

## BATTERIES

## Avoiding oxygen

In the development of lithium–air batteries, managing the phase change between gaseous oxygen and crystalline lithium peroxide is a key challenge. Now, a high-performing sealed battery with an oxygen anion-redox electrode is presented that does not involve any gas evolution.

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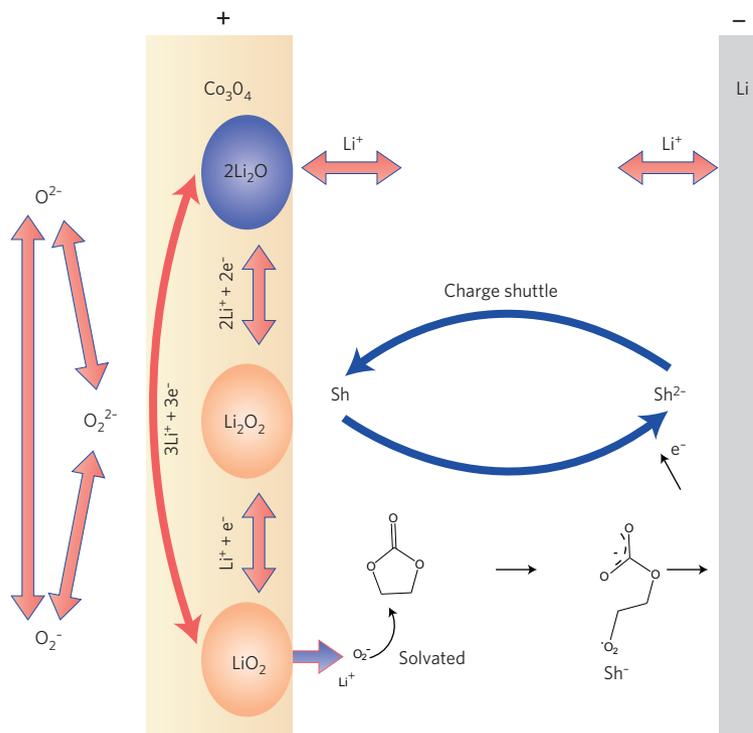
Energy storage in the form of rechargeable batteries is becoming increasingly important for a range of applications including transportation and grid reserves. Recent interest in non-aqueous metal–oxygen batteries, particularly lithium–oxygen ( $\text{Li}-\text{O}_2$ ), has stemmed from their high theoretical gravimetric energy densities<sup>1</sup>. In  $\text{Li}-\text{O}_2$  batteries, the reactant ( $\text{O}_2$ ) is not contained within the cell; instead, it enters from outside and undergoes reduction at the positive electrode, and is then combined with  $\text{Li}^+$  to form lithium peroxide ( $\text{Li}_2\text{O}_2$ ) during discharge. The product  $\text{Li}_2\text{O}_2$  has a much lower molecular weight to electron ratio than typical intercalation compounds used in Li-ion batteries (that is, 23 for  $\text{Li}_2\text{O}_2$  versus 98 for  $\text{LiCoO}_2$ ), which is the reason why the theoretical energy density of  $\text{Li}-\text{O}_2$  greatly surpasses that of Li-ion. The challenges, on the other hand, are related to mass transport, getting  $\text{O}_2$  to the electrode surface so it can be reduced at sufficiently fast rates in order to have a useful power capability and preventing blockage of the electrode pores during the precipitation of solid  $\text{Li}_2\text{O}_2$ . In addition, the air stream will have to be virtually free of moisture and  $\text{CO}_2$  to avoid deleterious side reactions. Writing in *Nature Energy*<sup>2</sup>, Ju Li and colleagues from Massachusetts Institute of Technology, Peking University and Argonne National Laboratory now demonstrate a sealed lithium-ion cell, as opposed to the open system of  $\text{Li}-\text{O}_2$  batteries, with an oxygen anion-redox ( $\text{O}^{2-}/\text{O}_2^-/\text{O}_2^{2-}$ ) electrode, which avoids the uptake and release of  $\text{O}_2$ .

The key idea behind the work is the development of an intimately mixed matrix of nanoscale lithium oxide, also known as lithia ( $\text{Li}_2\text{O}$ ), and cobalt oxide ( $\text{Co}_3\text{O}_4$ ).  $\text{Li}_2\text{O}$  exists as evenly dispersed domains on the order of 5 nm within the  $\text{Co}_3\text{O}_4$ . When oxidized,  $\text{Li}_2\text{O}$  can be transformed to lithium superoxide ( $\text{LiO}_2$ ) and  $\text{Li}_2\text{O}_2$  via redox reactions between  $\text{O}^{2-}/\text{O}_2^-$ ,  $\text{O}_2^-/\text{O}_2^{2-}$ , and possibly  $\text{O}_2^{2-}/\text{O}_2^-$ . In particular, the researchers showed that the  $\text{LiO}_2$  and  $\text{Li}_2\text{O}_2$  can be reduced back to  $\text{Li}_2\text{O}$  with a discharge

capacity of around 550 Ah  $\text{kg}^{-1}$ , and the cycle can be repeated over 100 times. When used as the positive electrode in a Li-ion cell, a specific energy of 1,000 Wh  $\text{kg}^{-1}$  was shown, which rivals the  $\text{Li}-\text{O}_2$  cell and outcompetes the state-of-the-art Li-ion technology by a factor of 2.5–3 at the materials level<sup>1</sup>. The cell also showed a minor voltage gap of 0.24 V between discharge and charge, implying possible high roundtrip efficiencies in operation.

A fascinating aspect of the study is the internal generation of a stable redox

shuttle, that is, a redox species that diffuses in-between both electrodes essentially allowing electrons to flow through the electrolyte. A redox shuttle in this example could be thought of as a ‘chemical short circuit’. As shown in Fig. 1, the redox shuttle ( $\text{Sh}^-$ ) is created from the reaction between surface exposed  $\text{LiO}_2$  and the electrolyte solvent (ethylene carbonate).  $\text{Sh}^-$  diffuses to the negative electrode where it is further reduced ( $\text{Sh}^{2-}$ ); subsequently the shuttle ( $\text{Sh}^{2-}$ ) diffuses back to the positive electrode where it is oxidized. The redox



**Figure 1** | Operation mechanism of the sealed Li-ion cell. A reversible lithium oxide–peroxy/superoxide positive electrode and lithium metal negative electrode are schematically shown. Nanoscale lithium oxide ( $\text{Li}_2\text{O}$ ) within a  $\text{Co}_3\text{O}_4$  matrix can be reversibly transformed to lithium peroxide ( $\text{Li}_2\text{O}_2$ ) and lithium superoxide ( $\text{LiO}_2$ ) at the positive electrode. The identity and transformation pathway of each redox active oxygen species is presented to the left of the Li-ion cell. Within the cell a redox shuttle (represented by ‘Sh’, ‘ $\text{Sh}^-$ ’ and ‘ $\text{Sh}^{2-}$ ’) is generated from the reaction of surface exposed  $\text{LiO}_2$  and the solvent ethylene carbonate. The shuttle ( $\text{Sh}^-$ ) diffuses to the negative electrode where it is further reduced ( $\text{Sh}^{2-}$ ); subsequently the shuttle ( $\text{Sh}^{2-}$ ) diffuses back to the positive electrode where it is oxidized by giving up two electrons ( $\text{Sh}$ ). The shuttle process protects the cell from oxygen gas release during overcharge.

shuttle therefore allows the movement of current through the electrolyte, preventing potential  $O_2$  evolution. Note that the redox shuttle maintains the electrode potential at 2.95 V vs  $Li^+/Li$  under a current load of  $0.12\text{ A g}^{-1}$  (based on the mass of  $Li_2O$ ). This is important because  $O_2$  can only be thermodynamically liberated from  $Li_2O_2$  above 2.96 V ( $Li_2O_2 \rightarrow O_2 + 2Li^+ + 2e^-$ ). Indeed, the researchers monitored the gas release from the cell and did not detect  $O_2$  during charging. Only when currents larger than  $5\text{ A g}^{-1}$  were used to charge the cell, was the limit of the shuttle's ability to prevent the oxidation to  $O_2$  reached. It is the ability of the redox shuttle to prevent  $O_2$  evolution that significantly advances the system pioneered by Okuoka and co-workers<sup>3</sup>. In that work  $Li_2O$  was also shown to convert to  $Li_2O_2$  during charge, but without an internal charge shuttle they could not prevent  $O_2$  gas release beyond a capacity of around  $200\text{ Ah kg}^{-1}$ .

The choice of electrolytes, it seems, is essential in the prevention of  $O_2$  release. In their report Okuoka *et al.*<sup>3</sup> used a concentrated (4 molar) lithium bis(fluorosulfonyl)amide salt dissolved in acetonitrile, whilst Li and colleagues<sup>2</sup> adopted the organic carbonate based electrolyte (ethylene carbonate and diethylene carbonate with the salt lithium

hexafluorophosphate) that is regularly used in Li-ion batteries. In oxygen-saturated organic carbonate electrolytes, any  $LiO_2$  generated, will irreversibly react<sup>4</sup>, forming a variety of soluble and insoluble side-reaction products, which was the scourge of early  $Li-O_2$  battery work while more stable solvents were being sought<sup>4,5</sup>. However, as demonstrated by Li and colleagues<sup>2</sup>, when the partial pressure of the  $O_2$  is low, a superoxoradical species maintains its stability and acts as the redox shuttle between the positive and negative electrode preventing  $O_2$  evolution during overcharge.

In order to confirm that  $Li_2O$  converts to both  $Li_2O_2$  and  $LiO_2$  during charge and returns back to  $Li_2O$  upon discharge, the research team also undertook Raman,  $^6Li$  nuclear magnetic resonance, electron paramagnetic resonance spectroscopy measurements at various charge capacities and then at the full discharge capacity. The spectral information from these techniques provided strong evidence for the proposed chemical reactions. Nevertheless, the exact chemical structure of the shuttle species still requires further investigation. Going beyond this work it will be interesting to see whether an analogous sodium version of this system can be demonstrated. Moreover, an examination of redox shuttles that operate at about 3 V versus  $Li^+/Li$  in similar and

alternative electrolytes could allow the prevention of  $O_2$  evolution at even higher current rates.

Developments in Li-ion batteries based upon intercalation chemistry are approaching their theoretical energy storage limit<sup>6</sup>. Worldwide, numerous alternative battery chemistries are undergoing intense research to move beyond what Li-ion may offer in terms of energy storage. As yet, no obvious front runner has emerged. The work from Li and colleagues has added a further promising high energy storage battery system into the mix. Importantly the study includes a detailed spectroscopic understanding of the underlying (electro)chemical reactions involved that will greatly facilitate a rational basis towards future development of this system.  $\square$

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