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COMMUNICATION

A new method to prevent degradation of lithium-oxygen batteries: reduction of superoxide by viologen

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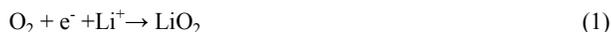
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Lithium-oxygen battery development is hampered by degradation reactions initiated by superoxide, which is formed in the pathway of oxygen reduction to peroxide. This work demonstrates that the superoxide lifetime is drastically decreased upon addition of ethyl viologen, which catalyses the reduction of superoxide to peroxide.

Lithium-oxygen batteries can potentially deliver 5 times more energy than lithium-ion batteries of the same weight.¹⁻⁷ The energy is provided by the electrochemical reaction between Li and O₂, typically forming Li₂O₂. Since all these compounds are very light, the mass of the battery can be very small, leading to a high specific energy (i.e. energy per mass). However, several factors hamper the practical performance of current lithium-oxygen batteries. First of all, superoxide is formed as the first product of the reduction of O₂.^{8,9}



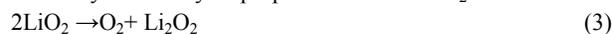
It has been shown that superoxide reacts irreversibly with most known electrolytes¹⁰ and it is also probably involved in the corrosion of carbon electrodes.¹¹ Intensive research has been done on finding alternative electrolytes and electrode materials that are resistant towards degradation by superoxide. A few solvents like dimethyl sulfoxide¹², some glymes^{13, 14} and pyrrolidinium or piperidinium based ionic liquids¹⁵⁻¹⁹ have been identified as promising electrolyte choices. Gold¹² and TiC²⁰ electrodes have shown much better capacity performance than carbon, in terms of cycling stability and suppression of side reactions.

An alternative approach to solve the superoxide problem is the introduction of catalysts to promote the reduction of superoxide to peroxide:



This would decrease the lifetime of superoxide and, with this, the long-term durability of the battery. If the superoxide lifetime were

short enough, it would be conceivable that a wider range of materials could be incorporated in lithium-oxygen batteries without serious problems of degradation reactions. In addition, such catalysts would also be beneficial in order to speed up the overall 2-electron reduction of oxygen to Li₂O₂. In the absence of such catalyst, Li₂O₂ is usually formed by disproportionation of LiO₂.^{8,9}



However, as will be shown below, the rate of this reaction is very slow at low superoxide concentrations.

Another important issue in lithium-oxygen batteries is that the discharge product, Li₂O₂, deposits on the surface of the electrode, blocking its electrochemical activity. This produces a very early end of discharge, with little discharge product being formed, and little capacity being delivered. An innovative solution to solve this problem is the introduction of soluble redox shuttles that can displace the formation of Li₂O₂ from the electrode surface to the solution, by reducing oxygen through a homogenous chemical reaction.^{21, 22} Soluble redox couples have also been used as mediators for the evolution of oxygen in lithium-oxygen batteries, resulting in major performance improvements.²³⁻²⁶

In the present work, we have studied the application of soluble redox couples with the dual purpose of preventing electrode passivation and enhancing the 2-electron oxygen reduction. We demonstrate that ethyl viologen acts as a homogenous electrocatalyst that enhances the 2-electron reaction of oxygen to Li₂O₂ while mitigating electrode passivation. It has been previously shown that superoxide and viologen react irreversibly forming a range of degradation products.²⁷ However, we demonstrate that under our experimental conditions the extent of degradation of viologen by superoxide attack is negligible, a fact that we attribute to the presence of an excess of lithium cations in solution.

Figure 1 shows the galvanostatic discharge and charge of a glassy carbon electrode in an oxygen-saturated solution with (a) and without (b) ethyl viologen, EtV^{2+} (see supplementary information for full experimental details). It is observed that, in the absence of EtV^{2+} , the discharge curve plateaus at ca. 2.39 V vs. Li/Li^+ , whereas with EtV^{2+} , a higher discharge voltage is observed, ca. 2.42 V vs. Li/Li^+ . This is associated to the mediation action of EtV^{2+} , which results in a lower overpotential for the reduction of oxygen. Consequently, the reduction of oxygen is triggered by the reduction of EtV^{2+} to EtV^+ , that plateaus at the standard potential $E^0(\text{EtV}^{2+}/\text{EtV}^+) \approx 2.42$ V vs. Li/Li^+ (supporting information, figure S2). This reaction is followed by the reduction of O_2 by EtV^+ :



Since the thermodynamic potential for the reduction of oxygen to Li_2O_2 is ca. 3 V vs. Li/Li^+ ,^{28, 29} the reaction above is thermodynamically favourable.

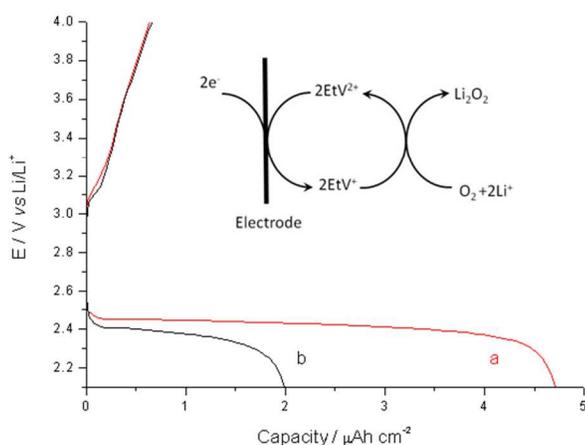
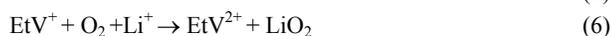


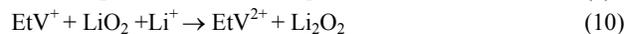
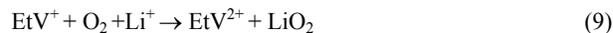
Figure 1. Galvanostatic discharge and charge of a glassy carbon electrode in oxygen-saturated $\text{Py}_{14}\text{TFSI}$ containing 0.1 M LiTFSI , with (a) and without (b) 2 mM EtV^{2+} . $I = 20 \mu\text{A cm}^{-2}$. The inset sketches the redox shuttle action of viologen, displacing the formation of Li_2O_2 from the electrode surface to the solution.

Another remarkable feature in figure 1 is the increase in the discharge capacity upon addition of viologen. This is due to the shuttle action of viologen (see inset figure 1). In the presence of viologen, Li_2O_2 is formed in solution, at a certain distance from the electrode surface. Therefore, the passivation of the electrode by Li_2O_2 deposition is less severe, affording a higher discharge capacity.

While the results in figure 1 demonstrate that viologen is a mediator of the oxygen reduction reaction, the reaction path is not unique. It is possible to propose that viologen acts as a mediator of the reduction of oxygen to superoxide, which will then disproportionate forming oxygen and peroxide:



Alternatively, viologen may mediate the 2-electron reduction of oxygen. In other words, viologen will not only reduce oxygen to superoxide, but it will also reduce superoxide to peroxide:



The second reaction path is more advantageous because the overall rate of the reaction would be faster (we will show below that the disproportionation step, reaction 7, is extremely slow at low superoxide concentrations). Furthermore, the lifetime of superoxide would be decreased, and consequently, the chemical stability of the battery would be improved for the reasons stated above.

In order to distinguish between these two reaction paths, we first studied the kinetics of LiO_2 disproportionation. For that purpose, we dissolved KO_2 in a solution containing an excess of Li^+ , and we followed the decrease in superoxide concentration by UV-vis measurements. This method was previously used in order to study the lifetime of superoxide anions in the absence of Li^+ , concluding that superoxide anions are long lived in some electrolytes such as dimethylsulfoxide,³⁰ glymes¹³ and pyrrolidinium based ionic liquids.¹⁹ In this work we have observed that superoxide anions are also stable in solutions with high concentration of Li^+ , for superoxide concentrations < 1 mM. Figure 2 shows that the absorption band of superoxide in a 0.1 mM KO_2 solution with 300 mM of LiTFSI decreases by less than 1% after 3 hours. Similar stability is observed at a KO_2 concentration of 1 mM (supporting information, figure S3). These measurements were done in acetonitrile, which is a solvent with low donor number. It has been suggested that the lifetime of lithium superoxide is longer in solvents with high donor number,^{31, 32} and we have observed that in tetraglyme the lithium superoxide lifetime is > 3 hours (supporting information, figure S4). Previous work showed that superoxide disproportionates to O_2 and Li_2O_2 in the presence Li^+ ,³³ but we have found that the disproportionation reaction is only fast for high superoxide concentrations, and particularly, in the presence of an excess of solid KO_2 .

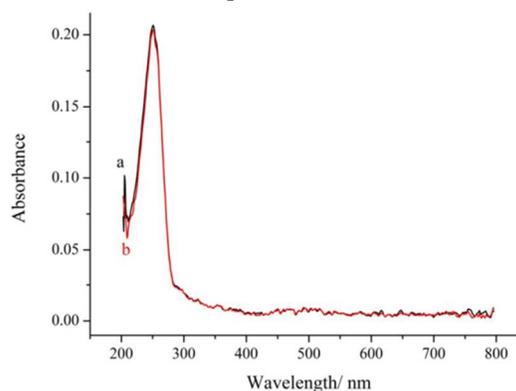


Figure 2. UV-vis spectra of a ca. 0.1 mM KO_2 solution in acetonitrile before (a) and 3 hours after the addition of 300 mM LiTFSI (b).

Next, we studied the reaction between LiO_2 and EtV^+ , and we observed that superoxide reacted rapidly in the presence of EtV^+ . Figure 3 shows the UV-vis spectra obtained during the titration of a EtV^+ solution with superoxide. As shown in figure 3, the absorption bands characteristic of EtV^+ at 600 and 400 nm decrease with the addition of superoxide aliquots, while the band at 260 nm characteristic of EtV^{2+} grows (see supporting information, figure S1

for the band assignment). Taking into account the decrease in the absorption at 600 nm, it is demonstrated that one mole of LiO_2 reacts with ca. one mole of EtV^+ (the details of the calculation are in the supporting information). The stoichiometry of the reaction thus demonstrates that a direct reduction of superoxide by viologen occurs as the second step of the 2- electron mediation suggested above (reaction 9).

In order to demonstrate the absence of a degradation reaction of viologen by the attack of superoxide, the oxidized viologen was re-reduced at the end of the experiment using $\text{Li}_7\text{Ti}_5\text{O}_{12}$:

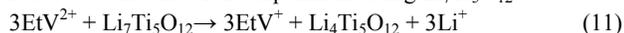


Figure 3 compares the spectrum of the EtV^+ before (curve a) and after (curve e) the reaction with superoxide followed by re-reduction with $\text{Li}_7\text{Ti}_5\text{O}_{12}$. An excellent agreement is observed, demonstrating that the extent of viologen degradation is negligible. In conclusion, the results in figure 3 are consistent with the viologen mediated reduction of superoxide to peroxide.

It is noteworthy that the mediation action of viologen for the 2- electron reduction of oxygen appears to hold in various solvents, including acetonitrile and $\text{Py}_{14}\text{TFSI}$ (supporting information, figures S5-7), and that the titration of a solution of EtV^+ with O_2 confirms that ca 2 moles of EtV^+ react with one mol of O_2 .

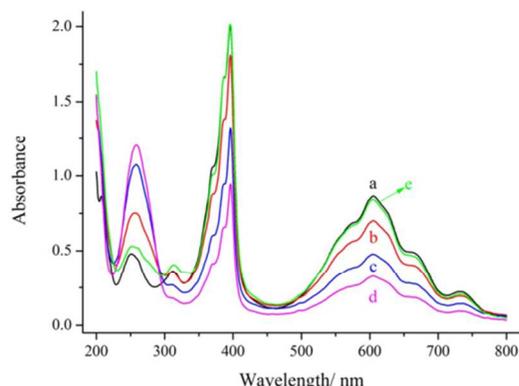


Figure 3. UV-vis spectra measured during the titration of 0.05 mM EtV^+ + 0.15 M LiTFSI in acetonitrile with: a) zero, b) one, c) two, and d) three additions of 0.0125 mM KO_2 . Curve (e) shows the spectrum obtained after re-reduction with $\text{Li}_7\text{Ti}_5\text{O}_{12}$.

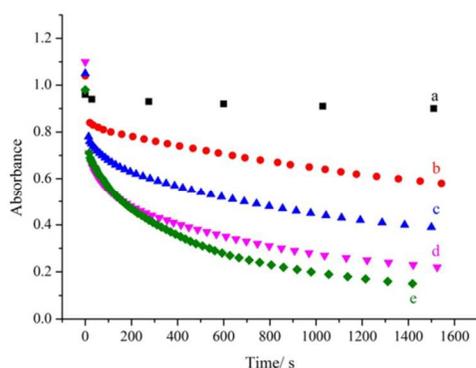


Figure 4. Absorbance at 590 nm of a solution that was initially 0.1 mM EtV^+ + 0.1 mM KO_2 in acetonitrile, measured as a function of time. The LiTFSI concentration is: a) 1, b) 75, c) 150, d) 300, and e) 600 mM.

Finally, the reaction rate between EtV^+ and superoxide was monitored by measuring the absorbance at 590 nm, which is proportional to the EtV^+ concentration, as a function of time (figure 4), at different Li^+ concentrations. These measurements provide a direct probe of the superoxide lifetime, and in addition, the analysis of the reaction kinetics confirms the direct reaction between EtV^+ and superoxide, since it is concluded that the reaction of EtV^+ and superoxide follows third order kinetics (see supporting information):

$$d[\text{EtV}^+]/dt = k[\text{Li}^+][\text{O}_2^-][\text{EtV}^+] \quad (12)$$

where the rate constant, k , equals to ca. $90 \text{ M}^{-2}\text{s}^{-1}$. The reaction between EtV^+ and O_2 is even faster, consistent with the reaction mechanism with reactions 8, 9 and 10 (see supporting information).

To finish, it should be emphasized that the presence of viologen produces an enormous decrease in the lifetime of superoxide. While in the absence of viologen, the lifetime of superoxide is > 3 hours for superoxide concentrations < 1 mM, in the presence of only 0.1 mM EtV^+ , the concentration of superoxide is decreased by half in only 3 minutes (figure 4).

Conclusions

We have shown that ethyl viologen acts as a homogeneous catalyst for the 2-electron reduction of oxygen in lithium-oxygen batteries. An enormous decrease in the lifetime of superoxide is observed upon addition of ethyl viologen to the solution, even at the sub-millimolar concentration. These findings open up a new strategy to improve the performance and durability of lithium-oxygen batteries.

The aim of this work was not to propose ethyl viologen as the perfect solution to lithium-oxygen batteries, since we are aware of some shortcomings (toxicity, slightly low redox potential, slow diffusion, etc.). The aim was to demonstrate, for the first time, the concept of employing a soluble redox couple in order to decrease the lifetime of superoxide in a lithium-oxygen battery by promoting the 2-electron reduction of oxygen.

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Notes and references

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Experimental details and additional experimental data are available in the

- Electronic Supplementary Information: See DOI: 10.1039/b000000x/
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