Promoting solution phase discharge in Li-O2 batteries containing weakly solvating electrolyte solutions

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Abstract

On discharge, the lithium-O2 battery can form a $\text{Li}_2\text{O}_2$ film on the cathode surface, leading to low capacities, low rates and early cell death, or it can form $\text{Li}_2\text{O}_2$ particles in solution, leading to high capacities at relatively high rates and avoiding early cell death. Achieving discharge in solution is important and may be encouraged by the use of high donor or acceptor number solvents or salts that dissolve the $\text{LiO}_2$ intermediate involved in the formation of $\text{Li}_2\text{O}_2$. However, the characteristics that make high donor or acceptor number solvents good (e.g. high polarity) result in them being unstable towards $\text{LiO}_2$ or $\text{Li}_2\text{O}_2$. Here we demonstrate that introduction of the additive 2,5-Di-tert-butyl-1,4-benzoquinone (DBBQ) promotes solution phase formation of $\text{Li}_2\text{O}_2$ in low polarity and weakly solvating electrolyte solutions. Importantly, it does so while simultaneously suppressing direct reduction to $\text{Li}_2\text{O}_2$ on the cathode surface, which would otherwise lead to $\text{Li}_2\text{O}_2$ film growth and premature cell death. It also halves the overpotential during discharge, increases the capacity 80-100 fold and enables rates > 1 mA cm$^{-2}$ areal for cathodes with capacities of > 4 mAh cm$^{-2}$ areal. The DBBQ additive operates by a new mechanism that avoids the reactive $\text{LiO}_2$ intermediate in solution.
The high theoretical specific energy of the rechargeable Li-O₂ battery has generated intense interest in the possibility of a practical device that could deliver energy storage significantly in excess of today’s lithium-ion batteries⁰⁻⁹. However, major challenges hinder the development of such a technology⁰⁻⁶,¹⁰⁻¹⁴. Typically a Li-O₂ battery is composed of a lithium metal anode separated by an aprotic electrolyte solution from a porous O₂ cathode. The reaction at the cathode involves, on discharge, the reduction of O₂ to form Li₂O₂, with oxidation of the latter on charge. Growth of Li₂O₂ on the cathode surface leads to low capacities, poor rates and early cell death¹⁵⁻¹⁷. In contrast, if Li₂O₂ can be induced to grow in the electrolyte solution then high discharge capacities at relatively high rates and avoiding early cell death is possible¹⁵. It is clearly important to operate a Li-O₂ battery in which Li₂O₂ grows in solution.

A number of groups have elucidated the mechanism of O₂ reduction to Li₂O₂ on discharge¹⁵,¹⁶,¹⁸⁻²¹. The reduction proceeds through the following general steps:

1. O₂ + Li⁺ + e⁻ → Li₂O₂
2. 2LiO₂ → Li₂O₂ + O₂
3. LiO₂ + Li⁺ + e⁻ → Li₂O₂

Whether Li₂O₂ grows in solution or as a film on the electrode surface depends on the solubility of the LiO₂ intermediate; if LiO₂ dissolves in the electrolyte solution then Li₂O₂ grows in solution. Solubility of LiO₂ depends on the strength of the cation and anion solvation, i.e. on the solvent and salt donor and acceptor numbers¹⁵,²²⁻²⁴. However, the very properties that make a good solvent for LiO₂, (high polarity) often makes the solvent more susceptible to nucleophilic attack or proton abstraction by the reactive O₂⁻ radical, leading to undesirable side-reactions⁵⁻²⁶. The challenge is to form Li₂O₂ in solution on discharge in low donor number (weakly solvating) solvents.

Soluble catalysts or salts with high donor numbers (DN) can in principle promote solution phase growth of Li₂O₂ in low donor number solvents (e.g. ethers)²²⁻²⁷,³⁰. High DN salts have been shown to increase the capacity 4 fold and reduce the discharge overpotential by ~30-50 mV over low DN salts²². Viologens²⁷⁻²⁸, phthalocyanines²⁹ and quinones³⁰ have been investigated as possible soluble reduction catalysts. While the studies of such catalysts are important, in most cases there is little or no direct evidence demonstrating that they promote formation of Li₂O₂ in solution and not on the electrode surface because they rely on electrochemical measurements alone. Yet past work on Li-O₂ batteries has shown how essential it is to provide more than electrochemical evidence in this field³¹. In some cases, soluble catalysts show an increase in discharge voltage (lower overpotential) as small as e.g. 40 mV²⁸,²⁹, which is very unlikely to be sufficient to shut-off the direct reduction of O₂ to Li₂O₂, essential to stop detrimental Li₂O₂ film formation. Also, none of the previous studies in low donor number solvents exhibited a significant increase in capacity on discharge at a relatively high rate, which is important for a successful Li-O₂ battery.

Here we demonstrate that addition of DBBQ (2,5-Di-tert-butyl-1,4-benzoquinone) to a weakly solvating (low DN) electrolyte solution, LiTFSI in ether²², promotes O₂ reduction to Li₂O₂ in solution while halving the discharge overpotential (increasing the discharge potential), suppressing the growth of a Li₂O₂ film on the electrode surface thus postponing cell death, increasing the discharge capacity 80-100 fold and permitting discharge at relatively high rates > 1 mA cm⁻² areal for an electrode capacity of > 4 mAh cm⁻² areal. It operates by a new mechanism that does not involve the reactive LiO₂ as an intermediate; the new mechanism also decouples the link between the nature of the
electrolyte solution (solvating power) and the nature of the product (particles or surface film). The search for truly stable electrolyte solutions for Li-O₂ batteries will focus on very low polarity and hence weakly solvating solvents. The significance of the present work is that if such stable solvents can be identified then DBBQ provides a route to solution growth of Li₂O₂ and hence potentially high rates, high capacities and sustained cycling, avoiding early cell death.

**CV studies with DBBQ**

The potential at which O₂ is reduced to Li₂O₂ (the discharge plateau in a Li-O₂ cell) is lower than the thermodynamic potential for O₂/Li₂O₂, 2.96 V. A CV corresponding to this process is shown in Fig. 1. To promote O₂ reduction to Li₂O₂ in solution in low DN solvents while suppressing the direct reduction of O₂ to form a Li₂O₂ film, which would otherwise passivate the electrode¹⁵,¹⁶,²¹, it is necessary to carry out the reduction of O₂ to Li₂O₂ in solution at a higher potential than the surface reaction, which also has the advantage of increasing the cell discharge potential closer to its thermodynamic potential of 2.96 V (reducing the overpotential). To achieve this, molecules with a redox potential somewhat higher than the potential at which O₂ is reduced (discharge plateau in a Li-O₂ cell) are required. Quinones were selected as they are known to exhibit potentials in the relevant range³⁰,³². Several quinones were investigated but most were found not to enhance O₂ reduction, see Supplementary Fig. S1. Electrolyte preparation and cell assembly are described in the Supplementary Information. DBBQ, in contrast, showed promising electrochemistry, Fig. 1. The cyclic voltammograms for DBBQ obtained in 1 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) and dimethoxyethane (DME) at a gold electrode under Ar exhibit quasi-reversible behavior, Fig. 1 and Supplementary Fig. S2. In the presence of O₂, the reduction peak is enhanced significantly. Such a CV is similar to that of a catalyzed reduction³³, where a redox active species, in this case DBBQ, is reduced and then takes part in a chemical reaction, here with O₂ to form Li₂O₂, resulting in the rapid regeneration of more DBBQ, giving rise to the increased reduction current. The reduction potential is significantly higher than for the direct reduction of O₂, thus effectively suppressing the direct reduction of O₂ to Li₂O₂ films on the electrode surface. The mechanism of O₂ reduction by DBBQ is discussed further later; demonstration of the efficiency of DBBQ in promoting Li₂O₂ formation in solution and not on the electrode surface, as well as increasing the discharge potential of Li-O₂ cells is presented below.

![Figure 1](image_url)  
**Figure 1 | CVs demonstrating the significant effect DBBQ has on O₂ reduction in ethers.** CVs for DBBQ in 1 M LiTFSI in (a) TEGDME and (b) DME. CVs under Ar (blue) and O₂ (red) and for direct O₂ reduction without DBBQ (black). DBBQ concentration was 10 mM and CVs were carried out at planar Au electrodes, scan rate 100 mV s⁻¹.
Enhancing the discharge of Li-O₂ cells with DBBQ

Li-O₂ cells were constructed as described in the Supplementary Information (Methods Section). The cathode was a binder-free carbon-fiber gas diffusion layer (GDL, Freudenberg), similar to cathodes used widely for aprotic O₂ cells. Carbon electrodes are relatively stable on discharge, which is our focus here. The anode consisted of LiₓFePO₄, as used in previous Li-O₂ studies instead of Li metal in order to avoid any oxidation of the anode by O₂. The LiₓFePO₄ potential vs. Li⁺/Li, 3.45 V, was used to express all potentials in this work on the Li scale. The electrolyte solution was in all cases 1 M LiTFSI dissolved in the low donor and acceptor number ethers, TEGDME or DME.

Cells containing TEGDME and DME saturated with O₂ (under 1 atm. of O₂), were each discharged at several different areal current densities with and without DBBQ, Fig. 2. In the absence of DBBQ, the cells died rapidly, exhibiting very small capacities and poor rate capability, in accord with previous observations. The cells with DBBQ discharged under the same conditions exhibited a dramatic improvement, delivering up to ~80 to 100 times higher discharge capacities before end of life. In TEGDME with DBBQ, a capacity of 10.6 mAh cm⁻² areal (equivalent to 9.1 mg of Li₂O₂) was obtained at a current density of 0.2 mA cm⁻² areal, while in DME with DBBQ, 7.3 mAh cm⁻² areal (equivalent to 6.3 mg of Li₂O₂) was obtained at 0.5 mA cm⁻² areal and 4 mAh cm⁻² areal (equivalent to 3.4 mg of Li₂O₂) at 1 mA cm⁻² areal. Moreover, areal current densities of 0.5 mA cm⁻² (in TEGDME) and 2 mA cm⁻² (in DME) were achieved, while halving the discharge overpotential, compared with the performance in the absence of DBBQ. To estimate the contribution of DBBQ reduction itself to the capacity, the cells were discharged under Ar, for DME and TEGDME, and at the same current densities as in Fig. 2. The discharge curves are given in Supplementary Fig. S3. A negligible capacity was observed. These values are all within the limits of the theoretical capacity for DBBQ reduction of 12.5 mAh m⁻² BET.

It has been shown that the limit of Li₂O₂ film growth is ~6 nm, which equates to a maximum capacity of ~15 mAh m⁻² BET (0.4 mAh cm⁻² areal). As is evident in Fig. 2, the cells without DBBQ exhibit end of life below this limit, indicating that Li₂O₂ formation is predominantly by the surface route. Whereas cells containing DBBQ are able to exceed the limit of film growth by an order of magnitude, signaling predominantly solution growth of Li₂O₂.
Figure 2 | Significant effect of DBBQ on discharge in ethers. Load curves of oxygen reduction at gas diffusion electrode discharged in 1 M LiTFSI in (a) TEGDME and (b) DME with 10 mM DBBQ (solid lines) and without DBBQ (dash lines) under O₂ at various areal current densities from 0.1 mA cm⁻² to 2 mA cm⁻². (c,d) enlarged section of load curves recorded without DBBQ in a,b. 200 μl of electrolyte was used. The roughness factor of the cathode is 270. The amounts of Li₂O₂ formed on discharge were 10.0, 9.1 and 5.2 mg cm⁻² areal in TEGDME and 9.1, 6.3, 3.4 and 2.0 mg cm⁻² areal in DME.

To confirm that Li₂O₂ grows primarily in solution, away from the electrode surface, in the presence of DBBQ, despite the use of low donor/acceptor solvents, the discharged cathodes with and without DBBQ were extracted and examined by SEM. The results are shown in Fig. 3. In both TEGDME and DME, in the absence of DBBQ, the surfaces of the carbon fibers that constitute the GDL were covered with a film and there was no evidence of Li₂O₂ particles. In contrast, identical cells discharged under the same conditions, except for the presence of DBBQ, show substantial growth of particles in the pores of the electrodes and with the toroidal morphologies expected for Li₂O₂, Fig. 3. Equally important is that DBBQ suppresses film growth on the electrode surface. This is shown in Fig. 3 (c,g) where there is little evidence of film growth when DBBQ was present until close to cell death. There will always be some direct reduction to form Li₂O₂ on the surface, even at the higher potential where DBBQ is reduced, as the direct reduction to form a Li₂O₂ film is suppressed but not eliminated completely. It has been proposed recently that the presence of H₂O can itself promote Li₂O₂ toroid formation in Li-O₂ batteries. Care was taken to rigorously dry the solvents, electrodes and all cell components used here. The H₂O content at the beginning and end of discharge did not exceed 30 ppm, considerably smaller than the quantities required to promote toroid formation; at least 200–500 ppm H₂O is needed. Overall, the SEM images demonstrate that DBBQ has successfully displaced the O₂ reduction away from the electrode surface, promoting growth of large Li₂O₂ particles in the adjacent solution within the pores of the electrode.
Figure 3 | SEM images showing the Li$_2$O$_2$ morphologies on discharge in 1 M LiTFSI in ethers with and without DBBQ. (a) the pristine GDL; (b-e) discharge in TEGDME and (f-i) in DME. (b,f) full discharge without DBBQ; (c,g) half discharge with 10 mM DBBQ and (d,e,h,i) full discharge with DBBQ.

To demonstrate the particles observed in SEM are indeed Li$_2$O$_2$, powder X-ray diffraction (PXRD), infrared spectrometry (IR) and Raman spectroscopy were carried out on the porous electrodes extracted from the cells. The results are presented in Fig. 4. The PXRD pattern collected on the GDLs discharged in ethers exhibits only peaks associated with Li$_2$O$_2$. The results are confirmed by the IR and Raman spectra in Fig. 4, which also show Li$_2$O$_2$ as the primary product. Although ethers are one of the more stable solvents in Li-O$_2$ batteries, it is known that they are not completely stable$^{38}$. Small peaks associated with lithium acetate/formate and some Li$_2$CO$_3$ are evident as minor by-products in the IR, as identified previously for discharge in ethers$^{39}$. There is little evidence of LiOH. To investigate the presence of any soluble by-products, NMR was carried out on the electrolyte solutions. The details are described in the Supplementary Information. In addition to the peaks
associated with the electrolyte solutions, only a tiny peak assigned to lithium acetate was observed, Supplementary Fig. S4. *In-situ* differential electrochemical mass spectrometry (DEMS) was carried out to investigate the gas consumption on discharge. The procedure is described in the Supplementary information and the results are presented in Fig. 5. No gases were detected other than O$_2$ and in particular there was no evidence of CO$_2$, consistent with the degree of side-reactions in ethers being small. The total O$_2$ consumed and total charge passed were measured and the integral gave a ratio of electrons to oxygen consumed of 2.03 e-/O$_2$, consistent with the dominant reaction on discharge involving Li$_2$O$_2$ formation$^{38,40}$. These results are in accord with charge/mass ratios seen previously for ethers$^{38}$. Taken together, the PXRD, IR, Raman and DEMS indicate that the dominant product on discharge in the presence of DBBQ in ethers is Li$_2$O$_2$ and that it forms relatively large particles in the pores rather than on the surfaces of the porous electrode. The amount of Li$_2$O$_2$ present in the electrode was quantified by chemical analysis using TiOSO$_4$ as described in the Supplementary information. The yield of Li$_2$O$_2$ (observed mass/mass predicted from charge passed) with DBBQ was 95% and 86% in DME and TEGDME, respectively. This compares with 91% and 81% reported previously for DME and TEGDME in the absence of DBBQ$^{38}$. The slightly higher yields indicates that the relatively high surface area of the Li$_2$O$_2$ film that grows on the electrode in the absence of DBBQ leads to more decomposition of the electrolyte solution than is the case for the large particles in solution. It has also been suggested that LiO$_2$ is responsible for solvent decomposition on discharge$^{26,41,42}$ and as discussed below, our analysis points to a mechanism that avoids this reactive intermediate.
Figure 4 | Characterization of the discharge product confirming Li$_2$O$_2$ is dominant. (a) PXRD pattern, (b) IR and (c) Raman spectra of GDLs discharged in 10 mM DBBQ - 1 M LiTFSI in TEGDME and DME under O$_2$. 
Figure 5 | In-situ DEMS in DBBQ-TEGDME showing 2.03 e\textsuperscript{-} per O\textsubscript{2} consumption, consistent with formation of Li\textsubscript{2}O\textsubscript{2}. (a) discharge current (blue), O\textsubscript{2} consumption (green) and CO\textsubscript{2} evolution (red) in 10 mM DBBQ \cdot 1 M LiTFSI in TEGDME; (b) voltage profile of the DEMS cell. Cyclic voltammetry was applied. e\textsuperscript{-}/O\textsubscript{2} ratio was obtained from the integral of charge passed and total O\textsubscript{2} consumption.

Attempts to charge the cells after discharge proved fruitless, see Supplementary Fig. S5. This is to be expected since the Li\textsubscript{2}O\textsubscript{2} is not well connected to the electrode surface and therefore direct electrochemical oxidation will be difficult. Therefore, especially in the presence of a reduction mediated discharge, it will be necessary to employ an oxidation mediator to charge the cell, as described previously\textsuperscript{36,43-45}.

The mechanism of O\textsubscript{2} reduction in the presence of DBBQ

As mentioned above, DBBQ does not operate as an electrocatalyst like, for example, the phthalocyanines described previously\textsuperscript{29,46} for which O\textsubscript{2} is bound to the electrocatalyst before, during and after reduction. Neither does it operate as a redox shuttle, transferring electrons from the electrode surface to reduce O\textsubscript{2} in solution to LiO\textsubscript{2} and further to Li\textsubscript{2}O\textsubscript{2} by an outer sphere reaction. Instead, it operates by a different mechanism that changes the pathway of O\textsubscript{2} reduction to Li\textsubscript{2}O\textsubscript{2} avoiding the reactive LiO\textsubscript{2} as an intermediate.

The reduction of quinones, such as DBBQ, in Li\textsuperscript{+} electrolyte solutions under Ar is known to form Li-quinone complexes, in this case LiDBBQ, Fig. 1\textsuperscript{47-49}. In the presence of O\textsubscript{2} the reduction potential for DBBQ/LiDBBQ does not change, Fig. 1, indicating that the same reduction reaction (DBBQ to LiDBBQ) occurs, i.e. there is no binding of O\textsubscript{2} to DBBQ prior to the initial electron transfer, unlike the phthalocyanines\textsuperscript{29}, the first step is as shown in equation (4). However, the reduction current is enhanced significantly, Fig. 1. The observed CV is similar to that of an EC\textsubscript{cat} reaction, electrochemical
reduction followed by a chemical step, in which the reduced form of the redox couple takes part in a chemical reaction that re-generates the oxidized form of the couple to feed the reduction. Here DBBQ is re-generated from LiDBBQ by the latter reducing O₂ in a chemical step, which goes on to form Li₂O₂.

In the absence of DBBQ, reduction of O₂ to Li₂O₂ proceeds via the LiO₂ intermediate, and it is the need to reach the potential for formation of LiO₂ that pins the O₂ reduction at a potential (discharge plateau in a Li-O₂ cell) significantly negative of the standard potential for Li₂O₂ formation, 2.96 V, Fig. 1. Where the energetics of an intermediate dictates the potential required to carry out an electrochemical reaction this is referred to as a “thermodynamic overpotential”. In the presence of DBBQ O₂ reduction effectively takes place at the potential for DBBQ reduction, Fig. 1, i.e. at a significantly higher potential than would be the case if O₂ reduction was occurring via the LiO₂ intermediate in solution. This indicates that O₂ reduction does not follow the usual path via the LiO₂ intermediate but involves formation of a different intermediate complex between LiDBBQ and O₂. By complexing Li⁺ and O₂ with DBBQ the reaction path and hence free energy of the intermediate (now a complex of the form LiDBBQO₂) is lowered (Fig. 6) and the potential correspondingly raised, as seen in the higher voltage for the discharge plateau in galvanostatic discharge of Li-O₂ cells, Fig. 2.

The sequence of proposed reaction steps at the cathode on discharging a Li-O₂ cell containing DBBQ is summarized in equations (4) to (6). Equation (4) is the initial electrochemical reduction. Equations (6a) and (6b) are examples of possible steps by which the intermediate formed in (5) could disproportionate or react with another LiDBBQ, to form Li₂O₂ that grows from solution, as observed in for example Fig. 3. Confirmation that LiDBBQ and O₂ react together to form Li₂O₂ was obtained by a direct chemical experiment in which O₂ was bubbled through a solution containing LiDBBQ and the quantity of Li₂O₂ measured by TiOSO₄ titration, see supplementary information for details.

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\begin{align*}
\text{DBBQ}_{(\text{sol})} + \text{Li}^+_{(\text{sol})} + e^- & \rightarrow \text{LiDBBQ}_{(\text{sol})} \quad (4) \\
\text{LiDBBQ}_{(\text{sol})} + \text{O}_2_{(\text{sol})} & \rightleftharpoons \text{LiDBBQO}_2_{(\text{sol})} \quad (5) \\
2 \text{LiDBBQO}_2_{(\text{sol})} & \rightarrow \text{Li}_2\text{O}_2_{(s)} + \text{O}_2_{(\text{sol})} + 2 \text{DBBQ}_{(\text{sol})} \quad (6a) \\
\text{LiDBBQ}_{(\text{sol})} + \text{LiDBBQO}_2_{(\text{sol})} & \rightarrow \text{Li}_2\text{O}_2_{(s)} + 2 \text{DBBQ}_{(\text{sol})} \quad (6b)
\end{align*}
\]
Figure 6 | Schematics (left) of reactions on discharge and (right) the effect of DBBQ on the potential determining step. DBBQ is reduced at the electrode surface forming LiDBBQ, and then LiDBBQ reacts with O₂, producing Li₂O₂ and itself being regenerated to DBBQ. Schematic of free energy plot is at E° for O₂/ Li₂O₂.

These reactions can be summarized by the schematic shown in Fig. 6, and the consequences of this scheme are relatively simple electron transfer and dominate solution phase product formation that translate into high rates and capacities during cell discharge.

As noted above, DBBQ does not act as a conventional catalyst, it does not bind O₂ and facilitate LiO₂ formation by stabilizing the superoxide intermediate. Instead DBBQ is reduced to LiDBBQ that binds O₂ to form LiDBBQ, (equation 5). The characteristics that make DBBQ suitable for this function are, a reduction potential positive of the potential for formation of LiO₂ thus avoiding direct formation of LiO₂, a reduction potential negative of the overall reduction potential to Li₂O₂ such that a driving force remains to push the reaction towards peroxide formation and the ability to bind O₂ when in the reduced form (LiDBBQ).

Outlook

O₂ reduction to Li₂O₂ by the DBBQ mediated route brings a number of benefits. The electrochemistry at the electrode surface is now DBBQ reduction rather than direct formation of Li₂O₂, in an electrolyte solution that does not dissolve LiO₂ (weakly solvating electrolyte solution). As a result, Li₂O₂ formation is moved into solution without the need for high donor/acceptor number solvents or salts. DBBQ shuts down the direct formation of a Li₂O₂ film on the cathode, thus postponing cell death, increasing capacity 80-100 fold and facilitates discharge rates of > 1 mA cm⁻² areal for cathodes with capacities of > 4 mAh cm⁻² areal. The discharge potential is also increased (overpotential is halved). O₂ reduction to Li₂O₂ in the presence of DBBBQ follows a new route that avoids the reactive LiO₂ in solution. The search for truly stable electrolyte solutions for Li-O₂ batteries will focus on very low polarity and hence weakly solvating solvents. The significance of the present work is that if such stable solvents can be identified then DBBQ provides a route to solution growth of Li₂O₂ and hence potentially high rates, high capacities and sustained cycling, avoiding early cell death. These results demonstrate the importance of moving to a mediated reaction on reduction and imply that the future of the lithium-air battery involves the mediated formation and decomposition of lithium peroxide, where the latter fulfills the role of storage medium only.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

‡These authors contributed equally to this work. X.G. and Y.C. designed experiments and analyzed the data. X.G. performed electrochemical and characterization of discharge products. Y.C. performed the UV-vis spectroscopy experiments and analyzed the data. P.G.B, X.G., Y.C., L.J. interpreted the data. P.G.B. wrote the paper.

Competing financial interests

The authors declare no competing financial interests.

Methods

Materials and methods

TEGDME was distilled under vacuum and DME was distilled under Ar. All solvents were further dried for several days over freshly activated molecular sieves (type 4Å, Aldrich) before use. The final water content was < 10 ppm (determined by Karl Fischer titration). Lithium bis(trifluoromethane)sulfonimide (LiTFSI, Aldrich) was dried at 70 °C under vacuum over several days. 3,5-di-tert-butyl-o-benzoquinone, 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) and thymoquinone were obtained from Aldrich. The prepared electrolyte solutions contain < 10 ppm water content (determined by Karl Fischer titration). High purity N5.5 O2 (BOC) was used in all measurements. O2 gas flow was further dried by an in-line moisture trap filled with activated 3 Å molecular sieves. All materials were stored in an Ar-filled glove box.

Cyclic voltammetry (CV) was performed using a VMP3 electrochemical workstation (Biologic) and a multi-necked, air-tight glass cell within a glove box. The measurements were carried out at room temperature and IR correction was used. 2 mm diameter polycrystalline Au disks (BAS Inc.) were employed as the working electrodes. A platinum wire served as the counter electrode and a partially oxidized LiFePO4 composite electrode behind a Vycor frit served as the reference electrode, as described previously15.
Swagelok Li-O₂ cells were constructed as described previously. Binder-free gas diffusion layers (GDL, H2315, Quintech) served as the O₂ electrode. The porosity of the GDLs is ~80%, roughness factor (total surface area/ areal area) is 90 and the Brunauer-Emmett-Teller surface area is below 1 m² g⁻¹. Three pieces of GDLs (4 mm x 4 mm) were stacked to form the cathode giving a final roughness factor of 270 (3 x 90), a glass fibre filter (Waterman) was used as the separator and a partially oxidized LiFePO₄ electrode was used as the anode. The two-phase LiFePO₄ has a fixed potential of 3.45 V vs. Li⁺/Li. 200 µl of electrolyte solution was used, consisting of either TEGDME or DME containing 1 M LiTFSI with DBBQ as indicated in the main article. All cell components were dried at 90 °C under vacuum prior to use. Assembled cells were placed in glass tubes, which were filled with dried O₂ inside the glove box. Cells were discharged inside an Ar-filled glove box.

**Characterisations of discharged electrodes**

For post-cycling characterisation, the cells were assembled in a glovebox and the cathode and separators were rinsed with a small amount of TEGDME or DME, the resulting solutions were subjected to Karl Fischer titration to determine the water content after discharge. The electrodes were rinsed again with DME and dried prior to further characterisation. The morphology of discharge electrodes were observed by FE-SEM using a Zeiss-Merlin. PXRD was carried out with a Rigaku X-ray diffractometer in an air-sensitive holder. FTIR spectra were measured with a Thermo IR spectrometer (Nicolet 6700) in a N₂-filled glove box. Raman spectra were measured with a Renishaw Invia spectrometer (10 mW laser power at 785 nm) with an air-sensitive sample holder. For NMR analysis, 100 µl of electrolyte was extracted from the discharge electrodes and separators then diluted with 0.7 ml of CDCl₃, measurements were recorded on a Bruker spectrometer (400 MHz). A DEMS cell was constructed as described previously. A GDL served as working electrode and a partially oxidised LiFePO₄ composite electrode served as anode. The electrolyte solution was 10 mM DBBQ in 1 M LiTFSI in TEGDME. A continuous 95% O₂ / 5% Ar gas flow was purged through the cell as a carrier gas at a flow rate of 0.3 ml min⁻¹.

The quantity of Li₂O₂ formed was determined by UV-vis spectrometry (Thermo Evolution 200) using a UV-vis titration method reported previously. The unwashed discharged electrode and separators were added to a vial containing a known amount of water; Li₂O₂ reacts with water to produce H₂O₂ in solution. 1 ml of this solution was mixed with 2 ml of 2 % TiOSO₄ dissolved in 1 M H₂SO₄ solution and a yellowish complex [Ti(O₂)]²⁺ (λₘₐₓ= 405 nm) was formed. The UV-vis absorption spectrum of the solution was measured and compared to a calibration curve, which was obtained by measuring solutions with known amounts of commercial Li₂O₂ (Aldrich). The purity of commercial Li₂O₂ was determined by titration using KMnO₄ and this was taken into account when constructing the calibration curve.

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