



Bifunctional Catalysts for Metal-Air Batteries

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Owing to the continued depletion of fossil fuels and rapidly increased dependency on electrical energy, it is more important now than ever to develop advanced energy storage systems with an efficient energy saving and emission reduction. As a class of efficient energy storage devices, batteries can be user friendly, highly compact, and portable with a high energy density and stability, attractive for electronic devices, electrical automobile vehicles, and even large-scale electric grids. Having reasonably high energy densities (typically, 200–250 Wh/kg), Li-ion batteries (LIBs) have been widely used in our electricity-dependent society. However, batteries with an even higher energy density and longer operation stability than those of LIBs are needed for various specific applications, including hybrid and/or fully electrical vehicles with a low greenhouse gas emission to replace fossil fuel vehicles. In this regard, metal-air batteries (MABs) with the combined features of LIBs and fuel cells, consisting of a metal anode, an air-breathing cathode and an electrolyte, are very promising candidates. The theoretical energy densities of MABs range from ca. 700–10 000 Wh/kg, which is 3–30 times higher than that of LIBs.

Depending on the types of electrolytes, MABs can be classified into aqueous and nonaqueous MABs, though various metals, such as Zn, Fe, Al, Mg, Li, Na, K and Ca, can be used as the anode. Zn-air, Al-air, Fe-air, and Mg-air batteries can be fabricated using aqueous electrolytes while Li-O₂, Na-O₂, K-O₂ and Ca-O₂ batteries typically work with nonaqueous electrolytes. Among them, Zn-air and Li-O₂ batteries have recently attracted enormous research attention owing to their high energy density and good performance consistency.

Compared with LIBs, Zn-air batteries are cheap with a low fabrication cost around 10 \$/kW/h and possess a high theoretical energy density of about 11 140 Wh/kg, which is very close to the gasoline energy density of 12 200 Wh/kg. However,

the practical advancement of MABs has been largely limited by the intrinsic sluggish kinetics of the oxygen-reduction reaction (ORR) and the oxygen-evolution reaction (OER) during the discharge and charge process, respectively. Therefore, efficient bifunctional catalysts and well-defined cathodes of a hierarchically structured tri-phase boundary for simultaneously interfacing with electrolyte and gaseous oxygen are highly desirable. Extensive research efforts have been made worldwide to develop efficient catalytic cathode materials for MABs. As a result, various transition metal oxides (TMO), TM-dioxides and even TM-triple oxides, alloyed and/or composited with various carbon nanomaterials, have been devised as the cathode in MABs, as illustrated by this special issue that comprises two critical review articles, three minireview articles and six research articles on recent advancements in this rapidly developing field.

The development of efficient and stable ORR and OER bifunctional electrocatalysts is most important and challenging. In this special issue, Hacker et al. provide an article on the long-term operation of Zn-air batteries using a perovskite-catalyzed cathode (10.1002/batt.201800094) while Metin et al. report the innovative synthesis of silica-coated ZnFe₂O₄ nanoparticles as cathode catalysts for rechargeable Li-air batteries (10.1002/batt.201800095). In the same issue, Zhang et al. report N-doped porous carbon formed by thermal sugar bubbling as efficient metal-free bifunctional catalysts for high-performance flexible solid-state Zn-air batteries with a high power density of 50 mW/cm² and good cycling stability over 50 hours (10.1002/batt.201800105). Besides, Zeolitic Imidazolate Frameworks (ZIF-8) have been used as the precursors for developing Co-based catalysts supported by hierarchically structured carbon materials, including the carbon-caged Co nanoparticles (reported by Chen et al., 10.1002/batt.201800143) and CoS₂/CoS₂ core-shell particles embedded into N-doped carbon supported by a graphene foil (reported by Hou et al., 10.1002/batt.201800098). Also, in this special issue, Risch et al. report the importance of electrochemical history of the cathode for bifunctional ORR-OER activities on the epitaxially (001)-oriented La_{0.6}Sr_{0.4}MnO₃ perovskite surfaces (10.1002/batt.201800119). The aforementioned advancements and more are reviewed by Shao et al. focusing on metal-organic framework derivatives as oxygen catalysts for Zn-air batteries (10.1002/batt.201800093), Wang et al. on functional electrocatalysts derived from Prussian blue and its analogues for metal-air batteries (10.1002/batt.201800116), Ivey et al. on direct deposition synthesis of bifunctional catalysts for metal-air batteries (10.1002/batt.201800069), Xia et al. on transition metal oxides as bifunctional catalysts for Li-air and Zn-air batteries (10.1002/

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An invited contribution to a Special Issue on Bifunctional Catalysts for Metal-Air Batteries



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Dr. Chunyi Zhi got his PhD degree in physics from the Institute of Physics, Chinese Academy of Sciences. After that, he started to work as a postdoctoral researcher in the National Institute for Materials Science (NIMS) in Japan, followed by a research fellowship in the International Center for Young Scientists in NIMS and a permanent position in NIMS as a senior researcher. He is currently an associate professor in the Department of Materials Science & Engineering, City University of Hong Kong. Zhi's research focuses on flexible/wearable energy storage devices etc. He received the NML award, CityU president award, outstanding research award for junior faculty and outstanding supervisor award.



Prof. Xinliang Feng has been a full professor and the head of the Chair of Molecular Functional Materials at Technische Universität Dresden since 2014. He received his BS degree in 2001 and MS degree in 2004. Then he joined the Max Planck Institute for Polymer Research (MPIP), where he obtained his PhD degree in April 2008. In December 2007, he was appointed as a group leader at the MPIP and in 2012 he became a distinguished group leader. His current scientific interests include graphene, synthetic two-dimensional materials, organic conjugated materials, and carbon-rich molecules and materials for electronic and energy-related applications.

batt.201800082), and Kang et al. on bifunctional oxygen electrocatalysts for Li-O₂ batteries (10.1002/batt.201800127).

In spite of the numerous progress that has been achieved, the catalytic mechanism, the design principle for efficient ORR/OER catalysts, and the structure-performance relationship for the

cathodic catalysts in MABs are still far from being well understood. More in-depth experimental and theoretical investigations are needed for potential commercial success. We hope this timely and informative special issue will help the scientific community to find an effulgent way forward.