Charging ahead rationally

Redox mediators facilitate the oxidation of the highly insulating discharge product in metal-oxygen batteries during recharge and offer opportunities to achieve high reversible capacities. Now, a design principle is suggested for selecting redox mediators that can more efficiently recharge the batteries.

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Energy storage systems such as lithium-ion batteries are key enablers to overcome societal energy challenges but require major breakthroughs to make more widespread impact in electrified transportation, grid-scale storage and other fields. New technologies are being sought that far exceed the potentials of lithium-ion batteries in terms of energy stored, eco-friendliness and cost[1]. This is why metal-air batteries such as the lithium-oxygen battery have spurred tremendous research in the last decade. They hold theoretically the highest energy per unit mass whilst using oxygen – drawn from the air – as the active cathode material instead of the widely used toxic and expensive cobalt in current commercial lithium ion batteries. This leap in theoretical performance comes with a fundamental change of how lithium ions are stored in the cathode. While in the lithium-ion battery the cobalt compound reversibly inserts and releases lithium ions upon discharge and charge, the lithium-oxygen battery works through the formation of lithium peroxide (Li_2O_2) in the discharged state that then entirely vanishes to release oxygen during recharge. The Li_2O_2 is highly insulating, unlike the active material in lithium-ion batteries, which is somewhat conductive. Thus, a major challenge to advance the lithium-oxygen battery is how to oxidize the Li_2O_2 on charging, that is, how to reduce the amount of Li_2O_2. Redox mediators have been proposed as one promising route. The mediator, dissolved in the electrolyte, acts as an electron-hole transfer agent between the solid electrode and the Li_2O_2 and allows recharging at far higher rates at lower overpotential (the voltage above the theoretical potential, representing energy loss).[2] Understanding the energetics of intermediate states of the mediator, which can be considered as a soluble catalyst, is important because they affect efficacy and selectivity in the batteries. Writing in *Nature Energy*, Kisuk Kang from Seoul National University and colleagues now propose a design principle for redox mediators that oxidize Li_2O_2 at as low an overpotential as possible but without harming the electrolyte in the process[3].

In lithium-oxygen batteries the cathode comprises a porous electron-conducting solid that is filled with electrolyte. Upon discharge, dissolved O_2 is reduced at the pore wall and

combines with Li ions to form Li_2O_2. The capacity per unit volume or mass of electrode at a given initial porosity is therefore determined by the degree of pore filling. Despite the low conductivity of Li_2O_2, relatively large capacities can be achieved. However, further discharge is hindered by the growing Li_2O_2. In particular, soluble intermediates formed during discharge could allow Li_2O_2 to crystallize in large particles, thus filling the pores to some extent[4,5] and consequently blocking O_2 from contact with electrons. During charge, the Li_2O_2 immediately in contact with the electrode is relatively easily oxidized, but the regions of Li_2O_2 further from the electrode surface are increasingly difficult to decompose. As a result the charge overpotential after a deep discharge climbs inexorably to as much as 1.6 V in some cases, even at low current densities. Such high voltages cause degradation of cell components and result in poor cycle life[6].

Redox mediators allow, in principle, charging of the cell at nearly zero overpotential. The mediator is oxidized at its own redox potential at the electrode, diffuses to oxidize the Li_2O_2 to produce Li ions and O_2 gas (O_2 evolution), and is itself in turn reduced to its initial form (Fig. 1a). Reports so far on the selection of appropriate mediators have focused on screening for redox potential and O_2 evolution efficiency, but mechanistic descriptors for stability have rarely been given. The study from Kang and colleagues approaches the task by considering the ionization energy (IE) value of redox mediator candidates as the key descriptor. The IE values can be used to estimate the redox potentials of the redox mediator candidates (i.e. organic molecule candidates in the study). To be able to charge the cell their redox potential needs to be at or above the equilibrium potential of Li_2O_2 formation and decomposition. Ionization energies are also available from databases for a large number of organic molecules, thus allowing for an efficient preselection. By narrowing the range of ionization energies to values corresponding to redox potentials between roughly 0 and 1 V above the equilibrium potential of Li_2O_2 they found new candidates from the family of alkylated aromatic amines that could allow recharging with an overpotential of less than 1 V. This was confirmed in battery experiments, where otherwise identical cells without the mediators have shown charge overpotentials of up to 1.6 V.

Earlier work has found that some redox mediators with suitable redox potentials oxidize Li_2O_2 with the expected amount of O_2 evolution whereas others with similar potentials evolve less O_2, implying that side reactions may have taken place[2]. Kang and colleagues explain this behaviour by considering the electron energies in the reduced and oxidized form of the mediators and of the electrolyte solvent by means of first principles calculations. For mediators that cause side reactions they found that the oxidized mediator has a singly

occupied orbital with an energy level in the right range to take an electron from the electrolyte (Fig. 1b). Thus, the electrolyte is oxidized and decomposed. This behaviour is seen by cyclic voltammetry that shows irreversible behaviour and quantitative gas analysis of the O_2 evolved. Stable mediators, in contrast, have the respective orbital at a sufficiently different energy not to oxidize the electrolyte (Fig. 1b).

It remains the central goal in the field to repeatedly achieve high discharge capacity, i.e., nearly complete pore-filling, and to be able to recharge the cell fully at high rate. There is a growing agreement that mediators may be key to achieve this. First, on discharge the Li_2O_2 growth in solution appears to be the only way to achieve high capacities[4,5]. Mediators could in principle decouple the discharge product formation from the electrode surface (reduction mediators), and thus enable a very high degree of pore-filling and capacity[7]. Second, once the cell has been deeply discharged, large particles of insulting and possibly detached Li_2O_2 particles have to be oxidized. There has been no approach for the oxidation so far apart from using mediators (oxidation mediators). Ideally, bifunctional mediators should be developed, which can work for both the reduction and the oxidation[8,9]. The drawback of mediators is of course their own susceptibility to decomposition. The work from Kang and colleagues gives important design principles for finding stable mediators with low charge voltage. Nevertheless, similar descriptors for the stability of mediators and electrolytes upon discharge and long term cyclability, which have not been addressed here, would equally be desirable.

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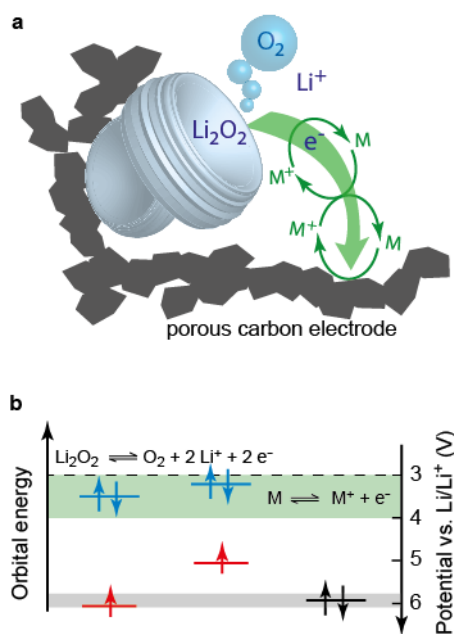9. Mourad, E. *et al. Electrochim. Acta*, doi: 10.1016/j.electacta.2016.02.211 (2016).

Fig. 1 | Working principle of a redox mediator for charging Li_2O_2 in the lithium-oxygen battery. **a**, The mediator M is oxidized to M^+ at the electrode surface and diffuses to the Li_2O_2 that often forms toroidal particles of some 100 nm size. M^+ oxidizes Li_2O_2 leading to O_2 evolution and is itself reduced to M. **b**, Energies of the highest occupied orbitals of M (blue) and M^+ (red), and corresponding voltages on the Li/Li^+ scale. The dashed line denotes the equilibrium potential of the cell reaction $O_2 + 2\ Li^+ + 2\ e^- \leftrightarrow Li_2O_2$. The green shaded area denotes suitable redox potentials of mediators. The data at the left and center refer to a typical mediator causing side reactions and a stable mediator, respectively. The energy of the highest occupied orbital of a typical electrolyte solvent is shown at the right. A non-filled mediator orbital with an energy value in the vicinity (grey shaded area) is prone to take an electron from the solvent. Figure 1b adapted from ref. 3.