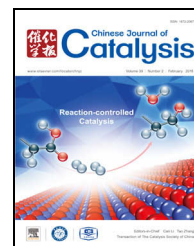


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Review

Metal-organic frameworks for highly efficient oxygen electrocatalysis



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ABSTRACT

Metal-organic frameworks (MOFs) are a series of highly porous crystalline materials, which are built from inorganic metal nodes and organic linkers through coordination bonds. Their unique porous structural features (such as high porosity, high surface areas, and highly ordered nanoporous structures) and designable structures and compositions have facilitated their use in gas capture, separation, catalysis, and energy storage and conversion. Recently, the design and synthesis of pure MOFs and their derivatives have opened new routes to develop highly efficient electrocatalysts toward oxygen reduction reactions (ORR) and oxygen evolution reactions (OER), which are the core electrode reactions in many energy storage and conversion techniques, such as metal-air batteries and fuel cells. This review first discusses recent progress in the synthesis and the electrocatalytic applications of pure MOF-based electrocatalysts toward ORR or OER, including pure MOFs, MOFs decorated with active species, and MOFs incorporated with conductive materials. The following section focuses on the advancements of the design and preparation of various MOF-derived materials—such as inorganic nano- (or micro-) structures/porous carbon composites, pure porous carbons, pure inorganic nano- (or micro-) structured materials, and single-atom electrocatalysts—and their applications in oxygen electrocatalysis. Finally, we present a conclusion and an outlook for some general design strategies and future research directions of MOF-based oxygen electrocatalysts.

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1. Introduction

Electrocatalytic oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) are very important in the realm of electrochemistry to achieve energy storage and conversion

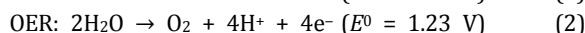
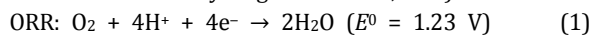
through the transformation between oxygen and water. ORR (cathodic) and OER (anodic) are half-cell reactions in regenerative fuel cells and rechargeable metal-air batteries. Typically, a four-electron transfer mechanism is favorable, as shown in the following reactions (the standard potential is reported in ref-

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erence to the reversible hydrogen electrode, *RHE*):



Although the elementary steps of ORR/OER may differ based on different mechanisms (dissociation (ORR)/recombination (OER), associative, or peroxy) and electrolytes (acidic, alkaline, or neutral), three types of oxygen species, OH^* , O^* and OOH^* , have been accepted as intermediates during ORR/OER processes (Fig. 1) [1]. High-energy barriers of bond breaking or formation and multiple steps of proton and electron transfer result in their sluggish kinetics. Meanwhile, the triple “liquid-solid-gas” interfaces, where the reactions occur, hinder fast kinetics. Therefore, efficient electrocatalysts are urgently required.

Among the as-developed oxygen electrocatalysts, platinum group metals (PGMs), such as Pt & Pd (for ORR) and Ir & Ru (for OER), are highly active but still suffer from high cost and low reserves. Another serious issue associated with PGMs is their poor durability under continuous operating conditions. Therefore, it is of great interest to develop low-cost and earth-abundant electrocatalysts with comparable or superior catalytic performance to PGMs [2–10]. For PGM-free electrocatalysts, metal-free electrocatalysts (typically with nonmetal dopants [11]) (e.g., N, S and P) and transition metal (TM)-based ones, such as metallic TM, TM-oxides, TM-hydroxides, TM-chalcogenides (sulfides and selenides), TM-phosphides, and TM-borates, have been widely investigated [12–14]. Most efforts aim to increase the number of exposed active sites and boost intrinsic activity. Many synthetic protocols have been proposed and put into practice [13,15]. Generally speaking, high loading or highly porous and open structures are required to increase the number of exposed active sites, while fine tuning the compositions via facile routes is expected to boost intrinsic activity. Most importantly, the structure and the composition of an oxygen electrocatalysts should be well matched, resulting in synergistic effects for achieving high activity. It is still challenging, however, to simultaneously increase the number of active sites and boost intrinsic activity to realize a highly efficient oxygen electrocatalyst. Fortunately, a class of porous materials with inherent nanopores (generally pore sizes

smaller than 100 nm), namely metal-organic frameworks (MOFs), provides a promising route to design and prepare highly efficient oxygen electrocatalysts.

MOFs are constructed with metal nodes and organic linkers via their coordination effects, which have high surface areas and high porosity. In comparison with other conventional porous materials, such as activated carbons, mesoporous silica, and zeolites, the most attractive advantages of MOFs are their tunable and designable pore structures, compositions, and functions, which can be easily realized by selecting the proper metal nodes and organic linkers [16–18]. In other words, MOFs can be designed on account of the features of metal nodes and the characteristics of organic linkers. To facilitate the design of MOFs with specific structures, the design methods of “reticular chemistry” and “net-based approach” have been proposed by Yaghi et al. [19] and Robson [20], respectively, both of which are based on the theory of network topology. To realize the predesigned MOFs, efficient synthetic methods have been explored, such as liquid diffusion, hydrothermal (or solvothermal) methods, microwave-assisted methods, and mechanochemical synthetic methods [21–23]. Over the past decade, numerous kinds of MOFs (more than 20000) have been successfully synthesized by combining these design methods and various synthetic methods [22]. Recently, as the development of the properties and functionality of MOFs approach practical demands, some possible synthetic methods that can produce MOFs on a large scale also have been developed, such as electrochemical synthetic methods, flow chemistry synthesis, and spray drying [24]. Some manufacturers, such as BASF, MOF Technologies, and MOF Apps, already have the capability of producing some kinds of MOFs and are promoting the commercialization of MOFs [24]. Note that a synthetic method, especially for large-scale production, should meet the following requirements: low cost, high environmental sustainability, and reproducibility.

MOFs have many potential applications [25], including gas separation and storage [26], catalysis [27], photocatalysis [28], luminescence [29], chemical sensing [30], drug delivery [31], and energy storage and conversion [32]. Among the numerous functions of MOFs, the intrinsic activity of pure MOFs in many

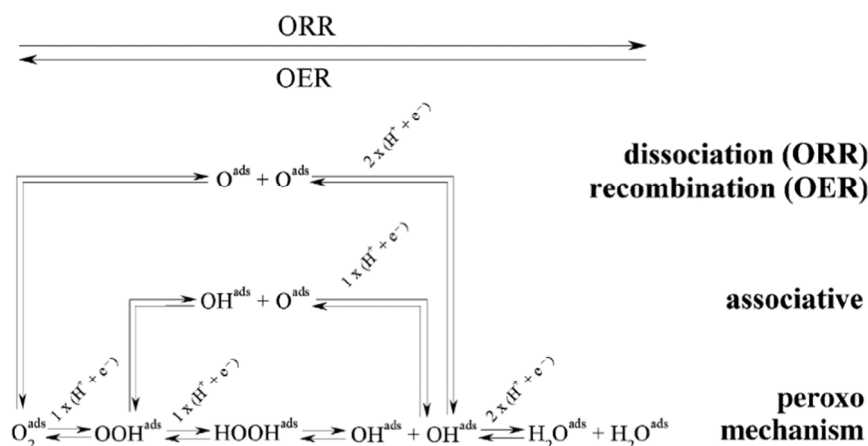


Fig. 1. Proposed ORR/OER mechanism. Reproduced with permission from Ref. [1], Copyright 2014 from WILEY-VCH.

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