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BATTERIES & SUPERCAPS
Editorial

Special Collection

Coming up for Air: Breathing Air with Metal for Energy Storage

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The current technology for Li-ion batteries cannot fully meet our increasing demand for energy. Therefore, rechargeable batteries with high energy density, high rate performance, long cycling life, and intrinsic safety are urgently needed. Among various candidates for next-generation batteries, metal–air batteries (MABs) have attracted broad attention because of their incomparably high theoretical energy density. This feature of MABs can enrich the application market of portable electronics, electric vehicles, and large-scale energy reserves. However, the rate performance and battery life are lackluster compared with conventional Li-ion batteries. These obstacles hinder the exploration and full demonstration of the merits of MABs. Throughout the history of MABs, pushing the capacity to their theoretical values and at the same time optimizing the rate capability and lifespan are top priorities.

Typically, a MAB consists of a metal anode (Li, Na, K, Ca, Zn, Mg, Fe, Al), the electrolyte, and a porous cathode. During discharge, the metal anode releases metal ions to the working electrolyte, while O_2 is reduced to combine with the metal ions from the electrolyte to form discharge products on the cathode. Charging follows the reverse process. The most widely accepted cathodes in MABs are carbon-based materials because of their abundant conductivity, light weight, tunable nanostructures and properties. By regulating cathodes with specific holes, heteroatoms, catalytic particles, both oxygen reduction and oxygen evolution reactions (ORR and OER) are enhanced to reduce polarization and the rate capabilities are improved. There are many works related to the rational design of cathodes to promote the performance of MABs. In this Special Collection, Liang and co-workers present a high-quality Review on recent work of carbon-based bifunctional oxygen catalysts for zinc-air batteries (10.1002/batt.201900052) with a comprehensive introduction to carbon-based catalysts. However, carbon-based electrocatalysts are not stable in MABs, leading to side products, which are detrimental to the cycling performance. Carbon-free cathodes can alleviate complex chemistry in MABs, so it is helpful to understand the intrinsic chemistry. In addition, carbon-free cathodes are very stable so that a longer life is achievable. Chen and co-workers provide a Minireview on carbon-free cathodes for Li–O_2 batteries in this collection (10.1002/batt.20180133).

The Li–O_2 battery is the most popular MAB because of its highest theoretical energy density. To probe the mechanisms during discharge and charge, many in situ and operando investigations have been proposed to shed fresh light on the invisible phenomena through ex situ characterizations. However, the reported findings are not consistent, often due to different experimental conditions. For instance, it is controversial what exactly initial interphase of Li_2O_2 decomposition is. Besides, traditional techniques cannot reveal interactions on the atomic level. Bulk Li_2O_2 has a high electric resistance, but the electrochemically formed Li_2O_2 in Li–O_2 battery is conductive. It is very difficult to probe the origins for the differences among various results. Therefore theoretical analysis is important and powerful as a supplement of experimental results. Moreover, theoretical calculations are especially useful to conduct high-throughput screening for stable solvents and catalysts. Here, in the Minireview on the first-principles computations on Li–O_2 batteries (10.1002/batt.201900010) by Zhou and co-workers, the ORR and OER on Li_2O_2 as well as cathode, electronic and magnetic properties of Li_2O_2, charge transfer and solvent stability are discussed, very useful for understanding the chemistry behind Li–O_2 batteries. Adding redox mediators (RMs) can further lift the capacity and rate capability. Different with the catalysts on cathodes, RMs dissolve well in electrolytes, thus OER and ORR can be catalyzed more effectively. He and co-workers deliver a Review on advances and challenges of redox mediators in aprotic Li–O_2 batteries (10.1002/batt.201900045), in which they present new insights into the mechanisms of how the RMs work to improve the capacity and rate performance as well as on the problems RMs bring. To lengthen the life of Li–O_2 batteries, a stable and safe anode is non-negligible. However, the Li situation in Li–O_2 batteries is different from that of Li-ion or Li–S batteries because the Li in Li–O_2 batteries is exposed to O_2 and moisture. Consequently, developing effective strategies that protect the Li anode, in particular in Li–O_2 batteries, is highly desirable. Yu, Huang, Zhang, and co-workers summarize the characterization techniques on dendrite growth and solid–electrolyte interface (SEI) evolution and various anode protection strategies

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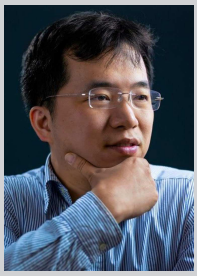

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(10.1002/batt.201900031) in this collection, which should inspire more efforts in this direction.

Compared to Li–O_2 batteries, Na–O_2 batteries have the advantage that Na is more abundant and cheaper than Li. Lithium reserves will become depleted in the next decades if we keep up the current rate of consumption, which will restrict its use in Li-ion and Li–O_2 batteries. In contrast, sodium is abundant in the ocean, so that Na–O_2 batteries are likely to replace Li–O_2 batteries once the lithium becomes scarcer. Therefore, Na–O_2 batteries have attracted much attention since 2012 when the first Na–O_2 was reported and the development since then has been swift. Li and co-workers present an overall review on the aprotic Na–O_2 batteries, including reaction mechanisms, anode, electrolyte, and cathode (10.1002/batt.201900015).

Even though recent research has delivered impressive results, some urgent problems such as safety, electrolyte decomposition, and the influence of air components on battery performance still need to be resolved. We hope this Special Collection can help the energy storage community understand the state of the art of MABs, which is beneficial to achieve high-performance MABs for practical applications.