Kinetics of lithium peroxide oxidation by redox mediators and consequences for the lithium–oxygen cell

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Lithium–oxygen cells, in which lithium peroxide forms in solution rather than on the electrode surface, can sustain relatively high cycling rates but require redox mediators to charge. The mediators are oxidised at the electrode surface and then oxidise lithium peroxide stored in the cathode. The kinetics of lithium peroxide oxidation has received almost no attention and yet is crucial for the operation of the lithium–oxygen cell. It is essential that the molecules oxidise lithium peroxide sufficiently rapidly to sustain fast charging. Here, we investigate the kinetics of lithium peroxide oxidation by several different classes of redox mediators. We show that the reaction is not a simple outer-sphere electron transfer and that the steric structure of the mediator molecule plays an important role. The fastest mediator studied could sustain a charging current of up to 1.9 A cm⁻², based on a model for a porous electrode described here.
The rechargeable aprotic lithium–O₂ (air) battery operates by the reduction of O₂ at the positive electrode forming Li₂O₂ on discharge, with oxidation of Li₂O₂ taking place on charge. Li₂O₂ is an insulating and insoluble solid. Ether-based electrolytes, such as dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (tetruglyme), have been used as the basis of electrolyte solutions in most Li–O₂ cells, because of their relative stability towards reduced oxygen species. However, they cannot dissolve LiO₂, the intermediate in the reduction of O₂ to Li₂O₂, resulting in Li₂O₂ being adsorbed on the electrode surface, and resulting in the growth of Li₂O₂ films on the electrode, leading to low rates, low capacities and early cell death. The problem is exacerbated by the formation of Li₂CO₃ between Li₂O₂ and carbon, the latter is usually employed as the material for the porous positive electrode. Use of redox mediators (RMs) on discharge, such as 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ), which are reduced at the electrode surface on discharge and then go on to reduce O₂ to Li₂O₂ in solution, can help to mitigate these problems, but result in the formation of Li₂O₂ disconnected from the electrode surface and therefore electronically isolated during charging. This introduces the need for a redox mediator to be employed on charging that can oxidise LiO₂, which are molecules capable of oxidation at the surface of the pores in the porous positive electrode on charging and then transfer of holes to the electronically isolated Li₂O₂ particles within the pores. As a result, Li₂O₂ is oxidised and O₂ released, the mediator molecule being reduced in the process and returning to the electrode surface for the cycle to be repeated.

Suitable oxidation mediators must have a redox potential above that for O₂/Li₂O₂, which is 2.96 V vs. Li⁺/Li, and can oxidise Li₂O₂, regenerating itself and contributing to a feedback loop, while concurrently, diffusion of the mediator to the tip is blocked by the surface. The balance of the two alter the current at the SEC tip, r, and the faster the kinetics of Li₂O₂ oxidation by the mediator the greater the current, see Supplementary Figure 1. As we do not know the mechanism by which the mediators oxidise the lithium peroxides, we can only obtain an apparent rate constant (k<sub>app</sub>) based on the feedback response; however, this provides a comparison between the different mediators and indicates the overall rate capability.

Fig. 1 shows the oxidation mediators studied. They are in three classes, amines, nitroxy and thiol compounds, chosen because they are classes of compounds known to exhibit reversible redox processes and include several of the compounds that have been used as oxidation mediators in Li–O₂ cells, such as tris-[4-(diethylamino)phenyl]amine (TDPA), 2,2,6,6-tetramethyl-1-piperidinolxy (TEMOPO) and 10-methylphenothiazine (MPT). k<sub>app</sub> for Li₂O₂ oxidation by the mediators are presented in Supplementary Table 1. The standard redox potential, E°, and standard heterogeneous electron transfer rate constant, k°, were measured for each mediator using cyclic voltammetry, as described in the Methods section. The diffusion coefficients, D, were obtained from the steady-state current at an ultramicroelectrode (UME), also as described in the Methods section. The values for each of the three parameters are also given in Supplementary Table 1. Three additional mediators, tetra-thiafulvalene (TTF), ferrocene (FC) and 5,10-dimethylphenazine (DMPZ), which do not belong to the above three classes, but have been commonly used as oxidation mediators, were also studied and are listed in Supplementary Table 1. The standard redox potentials are all positive for the O₂/Li₂O₂ reaction. The diffusion coefficients vary by no more than 0.04 for E° and 0.001 for k°.

Before considering the kinetics of the mediator oxidation in more detail, we first determine the surface composition of the disk and the possibility of passivation with, for example, Li₂CO₃. A disk of Li₂O₂ was immersed in 1 M LiTFSI in tetruglyme for 3 h and then examined by time of flight secondary ion mass spectrometry (TOF-SIMS), alongside a disk that was not exposed to the electrolyte solution. As shown in Fig. 2, for both disks, the major peaks are from Li₂O₂⁺, with the secondary peaks being ascribed to Li₂CO₃. These results show that although there is some Li₂CO₃, even on the surface of the pristine disk, a significant proportion of the surface remains as Li₂O₂ even after 3 h of
exposure to the electrolyte, confirming that the disk is suitable for the SECM measurements. Note that the sensitivity of TOF-SIMS to different species varies, consequently it is not possible to quantify the relative amounts of Li$_2$O$_2$ and Li$_2$CO$_3$ by simply comparing the areas under the peaks. Instead, the disk was etched until the signal from Li$_2$O$_2$ was constant, therefore corresponding to the bulk peroxide, i.e., 100% Li$_2$O$_2$. Comparing this signal with that for Li$_2$O$_2$ at the surface indicated that approximately 35% of the disk surface was Li$_2$O$_2$.

A disk of Li$_2$CO$_3$ was investigated with SECM using TEMPO as the oxidation mediator, as it has a sufficiently high potential to oxidise Li$_2$O$_2$ and shows fast kinetics with the Li$_2$O$_2$ disk. The results are shown in Supplementary Figure 2. The $k_{app}$ for oxidation of Li$_2$CO$_3$ by TEMPO is four orders of magnitude lower than the data collected on the Li$_2$O$_2$ disk, indicating that even for mediators with sufficiently high potentials the contribution of Li$_2$CO$_3$ oxidation to the $k_{app}$ is very small. The dominant reaction for the range of mediators studied here, even taking account of partial coverage by Li$_2$CO$_3$, is oxidation of Li$_2$O$_2$.

It has been reported previously by us and by others that several of the redox mediators used in Li–O$_2$ cells to date exhibit some degree of decomposition$^{24,39–41}$. Assembling a cell with commercial Li$_2$O$_2$ and the oxidation mediators TTF and AZO, and then charging to a capacity of $\sim$1 mAh results in notable decomposition of TTF and AZO as seen by $^1$HNMR of the electrolyte, see Supplementary Figure 3. In the SECM experiments, only a small amount of charge, $\sim$1 nAh, is passed, therefore the fraction of mediator that is decomposed is negligible.

**Inner-sphere process for mediator oxidising Li$_2$O$_2$**. To explore the possible correlations between $k_{app}$ and the electrochemical parameters of the redox mediators, $E^0$ and $k^0$, plots of $k_{app}$ vs. $k^0$ and $E^0$ and are presented in Figs. 3 and 4, respectively. There is no apparent dependence of $k_{app}$ on $k^0$, Fig. 3. The values of $k^0$ for the different redox mediators appear independent of the nature of the electrode used to measure them, as demonstrated by measuring these values at Au and glassy carbon electrodes, see Supplementary Figure 4 and Methods section, consistent with the RM$^+$/RM reactions occurring by outer-sphere electron transfer. If the oxidation of Li$_2$O$_2$ was also an outer-sphere electron transfer reaction, then $k_{app}$ would be proportional to $k^0$ of the redox mediator (and hence the reorganisation energy of the RM and surrounding solution), or the rate of the reaction Li$_2$O$_2$ $\rightarrow$ Li$_2$O$_2^+$ $+$ e$^-$. Since there is no dependence of $k_{app}$ on $k^0$, the former
Turning to the plot of $k_{\text{app}}$ vs. $E^o$, Fig. 4, it appears that the highest rates are observed for mediators with potentials above ~3.6 V. However, potential per se is not the explanation for the high rate, as there are examples of mediators with a high potential but low rate, e.g., BPPT. From the experiment on the Li$_2$CO$_3$ disk using TEMPO, we know higher rates at high potentials are not due to the onset of Li$_2$CO$_3$ oxidation contributing to the overall surface oxidation kinetics. Different crystal facets of Li$_2$O$_2$ will have different oxidation potentials. Mediators operating at higher potentials could oxidise these higher potential facets and hence access a greater Li$_2$O$_2$ surface area. However, the fact that the rates vary for different mediators above 3.6 V and several high potential mediators have relatively low $k_{\text{app}}$ suggests that this alone cannot be the reason for high rate mediators having a relatively high potential. As discussed below, we believe an important factor controlling the rate of the mediators is the nature of the oxidising centre and the degree of its steric hindrance.

Considering the molecules presented in Fig. 1 and the $k_{\text{app}}$ values shown in the figure, it is evident that the nitroxy radicals exhibit the fastest rates of Li$_2$O$_2$ oxidation. The thiol group also provides a high rate, in contrast to the amines that are all low rate. The chemistry of the redox centre appears to be an important factor for controlling the rate of oxidation, probably due to the interaction with Li$_2$O$_2$ surface. The oxidation rates decrease when the redox centre of the molecule is surrounded by bulky groups, Fig. 1. This suggests that a key factor influencing the kinetics of Li$_2$O$_2$ oxidation is the steric hindrance as the molecule approaches the surface of Li$_2$O$_2$. The fastest kinetics is exhibited by 2-azaadamantane-N-oxyl (AZO), 7.9 × 10$^{-3}$ cm s$^{-1}$, which has the most exposed redox centre of all the redox mediators studied here. This observation is in accord with the lack of evidence for an outer-sphere reaction and provides direct evidence for Li$_2$O$_2$ oxidation proceeding by an inner-sphere mechanism.

**Discussion**

In conclusion, we have measured the rate constants for the oxidation of Li$_2$O$_2$ particles by a series of molecular mediators spanning standard redox potentials, $E^o$ from 3.1 to 3.9 V and standard heterogeneous rate constants for electron transfer, $k^0$ from 0.007 to 0.078 × 10$^{-3}$ cm s$^{-1}$. The surface of Li$_2$O$_2$ particles in a typical electrolyte solution, LiTFSI in tetraglyme, is partially covered by Li$_2$CO$_3$, but the rate of Li$_2$CO$_3$ oxidation, a mediator that operates at 3.8 V, TEMPO, is four orders of magnitude lower than for Li$_2$O$_2$, therefore Li$_2$O$_2$ oxidation dominates. There is no correlation between the variation of $k^0$, the standard heterogeneous rate constant at the electrode surface for the mediators, and the rate of Li$_2$O$_2$ oxidation by the mediators, indicative of this not being an outer-sphere electron transfer process at the Li$_2$O$_2$ surface. There is evidence of Li$_2$O$_2$ oxidation rates depending on the nature of the oxidising molecule. Nitroxy radicals, especially those with low steric hindrances of access to the Li$_2$O$_2$ surface, exhibit the highest rates. Nevertheless, the mechanism of Li$_2$O$_2$ oxidation by molecular oxidants is still not well understood, and such understanding will be important in order to inform the design of optimised oxidation mediators. All mediators studied display kinetics sufficient to enable relatively high rates within a battery, charging current density exceeding 100 mA cm$^{-2}$. A mediator with a $k_{\text{app}}$ of 7.9 × 10$^{-3}$ cm s$^{-1}$ can sustain an areal current density of up to 1.9 A cm$^{-2}$, based on the same model. It is important to note that stability is still a challenge for the Li–O$_2$ battery and here we observe significant mediator decomposition when passing large amounts of charge. More stable electrolytes and mediators are required to minimise side reactions and hence improve cycleability.
Methods

Materials preparation. Li2O2 and Li2CO3 disks were obtained by pressing Li2O powder (Aldrich) and Li2CO3 powder (Aldrich) with a die set in an Ar-filled glove box. Disks of 13 mm diameter and ~1 mm of thickness were prepared and served as substrate. A Au microelectrode (diameter 25 μm, CHI) served as an SECME probe tip. Prior to measurement, the Au tip was polished with a microelectrode beveler (Sutter) and checked with a microscope. A silver wire reference electrode (RE) and a platinum counter electrode (CE) were used. Tetrakis(ethylenediamine)pentacyanoferrate(III) (TEPMA), 2-azadamanant-3-N-oxyl (AZO), 1-methyl-2-azadamanant-3-N-oxyl (MAZO), tris(4-diethylamino)phenylamine (TDA), 1,4-bis(diphenylamino) benzene (DPAB), N,N,N’N’-tetramethyl-p-phenylenediamine (TMDP), 10-methylphenothiazine (MPT), 10-isopropylphenothiazine (PTT), 10-(4-biphenylyl) phenothiazine (BPPT), tetrafluorobenzene (TFB), ferrocene (FC) and 5,10-dimethylphenylene diamine (DMPM) are from Aldrich. 10 mM redox mediators are dissolved in 100 mM LiTFSI–tetraglyme solution for electrolyte solution.

A Swagelok cell was assembled as reported previously35, using a piece of gas diffusion layer electrode (GDL) as the positive electrode. A lithium super ionic conductor disc (LSICON, Ohara) was used to protect Li metal as the negative electrode. A Li2O2 disk was placed between the GDL and the LSICON essentially placing the cell in a discharged state. TTF and AZO were chosen as the oxidation mediators. The cell was charged by holding at 3.4 V for TTF and 3.7 V for AZO until 1 mAh charge passed prior to further chemical characterisations. For NMR measurements, the electrodes and separators were rinsed with 0.7 ml of CDCl3, and measurements were recorded on a Bruker spectrometer (400 MHz).

Electrochemical measurements. SECM experiments were performed with SECM bipotentiostat (CHI 920) in an Ar-filled glovebox. Prior to kinetics measurement, the NG factor of Au tip was determined by approaching a completely insulating surface and fitting the negative approach curve. The data processing and fitting procedure were described elsewhere35–37. A dimensionless rate constant, k, was obtained by data fit, which equals to kapp/πr², where r is the radius of tip and D is the diffusion coefficient of redox mediators. D of various mediators were determined by measure steady-state current of a Au microelectrode with known radius r, according to k = iDπ/4r. The redox potential and heterogeneous electron transfer rate constants kθ of redox mediators itself were determined using cyclic voltammetry(CV) measurements. The redox potential is determined by the centre of two redox peaks, which is measured in a 100 mM LiTFSI–tetraglyme solution with 10 mM of various mediators at a Au electrode. Partially charged LiFeO4 (LFP) protected by a TTF mediation itself were determined using cyclic voltammetry(CV) various mediators at a Au electrode. Partially charged LiFeO4 (LFP) protected by a TTF mediation itself were determined using cyclic voltammetry(CV) various mediators at a Au electrode. Partially charged LiFeO4 (LFP) protected by a TTF mediation itself were determined using cyclic voltammetry(CV) various mediators at a Au electrode. Partially charged LiFeO4 (LFP) protected by a TTF mediation itself were determined using cyclic voltammetry(CV) various mediators at a Au electrode. Partially charged LiFeO4 (LFP) protected by a TTF mediation itself were determined using cyclic voltammetry(CV) various mediators at a Au electrode. Partially charged LiFeO4 (LFP) protected by a TTF mediation itself were determined using cyclic voltammetry(CV) various mediators at a Au electrode.

Characterisations. For the surface characterisations, the Li2O2 disk was immersed in 1 M LiTFSI–tetraglyme solution for 3 h prior to XPS and TOF-SIMS experiments. Both pristine disk and treated disk were characterised in an air-sensitive box. Disks of 13 mm diameter and ~1 mm of thickness were prepared and served as substrate. A Au microelectrode (diameter 25 μm, CHI) served as an SECM probe. A Si substrate. A Au microelectrode (diameter 25 μm, CHI) served as an SECM probe.
cyclic voltammetry and scanning electrochemical microscopy. J. Phys. Chem. B 112, 13292–13299 (2008).

38. Meini, S., Elazzari, R., Rosenman, A., Garsuch, A. & Aurbach, D. The use of redox mediators for enhancing utilization of Li2S cathodes for advanced Li–S battery systems. J. Phys. Chem. Lett. 5, 915–918 (2014).

39. Bergner, B. J. et al. How to improve capacity and cycling stability for next generation Li–O2 batteries: approach with a solid electrolyte and elevated redox mediator concentrations. ACS Appl. Mater. Interfaces 8, 7756–7765 (2016).

40. Gao, X., Chen, Y., Johnson, L. R., Jovanov, Z. P. & Bruce, P. G. A rechargeable lithium–oxygen battery with dual mediators stabilizing the carbon cathode. Nat. Energy 2, 17118 (2017).

41. McCloskey, B. D. & Addison, D. A viewpoint on heterogeneous electrocatalysis and redox mediation in nonaqueous Li–O2 batteries. ACS Catal. 7, 772–778 (2017).

42. Mo, Y., Ong, S. P. & Ceder, G. First-principles study of the oxygen evolution reaction of lithium peroxide in the lithium–air battery. Phys. Rev. B 84, 205446 (2011).

43. Bard, A. J. & Faulkner, L. R. Electrochemical Methods. Fundamentals and Applications 2nd edn (Wiley, New York, 2000).

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Author contributions

Y.C., X.G. and L.R.J. designed the experiments and analysed the data. Y.C. and X.G. performed the electrochemical measurements and characterizations. Y.C., X.G., L.R.J. and P.G.B. interpreted the data. P.G.B. wrote the paper.

Additional information

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