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Review

Recent developments in metal phosphide and sulfide electrocatalysts for oxygen evolution reaction

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ABSTRACT

Oxygen evolution reaction (OER), as an important half-reaction involved in water splitting, has been intensely studied since the last century. Transition metal phosphide and sulfide-based compounds have attracted increasing attention as active OER catalysts due to their excellent physical and chemical characters, and massive efforts have been devoted to improving the phosphide and sulfide-based materials with better activity and stability in recent years. In this review, the recent progress on phosphide and sulfide-based OER electrocatalysts in terms of chemical properties, synthetic methodologies, catalytic performances evaluation and improvement strategy is reviewed. The most accepted reaction pathways as well as the thermodynamics and electrochemistry of the OER are firstly introduced in brief, followed by a summary of the recent research and optimization strategy of phosphide and sulfide-based OER electrocatalysts. Finally, some mechanistic studies of the active phase of phosphide and sulfide-based compounds are discussed to give insight into the nature of active catalytic sites. It is expected to indicate guidance for further improving the performances of phosphide and sulfide-based OER electrocatalysts.

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1. Introduction

Growing society concerns has been focused on the environmental pollution and global energy crisis caused by consumption of fossil fuels. Hydrogen (H_2), with high energy density, small molecular mass and only clean water as the combustion product, is regarded as an ideal energy carrier for future energy storage and supply [1–5]. In addition, H_2 is also a critical chemical feedstock in the modern industry, for example, in synthesis of ammonia for fertilizer and hydrocracking in petroleum refining [6]. At present, the main strategy adopted to produce hydrogen is the steam reforming process from fossil resources, which uses both H_2O and CH_4 as the primary source for large-scale production of H_2. However, this production route not only aggravates the consumption of fossil fuels, but also contributes to the global CO_2 emission [7,8]. Therefore, there is an urgent need to search a clean, renewable and efficient route for H_2 production.

With a number of advantages such as using abundant water as starting material, no emission of greenhouse gases and other polluted gases, high hydrogen production efficiency and high-purity product, electrochemical water splitting for hydrogen and oxygen production is considered as a promising approach to provide affordable clean energy if renewable energy or surplus electricity is fully available [6]. Electrocatalytic water splitting, which is a reverse process of fuel cell reactions, involves the cathodic hydrogen evolution reaction (HER), and the anodic oxygen evolution reaction (OER). Compared to the

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more developed HER catalysts, OER catalysts is more complex and challenging [9]. Actually, as for the HER, which is based on a two-electron transfer ($2e^-$), it proceeds at a high rate in acidic conditions, where plenty of protons are available. In alkaline conditions, the scanty proton make the HER kinetics comparatively more sluggish, and its reaction rate directly depends on the anodic OER which supplies the protons to the cathode by the deprotonation of hydroxide ions. On the other hand, the OER, which involves a four sequential electron transfer mechanism ($4e^-$) as well as oxygen-oxygen bond formation, is a complicated and sluggish process, affecting the overall Faradaic efficiency of the electrolysis cell to a greater extent [10].

In practice, an electrolysis cell can never be performed under the theoretical decomposition potential because of various thermodynamic and kinetic hindrances. The absolute difference between the experimental potential and the thermodynamical potential is named as overpotential. Additional energy is demanded to overcome the overpotential, which is caused by polarization of various electrode processes. In order to ensure the electrolyzer practically efficient, both reactions require active and robust electrocatalysts to accelerate reaction process and finally reduce the electrolysis overpotential. Precious metal oxides (IrO_2/RuO_2) possess the best performance (activity and durability) for the OER, while large-scale industrial application of an electrolyzer has been impeded by their high cost and scarcity [11,12]. In order to speed up the industrialization of electrocatalytic water splitting and lower its industrial cost, numerous efforts have been stimulated to search for new electrocatalysts based on noble metals free elements [13]. Fortunately, nowadays there are increasingly many reports that claim that transition metal oxides, sulfides, selenides, nitrides, phosphides, and so forth are also highly efficient OER catalysts [14–24]. Among them, metal phosphide and sulfide electrocatalysts show super-activity for OER even as good as the traditional IrO_2 benchmark OER catalyst in alkaline media [25–28]. Therefore, it is necessary to summarize the new progress in this aspect.

In this review, after a brief description of the reaction mechanisms of OER in alkaline and acid electrolytes, we discuss the main barriers against accelerating the kinetic and thermodynamic process of OER in terms of activity. We try to categorize the findings reported in the literatures to provide a picture about metal phosphide and sulfide electrocatalysts for OER. The influence of some of important parameters, such as electrical conductivity, mass transport, active area and interface chemistry etc., on OER activity is discussed and commended. Then, the dominant role of less studied in situ evolution surface of metal phosphide and sulfide electrocatalysts is further summarized, which essentially include the catalytic property of metal cations and oxide/hydroxide anions in terms of the nature of true catalytic sites. Finally, we try to outline the further direction to facilitate the property of phosphide and sulfide catalysts for OER.

2. Reaction mechanisms and thermodynamics of the OER

An electrolyzer for electrocatalytic water splitting has four component parts: an electrolyte, a diaphragm, a cathode and an anode. In order to speed up the electrocatalytic water splitting reaction, hydrogen evolution catalysts (HEC) and oxygen evolution catalysts (OEC) are coated on the cathode and anode, respectively [29,30]. Although the thermodynamic potential for the electrocatalytic water splitting is 1.23 V under standard conditions (25 °C and 1 atm), an overpotential is required in a practical process. When an external voltage is applied to the electrodes, water molecules are decomposed and oxidized into oxygen at anode, meanwhile electron and proton combine to form hydrogen at cathode [31]. The hydrogen can be stored as fuels and the oxygen is released into the atmosphere. As stated in the introduction, though the production of purest H_2 is the main objective, more attention should be pay to the counter-reaction (OER), as it is one of several bottlenecks for the electrocatalytic water splitting and decides the overall Faradaic efficiency of the electrolytic cell.

In general, the electrochemical reaction occurred at the anode is proceeded via several proton/electron-coupled procedures [9]. The OER is highly pH sensitive, and the kinetics of the OER is quite different in acidic to alkaline media. In acidic and neutral conditions, two water molecules (H_2O) are oxidized into four protons (H^+) and oxygen molecule (O_2), while hydroxyl groups (OH^-) are oxidized and transformed into H_2O and O_2 in basic conditions. However, the anode catalysts for catalyzing OER in acid condition are mainly based on the precious Ir, Ru metals and their oxides. Other metals and their derived materials are not suitable for using as OER electrocatalysts due to their poor anti-acid corrosion [32–34]. Accordingly, almost all the metal phosphide and sulfide based materials are applied as OER electrocatalysts in alkaline electrolytes. In 1986, a detailed review on various reported OER mechanisms in acidic and alkaline media were reported by Matsumoto and Sato [35], including the Krasil'shchkov, Bockris [36], Yeager, and Wade [37] pathways in addition to the electrochemical oxide pathway [38]. Nowadays, the most recognized OER partway in alkaline media are shown as follows:

$$M + OH^- \rightarrow M\text{-}OH_{ads} + e^- \quad (1)$$

$$M\text{-}OH_{ads} + OH^- \rightarrow M\text{-}O_{ads} + H_2O + e^- \quad (2)$$

$$M\text{-}O_{ads} + M\text{-}O_{ads} \rightarrow 2M + O_2 \quad (3)$$

$$\text{or } M\text{-}O_{ads} + OH^- \rightarrow M\text{-}OOH_{ads} + e^- \quad (4)$$

$$M\text{-}OOH_{ads} + OH^- \rightarrow M + O_2 + H_2O + e^- \quad (5)$$

where, M represents the active site of catalyst surface, and "ads" is the adsorption species on the catalyst surface. All of the proposed mechanisms begin with an essential elementary step of hydroxide coordination to the active site under alkaline conditions, and then proceed via two main pathways with different proposed other elementary steps [36]. The first one is the direct coupling of two $M\text{-}O_{ads}$ intermediates, processing through the steps of (1)→(2)→(3). In the second pathway via (1)→(2)→(4)→(5), intermediate $M\text{-}OOH_{ads}$ is formed at first by the reaction of $M\text{-}O_{ads}$ with OH^-, and subsequently combined with another OH^- to produce O_2. In general, the thermodynamic barrier of Reaction (3) is always larger than those of reactions (4) and (5).

As for metal phosphides and sulfides, the OER reaction generally go through the second pathway [39]. The overpotential

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