

BATTERIES

Thousands of cycles

Potassium-air batteries, which suffer from oxygen cathode and potassium metal anode degradation, can be cycled thousands of times when an organic anode replaces the metal.

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Mobile energy sources are the engine of modern society. One of the most advanced sources, lithium-ion batteries, are approaching the limits of their development potential in terms of energy storage. Moreover, with the widespread adaptation of batteries into large scale applications, other properties such as eco-friendliness and cost are becoming more important¹. These additional requirements have spurred tremendous research into alternatives², such as metal-air batteries³. Theoretically, these store more energy per unit mass because they use alkali metals (lithium, sodium, or potassium) at the anode and oxygen – drawn from air – at the cathode, instead of expensive and toxic cobalt at the cathodes in current lithium-ion batteries. Whilst metal-air batteries involve seemingly simple reactions, parasitic reactions degrade cell components, severely limiting cycle life. Now, in *Nature Materials*, Yi-Chun Lu and coworkers show that one variant, the potassium-O₂ (K-O₂) battery, can achieve an impressive cycle life of several thousand cycles by meticulously excluding the origins of degrading processes⁴.

Reversible cycling of metal-O₂ cells has been claimed before. However, these studies mostly forced discharge and charge capacity to match without substantiating claims by using quantitative measures of the involved electroactive species. The far fewer studies that quantified species invariably found significant deviations from the ideal³. For the K-O₂ cell, the electrochemical reaction $O_2 + e^- + K^+ \rightleftharpoons KO_2$ establishes a clear link between charge passed, O₂ consumed and KO₂ formed. Lu and coworkers used complementary quantitative measures to show that their cell obeys these requirements very closely over hundreds of cycles, much better than other cells. The reasons are rooted in the fundamental electrochemistry at the cathode whilst obeying the anode.

Considering the anode, K metal is incompatible with the commonly used dimethylsulfoxide electrolyte and also cycles poorly in other organic electrolytes. The authors replaced K metal by a liquid aromatic hydrocarbon that can undergo reversible electroreduction in the presence of alkali metal ions. Such reactions have been known such as for Na with naphthalene. Now Lu and coworkers push this to the limit for K⁺ storage using a new modification, biphenyl with a methyl group attached, which stores K⁺ at only ~0.14 V higher than K metal (Fig. 1a). This makes the cell voltage (the difference between K metal/K⁺ and the O₂/KO₂ couples) as large as possible by getting as close as possible to the K metal/K⁺ couple.

Oxygen redox chemistry, the reactions at the heart of the K-O₂ cell's cathode, is also central to energy storage in biology. Prominent examples include cellular respiration, where O₂ is reduced, and photosynthesis, where O₂ is released. Accessed redox states are molecular O₂, superoxide (O₂⁻), peroxide (O₂²⁻), and oxide (O²⁻). Broadly speaking, metal-O₂ cells resemble these processes during discharge and charge. Li⁺, Na⁺, and K-O₂ cells with an organic and proton-free electrolyte are most widely investigated. Consequently, cells have been described, where on discharge O₂ is reduced in presence of alkali metal cations to, e.g., Li oxide (Li₂O)⁵, Li or Na peroxide (Li₂O₂ or Na₂O₂)^{3,6}, or Na or K superoxide (NaO₂ or KO₂)^{6,7}. Potassium is the only cation amongst H⁺, Li⁺, Na⁺ and K⁺ that prefers the superoxide (Fig. 1b).

The reduction states of O₂ and the ways to reach them determine possible unwanted reactions. Amongst challenges towards practical metal-O₂ cells, most vexing are parasitic reactions that decompose cell components, leading to early cell failure. Researchers have long been puzzled by these parasitic reactions. Reactivity of the superoxide or peroxide with the electrolyte was assumed to be responsible, since they are strong nucleophiles and bases. However, research now casts serious doubt that typically used organic electrolytes react significantly with reduced oxygen species.⁸ Lu and colleagues now provide more evidence that the more reactive superoxide, specifically KO₂, is compatible with organic electrolytes and can be cycled reversibly. They argue forcefully that excluding impurities, e.g., proton-containing by-products formed at a K metal anode, is required for stability. For this purpose, they introduced a ceramic K⁺ conducting membrane. Protons would drive superoxide to convert to unwanted peroxide which then triggers further side reactions (Fig. 1b).

A natural expansion of this work is to fully exploit the energy density that the biphenyl–KO₂ cell promises. The large cycle number has been demonstrated by limiting cathode capacity to about half the full discharge capacity. The available pore space in the porous cathode is not fully filled with KO₂ on discharge. Furthermore, biphenyl concentration at the anode was a third of the maximum solubility. Restricting the capacity below the theoretical maximum often allows for better cyclability, but cuts energy⁹. Further work should therefore aim to fully fill pore space at the cathode with KO₂ at high rates, while at the anode biphenyl solubility may be expanded or even suspensions used.

Looking forward, this work provides an encouraging perspective for other metal-O₂ cells. In terms of energy, both cycling peroxide and using Na⁺ or Li⁺ instead of the heavier K⁺ would be preferable. Li₂O₂, used in Li-O₂ cells, provides a factor of ~4 larger energy density than KO₂. Given that as the most reactive considered superoxide can cycle that reversibly, reactivity of Li₂O₂ is not expected to be the actual barrier. Instead, highly reactive singlet oxygen (¹O₂) is now recognized as the major driver of parasitic chemistry¹⁰. The thermodynamics of K⁺ appears to avoid singlet oxygen. Biological systems also face singlet oxygen formation when passing between O₂, superoxide and peroxide and have learned to cope. Better understanding of the singlet oxygen formation mechanisms in Li- and Na-O₂ cells may hence enable similar cyclability, as now demonstrated for the K-O₂ cell.

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References:

1. Larcher, D. & Tarascon, J. M. *Nat. Chem.* **7**, 19-29, (2014).
2. Choi, J. W. & Aurbach, D. *Nat. Rev. Mater.* **1**, 16013, (2016).
3. Aurbach, D., McCloskey, B. D., Nazar, L. F. & Bruce, P. G. *Nat. Energy* **1**, 16128, (2016).
4. Cong, G., Wang, W., Lai, N.-C., Liang, Z. & Lu, Y.-C. *Nat. Mater.*, doi:xxx (2019).
5. Xia, C., Kwok, C. Y. & Nazar, L. F. *Science* **361**, 777-781, (2018).
6. Hartmann, P. et al. *Nat. Mater.* **12**, 228–232, (2012).
7. Xiao, N., Rooney, R. T., Gewirth, A. A. & Wu, Y. *Angew. Chem. Int. Ed.* **57**, 1227-1231, (2018).
8. Bryantsev, V. S. et al. *J. Electrochem. Soc.* **160**, A160-A171, (2013).
9. Freunberger, S. A., *Nat. Energy* **2**, 17091, (2017).
10. Mahne, N. et al. *Nat. Energy* **2**, 17036, (2017).

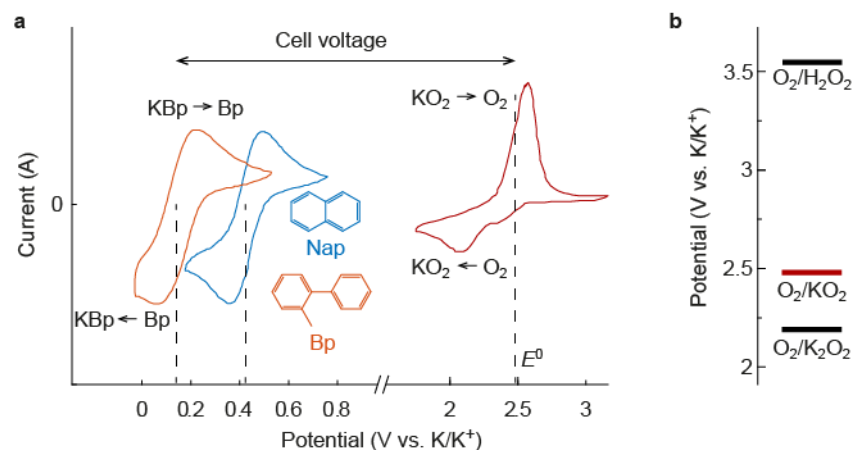


Figure 1 | Thermodynamics of the potassium-O₂ cell. **a**, Redox processes in the reported cell with naphthalene (Nap, blue) or 2-methylbiphenyl (Bp, orange) anode, K⁺ electrolyte, and O₂ cathode (red) as measured by cyclic voltammetry. The vertical dashed lines indicate the standard redox potentials E^0 (generally half way between the negative and positive current peak) of the processes. Bp and KBp indicate the oxidized (K⁺ free) and reduced (K⁺ containing) form of Bp, respectively. **b**, Standard redox potentials E^0 of the O₂/K₂O₂, O₂/KO₂, and O₂/H₂O₂ redox couples on the K/K⁺ scale. A higher value means a thermodynamically more favourable process. Hence, KO₂, the discharge product in the K-O₂ cell will not spontaneously convert to K₂O₂. However, in the presence of protons (H⁺) it will spontaneously convert to H₂O₂ (and further to H₂O, not shown, at 4.15 V on the K/K⁺ scale). Panel **a** adapted from ref. 4, NPG.