

LI-AIR BATTERIES

Decouple to stabilize

The utilization of porous carbon cathodes in lithium–air batteries is hindered by their severe decomposition during battery cycling. Now, dual redox mediators are shown to decouple the complex electrochemical reactions at the cathode, avoiding cathode passivation and decomposition.

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Rechargeable batteries power devices such as mobile electronics and electric vehicles, and can store electricity generated from various renewable energy sources. Lithium-ion (Li-ion) batteries are an efficient energy-storage system, but the energy density is approaching their theoretical limit. The ever-growing need for energy storage therefore necessitates the pursuit of next-generation batteries¹. Lithium–air (Li–air) batteries are promising because they have a theoretical energy density that is nearly 10 times as much as that of a conventional Li-ion battery². However, many challenges must be addressed before Li–air batteries can compete with current rechargeable batteries, the most difficult of which is the significant decomposition of the carbon cathode and electrolyte during cycling, which severely limits the battery cycle life³. Carbon modification (for example, improving crystallization) or surface treatment (for example, coating surface defects with inorganic particles) are commonly adopted to stabilize the cathode, because these approaches decrease the contact between the active site of the carbon cathode and highly active species (LiO_2 and Li_2O_2) and hence improve resistance to decomposition⁴. However, these highly active species are still present in batteries and are able to degrade the carbon cathode. Writing in *Nature Energy*⁵, Peter Bruce and colleagues from the University of Oxford, UK, now propose a strategy of using dual redox mediators to stabilize the carbon cathode without any carbon modification or surface treatment.

A typical Li–air battery is composed of a lithium anode and a porous carbon cathode, separated by an aprotic electrolyte. Its chemistry can be written $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$, with the forward and reverse reaction describing discharge and charge, respectively. As shown in Fig. 1a, during discharge O_2 undergoes a one-electron reduction on the cathode surface to generate O_2^- that then binds with Li^+ to form LiO_2 ; further reduction

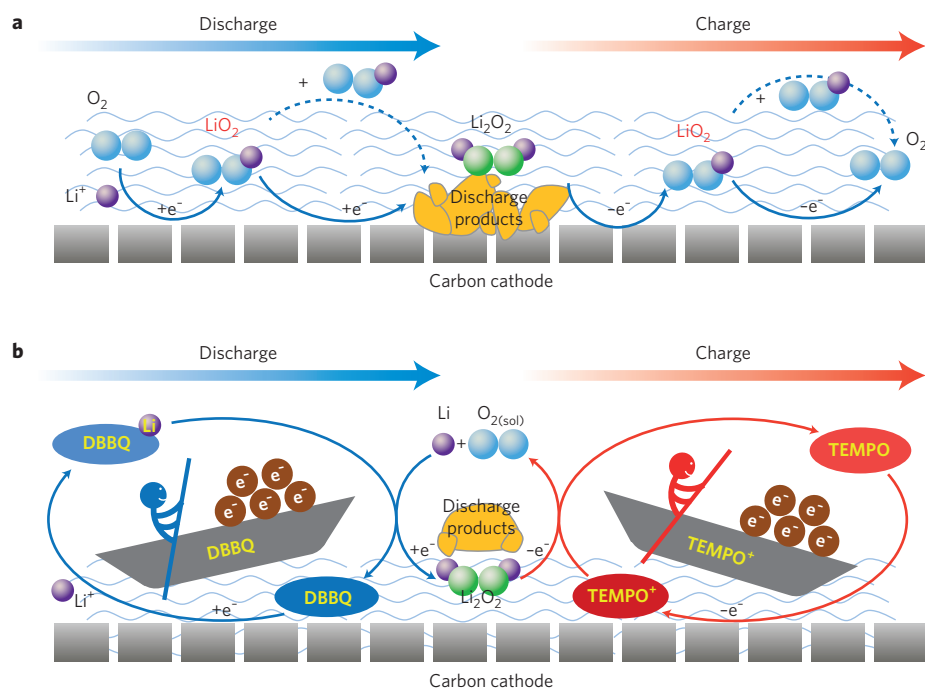


Figure 1 | Reaction mechanisms at the carbon cathode. **a**, The cathodic reactions upon discharge and charge in the absence of any mediators. Upon discharge, O_2 is reduced to form O_2^- that binds with Li^+ to produce LiO_2 . Subsequently, Li_2O_2 forms by disproportionation (represented by dotted curved arrows) or further reduction (represented by solid curved arrows) of LiO_2 . Upon charge, Li_2O_2 is oxidized to LiO_2 , and then O_2 is released via disproportionation (dotted curved arrows) or a second oxidation (solid curved arrows) of LiO_2 . The electrolyte is represented by wave-like features. **b**, The cathodic reactions upon discharge and charge in the presence of DBBQ and TEMPO. Upon discharge, DBBQ is reduced at the cathode surface, forming LiDBBQ . Then, LiDBBQ reacts with O_2 to produce Li_2O_2 and regenerate DBBQ. Upon charge, TEMPO is oxidized at the cathode surface, forming TEMPO^+ , which in turn oxidizes Li_2O_2 to produce O_2 and regenerate TEMPO. The $\text{O}_{2(\text{sol})}$ indicates the O_2 dissolved in the electrolyte. The left and right boats schematically illustrate that DBBQ transfers electrons from the cathode surface to O_2 , and TEMPO transfers electrons from Li_2O_2 to the cathode surface, respectively.

or disproportionation of LiO_2 leads to the formation of Li_2O_2 . The reverse reactions occur during charge. As a strong nucleophile, LiO_2 is unfortunately too reactive towards the carbon cathode and the aprotic electrolyte, forming undesired by-products such as Li_2CO_3 and Li carboxylates⁶. The by-products passivate the cathode, which results in severe capacity fading upon cycling and even premature

cell death. Furthermore, Li_2O_2 is also problematic: when Li_2O_2 is in contact with the carbon cathode, it forms Li_2CO_3 (ref. 7). In addition, the high charging voltage required to oxidize the insulating Li_2O_2 can also induce carbon-cathode decomposition.

Recently, a concept of using dissolved redox mediators as a soluble catalyst to reduce the overvoltages has been

proposed⁸. Overvoltages are gaps between the practical and theoretical potential, representing the energy loss in operation. It has been demonstrated that redox mediators can facilitate either the discharge or charge process. In this work, Peter Bruce and colleagues show that using a dual redox mediator can facilitate both discharge and charge processes as required, and importantly can stabilize the carbon cathode.

Specifically, the dual redox mediator consists of 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). During discharge, the DBBQ is first reduced at the cathode surface; the reduced species (DBBQ–Li, shown in Fig. 1b) then transfers the electrons to O₂ that is dissolved in the electrolyte solution (O_{2(sol)}), and the final discharge product Li₂O₂ is formed. Meanwhile, DBBQ–Li is oxidized to DBBQ. During charge, TEMPO is first oxidized at the cathode surface, and the oxidized species (TEMPO⁺) then obtains electrons from Li₂O₂ to produce O₂. Clearly, both DBBQ and TEMPO act as an electron-transfer agent and are discharge and charge mediators, respectively, in the battery process.

The approach shown in this work bypasses the formation of the troublesome

intermediate LiO₂. Importantly, it decouples the electrochemical reactions at the cathode surface from the formation and decomposition of Li₂O₂ from solution: the electrochemistry at the cathode surface only involves the redox reactions of DBBQ and TEMPO molecules, whereas the Li₂O₂ formation and decomposition occurs away from the carbon surface. Therefore, the detrimental reaction between Li₂O₂ and the carbon surface is minimized (Fig. 1b). In addition, the use of dual mediators ensures that Li₂O₂ particles in solution are efficiently oxidized without having to increase the charge voltage of the carbon cathode in the conventional approach, greatly alleviating high-potential-induced carbon-cathode decomposition. Taking all these factors together, a much better cycling performance is obtained in the Li–air cell (<0.008% carbon decomposition per cycle) than in the cell without any mediators (0.12% per cycle).

Owing to its high conductivity, light weight, and rich porous structure, carbon is by far the most attractive cathode selection in Li–air batteries. This work by Bruce and colleagues overcomes one of the major barriers for the application of carbon cathodes in Li–air batteries. However, the fact that the Li₂O₂ growth and decomposition now occurs in the electrolyte would increase the contact between Li₂O₂

and the electrolyte. Hence, the issue of the electrolyte stability needs to be addressed. In addition, because of the decoupling of the electrochemical reactions at the cathode surface from the formation and decomposition of Li₂O₂ from the electrolyte solution, the performance of a Li–air battery is no longer limited by the charge transport of Li₂O₂ but rather by the O₂ mass transport within the porous carbon cathode. We note that the carbon cathode in this work, which is flooded with the electrolyte, may lack efficient gas diffusion channels for O₂. This would limit the advantages of the mediators, and thus future work should also focus on the design of a porous cathode that delivers rapid mass transport. □

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