 % decomposition after 1500 cycles, assuming a constant rate of decomposition, as its surface area is 150 fold lower than the ^{13}C -carbon electrode for the same geometrical area of cathode. Carbon is the most attractive choice for the cathode in $\text{Li}-\text{O}_2$ cells, due to its low mass, low cost and high conductivity. Alternatives such as TiO_x are less attractive. If carbon can truly be used as the cathode in $\text{Li}-\text{O}_2$ cells, it would remove one of the major barriers to progress of $\text{Li}-\text{O}_2$ batteries.

Given that the amount of carbon decomposition is very small, the major contribution to the side reactions, and hence amount of Li_2CO_3 seen in the FTIR in Fig. 3, must come from reactions between the reduced oxygen species and the electrolyte solution. This is confirmed by analysing the amounts of $\text{Li}_2^{12}\text{CO}_3$ formed, as this arises from electrolyte decomposition whereas $\text{Li}_2^{13}\text{CO}_3$ was from carbon decomposition. As shown in Supplementary Fig. S7, the $\text{Li}_2^{12}\text{CO}_3$ is significantly greater than the

$\text{Li}_2^{13}\text{CO}_3$. The growth of both appears approximately linear with cycling. It should be noted that as a result of suppressing the carbon decomposition, the main factor now limiting reversibility is the electrolyte solution stability, emphasising the importance of addressing this problem in future work. Note that the quantity of $\text{Li}_2^{12}\text{CO}_3$ from the electrolyte solution decomposition with the mediators is less than 1/3 of the cell without, consistent with our previous studies of discharge using DBBQ³². On the other hand, the long term stability of the mediators themselves must also be addressed, posing a new challenge.

The Li-O_2 cell described here decouples the process of energy storage (Li_2O_2 formation/decomposition from solution) from the surface electrochemistry. This is represented schematically in Fig. 5. The mechanisms of DBBQ mediated O_2 reduction and Li_2O_2 oxidation by TEMPO have been described^{32,39}. On discharge, DBBQ is first reduced to LiDBBQ at the surface of the positive electrode. LiDBBQ then reacts with O_2 in solution to form the intermediate LiDBBQO₂, which can either disproportionate or undergo a second reduction to form Li_2O_2 and regenerate DBBQ, Fig. 5. On charging, TEMPO is first oxidised at the positive electrode surface to TEMPO⁺, which in turn oxidises Li_2O_2 particles in solution and in doing so regenerates TEMPO.

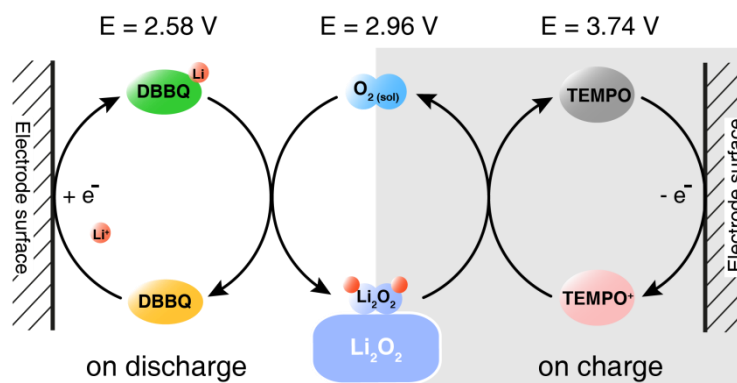


Figure 5 | Schematics of positive electrode reactions on discharge and charge in the presence of DBBQ and TEMPO.

Cell with protected lithium anode

Although LiFePO_4 has been used here as the negative electrode, as in many previous studies^{19,32,39,40}, in practical cells a lithium anode is required for a viable cell potential, and such an electrode will have to be protected by a Li^+ conducting solid electrolyte. Fig. 6 shows cycling results for such a cell, employing a Lithium super ionic conductor disc (LiSICON, Ohara) to separate the GDL cathode and Li anode. 25 mM DBBQ-25 mM TEMPO-0.3 M LiClO_4 in DME serves as catholyte and 0.3 M LiClO_4 dissolved in tetraglyme serves as anolyte. This design protects the Li metal anode from the catholyte solution containing the redox mediators. After correction for iR loss across the LiSICON, the results are very similar to those obtained using LiFePO_4 . The yield of Li_2O_2 in the protected lithium anode cell was 87 %, close to the figure of 88 % from the cell with a LiFePO_4 anode, confirming the similar behaviour of the two cells.

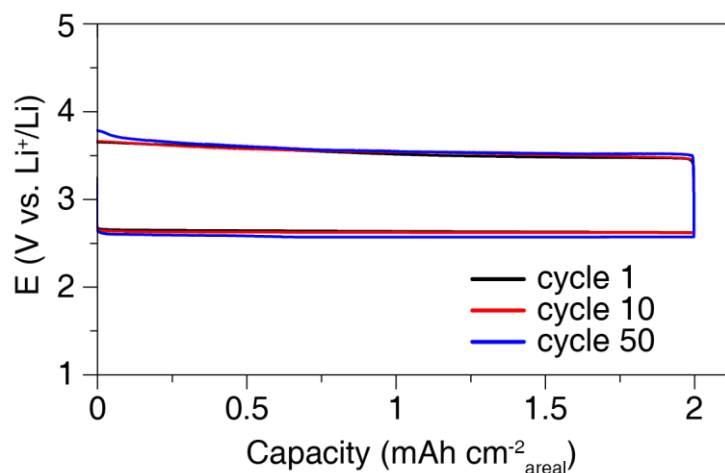


Figure 6 | Cycling profile of a dual-mediator Li-O₂ cell with a Li metal anode protected with Ohara glass: 25 mM DBBQ-25 mM TEMPO-0.3 M LiClO₄ in DME used as catholyte and 0.3 M LiClO₄ in tetraglyme used as anolyte. The cell was cycled under 1 atm O₂ at an areal current density of 1 mA cm⁻². The data have been corrected for the iR drop associated with the resistance of the Ohara glass membrane, recognising that higher conducting membranes would be required for practical cells.

Conclusions

A Li-O₂ cell using dual mediators has been cycled with capacities of 2 mAh cm⁻²_{areal} at a rate of 1 mA cm⁻²_{areal} and discharge/charge potentials of 2.7 and 3.6 V, respectively. By decoupling the electrochemical reactions at the cathode surface from the energy storage (growth/decomposition of Li₂O₂ from solution) using dual mediators, Li-O₂ cell performance is no longer limited by the insulating and insoluble nature of Li₂O₂, but rather by O₂ mass transport and associated pore clogging at the electrode/gas interface. The results imply that combining dual mediators with a true gas diffusion electrode could deliver an encouraging capacity of 40 mAh cm⁻²_{areal} and meet the goal for a practical cell with 500-600 Wh kg⁻¹. Future work should focus, in part, on the design of gas diffusion electrodes that deliver facile mass transport, as for fuel cell electrodes. The carbon cathode is significantly more stable in the presence of dual mediators, exhibiting less than 0.008 % decomposition per cycle compared with 0.12 % without mediators, and it does not have a deleterious effect on the cell performance, unlike in the absence of mediators. This may be attributed to Li₂O₂ growth/decomposition no longer taking place at the carbon surface, charging occurring at 3.6 V rather than 4 V, and the electron transfer reactions associated with the mediators at the carbon surface being less sensitive to the presence of Li₂CO₃. Carbon is by far the most attractive material for Li-O₂ cell cathodes due to its low cost, high conductivity and low mass, but has been dismissed due to instability. Coupled with dual mediators it may be possible to use carbon cathodes, and if so remove one of the major barriers to progress of Li-O₂. The results also show that now, the major source of side reactions and hence limitation of cycling and reversibility arises from reactions with the electrolyte solution. This emphasises that future research should focus on the search for more stable solvents and mediators, with the latter including investigation of oxidation mediators able to operate at lower potentials to further reduce the charging voltage. Using mediators on both discharge and charge can reduce one of the important sources of side reactions, i.e. carbon instability, and can mitigate another barrier to cell performance, namely the limitations on rate and capacity imposed if Li₂O₂ is formed and decomposed as a film on the cathode surface. If stable electrolyte solutions and appropriate mediators can be found, then our results suggest a Li-O₂ cell with mediation at the cathode could sustain cycling.

Acknowledgements

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Author contributions

‡These authors contributed equally to this work. X.G. and Y.C. designed experiments and analysed the data. X.G. performed electrochemical performance tests and characterisations. Y.C. performed the ¹³C-carbon experiments and analysed the data. P.G.B, X.G., Y.C., L.J., Z.J. interpreted the data. P.G.B. wrote the paper.

Competing financial interests

The authors declare no competing financial interests.