

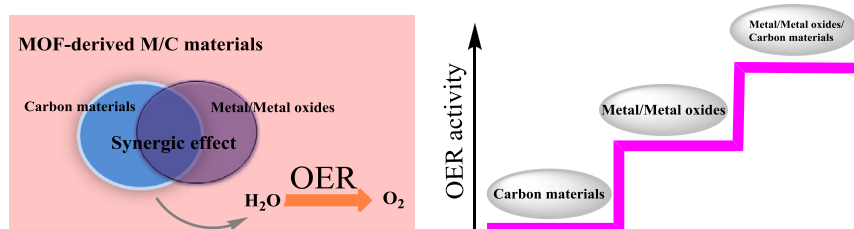
## MOF-derived metal/carbon materials as oxygen evolution reaction catalysts

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Water splitting has acquired much attention as the most appealing technology for hydrogen production in order to deal with urgent energy requirements and environmental issues. However, implementation of this technology in a future global-scale sustainable energy supply system is impeded by the slow kinetics of oxygen evolution reaction (OER). Several electrocatalysts have been developed so far to accelerate this reaction. Currently, metal organic frameworks (MOFs) have emerged as both the precursor and template of metal/carbon materials by in situ carbonization, which can catalyze OER efficiently. Recent progress in MOF-derived metal/carbon materials as OER catalysts is summarized here, including their structures, synthetic procedures and specifically highlighting the applications of these materials in OER. At the end, the existing key challenges and research directions for enhancing their performance are pointed out.

## 1. Introduction

The ever-increasing demand for clean fuels and sustainable energy sources triggers intense research efforts that focus on the development of new techniques for the production of hydrogen and oxygen via water splitting [1, 2]. Water splitting, either electrochemical or photoelectrochemical, consists of two half reactions: cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER) [3], which requires electricity or light as the source of energy, cathode and anode electrodes having appropriate catalytic properties and a supporting electrolyte, which could be alkaline or acidic [4]. However, the process is rarely applied in industrial applications till date because the OER is vigorously uphill and involves much large overpotentials, for which highly efficient and robust electrocatalysts are essentially required to

facilitate this reaction [5]. Precious metal oxides, such as  $\text{RuO}_2$  and  $\text{IrO}_2$ , are the most effective electrocatalysts known for OER, but their use for large-scale implementation is highly impeded by their scarcity, high cost and limited durability [6–8]. In recent years, various transition metal-based materials have been widely exploited as a family of earth-abundant alternatives to OER catalysts [9, 10]. Among these alternatives, 3d transition metals, including Fe, Co, Ni, Mn, Cu [11–21], and their oxides [21–24], mixed-metal oxides [25–29] have drawn much interest by offering high activities and excellent stabilities in OER [30].

However, the use of these electrocatalysts especially for applications involving electrochemical processes is restricted by the low electrical conductivity of transition metal oxides and their large volume changes during cycling, poor charge transfer, sensitivity to pH and

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unsatisfactory catalytic performance [31, 32]. Hence, novel strategies are highly desirable to develop new materials and/or enhance the electrocatalytic activity and stability of existing materials. One of such approaches comes with transition metals/metal oxides and carbon based materials, involving direct nucleation, growth and anchoring of inorganic nanomaterials on the functional groups of nanocarbon substrates. This approach affords strong chemical attachment and electrical coupling between the electrocatalytic inorganic nanomaterial and nanocarbon, leading to non-precious metal/carbon based electrocatalysts with superior catalytic activity and durability for OER, HER and ORR for fuel cells [33]. In these materials, the carbon nanostructures not only serve as the physical support of metals and metal oxides but also provide the channels for charge transport, promoting the good cyclic stability [34, 35] and the resulting excellent activity of the materials owes to the synergetic effect between the metals/metal oxides and nanocarbon [36–38]. In past few years, MOFs emerged as precursors and templates to prepare porous oxides, metal/carbon and metal oxide/carbon materials which can supply porous carbon species to couple with metal species by in situ carbonization to further enhance the relevant properties of electrocatalysts as water oxidation catalysts (WOCs) [39]. MOF-derived resulting products show excellent water oxidation performance because of inherited porous structure from MOFs, large surface area and narrow pores size distributions [40]. Since Chaikititilp and co-workers first adopted Co-based MOF (ZIF-9) as a precursor for the preparation of a nanoporous  $\text{Co}_x\text{O}_y\text{-C}$  hybrid as an electrocatalyst for the OER [41], various types of MOF-derived materials have been widely reported for OER. Very recently, Xia et al. have demonstrated the direct use of nanoporous carbon materials in water splitting [42].

This paper reviews the recent progress and advancements in developing MOFs based inorganic/carbon materials, with main focus on metal/carbon (M/C), mixed metals/carbon (MM/C), metal oxide/carbon (MO/C) and mixed metals oxides/carbon (MMO/C) nanostructures and also highlight several important examples of these materials for OER electrocatalysis. This review may guide the further scientific activities to design and synthesize high performance electrodes for water oxidation.

### 1.1. Thermodynamic potential of water splitting

An attractive, carbon-neutral alternative is solar-driven and electrochemical water splitting to produce hydrogen, a promising substitute to traditional fossil fuels (Fig. 1). All the materials required for efficient water splitting must consist of earth-abundant elements to attain global scalability [43].

Water oxidation demands a minimum potential of 1.23 V for supplying of electrons and protons to the other half reaction, which is accepted as the thermodynamic equilibrium potential (Eq. (1)) [44, 45].



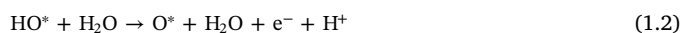
However, the potential practically required is larger than the thermodynamic equilibrium potential. Depending on solution pH, water

splitting proceeds by different half reactions (Fig. 2). In aqueous acid, the water oxidation half reaction has  $E^\circ = -1.23 \text{ V}$ , while the proton reduction half reaction has  $E^\circ = 0.00 \text{ V}$ . At pH 14,  $E^\circ$  is  $-0.83 \text{ V}$  for the hydrogen evolution half reaction and  $-0.40 \text{ V}$  for the water oxidation half reaction. These potentials are milder relative to the normal hydrogen electrode, which could have implications on catalyst stability and device design. It is worth noting that dioxygen reduction may compete with proton reduction under the acidic conditions [4].

The HER is a two-electron transport process which involves electrochemical  $\text{H}^+$  adsorption and electrochemical/chemical desorption of  $\text{H}_2$  to produce a single  $\text{H}_2$  molecule. The OER undergoes a four-electron transport together with the breaking of the O–H bond, and the O–O bond formation; thus, for a kinetically hindered process, a high potential is required to overcome the energy barriers [46].

### 1.2. OER mechanism

OER process involves four electron–proton coupled reactions, which occurred at surface of the catalyst to generate gaseous oxygen. From a thermodynamic viewpoint, the thermodynamic kinetics of the OER reactions under alkaline or acidic conditions is equivalent [47]. However, different mechanisms are involved under alkaline and acidic conditions. The proposed reaction mechanism for the OER under acidic conditions necessitates water binding to the surface and then irreversible removal of one proton and one electron to form a hydroxide (Eqs. (1.1)–(1.4)) [48]. Whereas, in alkaline media a reversible binding of hydroxide ion combined with a one electron oxidation is considered to precede a turnover-limiting electrochemical step resulting in the removal of one proton and one electron to generate a surface oxide species (Eqs. (1.5)–(1.8)) [49, 50]. This shift in mechanism between the pH extremes has been related to the kinetic facility of oxidizing hydroxide ion relative to water [51]. Density Functional Theory (DFT) calculations have also clearly shown that the slow kinetics of OER can be largely linked to the weak adsorption of intermediate  $^*\text{OOH}$  on the surface of the catalyst. Relatively high kinetic activities of the noble metal catalysts such as Ru and Ir-based catalysts are attributed to most favorable binding energy of the  $^*\text{OOH}$  and the better metallic conductivity of their oxides [52, 53]. The normally accepted mechanism under acidic conditions could be expressed as follows:



and for basic conditions:

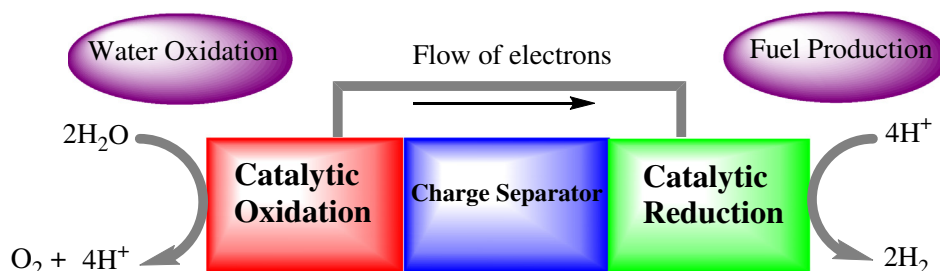


Fig. 1. Schematics of water splitting.

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