

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 (Li-O₂), has stemmed from their high theoretical gravimetric energy densities.¹ In Li-O₂ batteries, the reactant (O₂) is not contained within the cell; instead, it enters from outside and undergoes reduction at the positive electrode, and is then combined with Li⁺ to form lithium peroxide (Li₂O₂) during discharge. The product Li₂O₂ has a much lower molecular weight to electron ratio than typical intercalation compounds used in Li-ion batteries (i.e. 23 for Li₂O₂ vs. 98 for LiCoO₂), which is the reason why the theoretical energy density of Li-O₂ greatly surpasses that of Li-ion. The challenges, on the other hand, are related to mass transport, getting O₂ 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 Li₂O₂. In addition, the air stream will have to be virtually free of moisture and CO₂ to avoid deleterious side reactions. Writing in *Nature Energy*², 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 Li-O₂ batteries, with an oxygen anion-redox (O²⁻/O₂⁻/O₂²⁻) electrode, which avoids the uptake and release of O₂.

The key idea behind the work is the development of an intimately mixed matrix of nanoscale lithium oxide, also known as lithia (Li₂O), and cobalt oxide (Co₃O₄). Li₂O exists as evenly dispersed domains on the order of 5 nm within the Co₃O₄. When oxidised, Li₂O can be transformed to lithium superoxide (LiO₂) and Li₂O₂, via redox reactions between O²⁻/O₂⁻, O²⁻/O₂²⁻, and possibly O₂²⁻/O₂⁻. In particular, the researchers showed that the LiO₂ and Li₂O₂ can be reduced back to Li₂O with a discharge capacity of around 550 Ah 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 1000 Wh/kg was shown, which rivals the Li-O₂ cell and out-competes the state-of-the-art Li-ion technology by a factor of 2.5-3 at the materials level.¹ 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 (Sh⁻) is created from the reaction between surface exposed LiO₂ and the electrolyte solvent (ethylene carbonate). Sh⁻ diffuses to the negative electrode where it is further reduced (Sh²⁻); subsequently the shuttle (Sh²⁻) diffuses back to the positive electrode where it is oxidised. The redox shuttle therefore allows the movement of current through the electrolyte, preventing potential O₂ evolution. Note that the redox shuttle maintains the electrode potential at 2.95 V vs. Li⁺/Li under a current load of

0.12 A g⁻¹ (based on mass of Li₂O). This is important because O₂ can only be thermodynamically liberated from Li₂O₂ above 2.96 V (Li₂O₂ → O₂ + 2Li⁺ + 2e⁻). Indeed, the researchers monitored the gas release from the cell and did not detect O₂ during charging. Only when currents larger than 5 A g⁻¹ were used to charge the cell, was the limit of the shuttle's ability to prevent the oxidation to O₂ reached. It is the ability of the redox shuttle to prevent O₂ evolution that significantly advances the system pioneered by Okuoka *et al.*³. In that work Li₂O was also shown to convert to Li₂O₂ during charge, but without an internal charge shuttle they could not prevent O₂ gas release beyond a capacity of around 200 Ah kg⁻¹.

The choice of electrolytes, it seems, is essential in the prevention of O₂ release. In their report Okuoka *et al.*³ used a concentrated (4 molar) lithium bis(fluorosulfonyl)amide salt dissolved in acetonitrile, whilst Li and colleagues² 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 LiO₂ generated, will irreversibly react,⁴ forming a variety of soluble and insoluble side-reaction products, which was the scourge of early Li-O₂ battery work in searching for more stable solvents.^{4,5} However, as demonstrated by Li and colleagues², when the partial pressure of the O₂ is low, an organic LiO₂ species maintains its stability and acts as the redox shuttle between the positive and negative electrode preventing O₂ evolution during overcharge.

In order to confirm that Li₂O converts to both Li₂O₂ and LiO₂ during charge and returns back to Li₂O 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 ca. 3 V vs. Li⁺/Li in similar and alternative electrolytes could allow the prevention of O₂ evolution at even higher current rates.

Developments in Li-ion batteries based upon intercalation chemistry are approaching their theoretical energy storage limit.⁶ 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.

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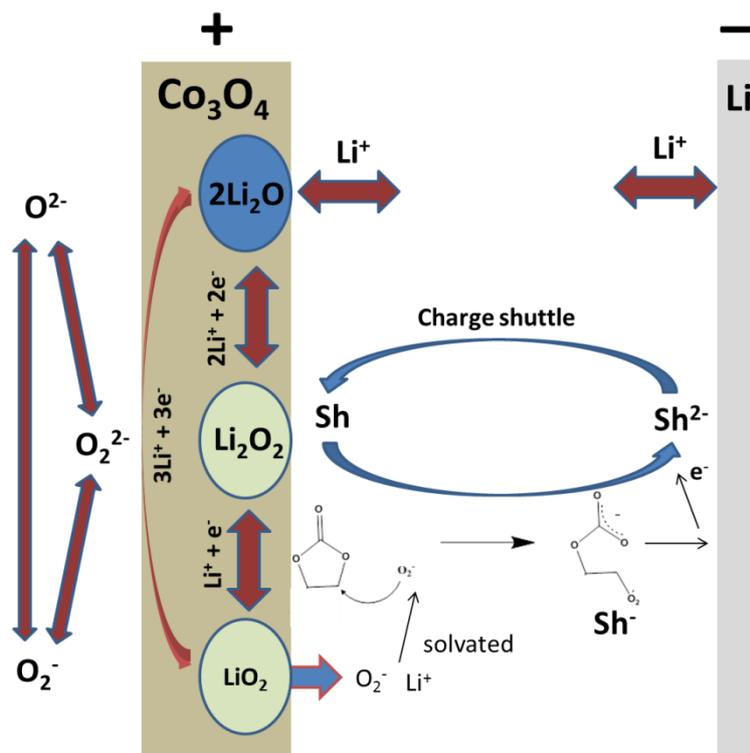


Figure 1: Operation mechanism of the sealed Li-ion cell. A reversible lithium oxide-peroxy/superoxide positive electrode and lithium metal negative electrode are schematically shown. Nanoscale lithium oxide (Li_2O) within a Co_3O_4 matrix can be reversibly transformed to lithium peroxide (Li_2O_2) and lithium superoxide (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 the symbols of 'Sh', 'Sh⁻' and 'Sh²⁻') is generated from the reaction of surface exposed LiO_2 and the solvent ethylene carbonate. The shuttle (Sh^-) diffuses to the negative electrode where it is further reduced (Sh^{2-}); subsequently the shuttle (Sh^{2-}) diffuses back to the positive electrode where it is oxidised by giving up two electrons (Sh). The shuttle process protects the cell from oxygen gas release during overcharge.

References

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