



Review article

Iron-based heterogeneous catalysts for oxygen evolution reaction; change in perspective from activity promoter to active catalyst



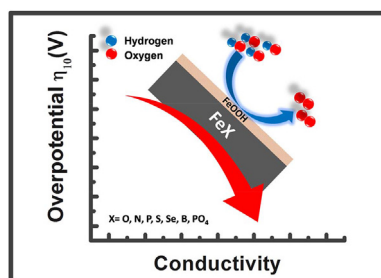
Harshad Bandal, K. Koteswara Reddy, Avinash Chaugule, Hern Kim*

Department of Energy Science and Technology, Smart Living Innovation Technology Center, Myongji University, Yongin, Gyeonggi-do, 17058, South Korea

HIGHLIGHTS

- Recent progress in development of Fe-based heterogeneous catalyst are reviewed.
- Role of Fe in mixed metal catalyst is also highlighted.
- A brief overview of existing challenges and future directions is summarized.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxygen evolution reaction is an integral part of energy storage technologies such as metal air batteries, water splitting, and regenerative fuel cells. However, oxygen evolution is 4 electron transfer process that suffers from sluggish reaction kinetics and indolent thermodynamics which mandates the use of a suitable noble metal catalyst. Considering the availability and cost of these precious metal catalysts, development of catalyst based on more abundant metal such as Fe is of vital interest for practical implication of these technologies. In this regards, over past few years several Fe based heterogeneous electrocatalysts are investigated for their electrocatalytic activity. Significant advances in improving the catalytic activity as well as exploring the catalytic mechanism are achieved in this area. Herein, we present an in-depth review on the recent progress in this field. Specific attention is given to design, synthesis, catalytic performance and strategies for improving their performance. A brief overview of existing challenges and future directions in the field of OER catalyst is also summarized.

1. Introduction

Continually rising energy demands, depletion of petroleum reserves and imminent threat of global warming has prompted extensive research on efficient utilization of clean and sustainable energy sources. However, these renewable sources of energy such as solar energy are characterized by their intermittent nature i.e. their availability varies depending on the time, season and geographic location [1]. Furthermore, solar energy is not concentrated source of energy and large solar panels must be constructed to obtain required power output [2].

Electricity harvested from solar energy must be stored with the help of a suitable energy storage system, like supercapacitor [3,4] or secondary batteries [5]. Alternatively, the electricity derived from the solar cell can be utilized to accomplish certain electrochemical transformation such as water electrolysis [6] or CO₂ reduction [7]. In this way, the intermittent solar energy can be stored indefinitely in the form of chemical fuels such as H₂ and hydrocarbons. Utilization of solar energy to drive water electrolysis is especially beneficial as hydrogen obtained during this transformation is a versatile carbon neutral energy carrier [8] that can be utilized directly in a fuel cell [9] or used as a reducing

* Corresponding author.

E-mail address: hernkim@mju.ac.kr (H. Kim).

agent to transform biomaterials [10] and CO₂ [10] into fuel.

The process of water electrolysis consists of two half reactions namely, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) both of which are critical for overall efficiency of water electrolysis [10]. HER is comparatively simple and can occur at relatively low overpotential in presence of several metal catalysts. The OER, on the other hand, involves 4 successive electron transfer and hence, it is defined by indolent kinetics and unreceptive thermodynamics [11]. As a result, under practical conditions OER occurs at an applied potential much higher than the equilibrium potential of OER. This excess overpotential is required to compensate activation barriers at cathode and anode and some other resistances [12]. Uncompensated resistance can be minimized by improving the cell design whilst, activation barriers can be reduced by implementing a suitable catalyst [12]. Until now, RuO₂ is considered as the best catalysts for OER but high price and low availability are limiting factors. In addition, RuO₂ get oxidize to soluble RuO₄ species under anodic potential leading to the poor stability under acidic and alkaline conditions [13,14]. Another precious metal oxide IrO₂ exhibited comparable catalytic activity and much better stability in acidic and alkaline conditions, but it is also oxidized to IrO₃ under anodic bias causing slow dissolution of IrO₂ during the OER. Thus, considering the low stability and high cost of these noble metal catalysts it is imperative to develop alternative non noble metal based electrocatalyst for OER.

Iron is one of the most abundant elements in the earth's crust, it also has less toxicity relative to other transition metals. Moreover, iron has very rich redox properties for activation of O₂ in biological system so, iron is extensively used for development of biomimetic complexes for oxygen activation [15,16]. Based on these consideration iron based compounds can be effective electrocatalyst for the OER. Unfortunately, hydrated oxide of iron which is the principal catalytic species during OER (under the anodic bias surface of most metals is oxidized to form layer of hydrated oxides) is poor conductor of electricity [17]. This causes the formation of schottky barrier between catalyst and electrolyte, as well as between catalyst and current collector leading to the poor activity of Fe based catalyst. In sharp contrast, deliberate or accidental doping of the iron into nickel and cobalt based catalysts such as oxides, hydroxides, sulfides, phosphides can dramatically improve their activity [18–21]. This enhancement in the catalytic activity can be partly attributed to the concurrent improvement in the electrical conductivity on doping of Fe. However, observed improvement in the electrical conductivity isn't sufficient to explain the corresponding improvement in catalytic activity [22]. To gain further insight in the origin of the high activity of these composites different in situ techniques such as X-ray adsorption fine structure (XAFS) [23], Raman [24], and Mossbauer [25] spectroscopy were used. The results of these experiments indicate that in these mixed metal catalysts Fe is the principal active center. Whereas, bulk of the catalyst provides a conducting matrix that can stabilize Fe in higher oxidation state. In light of these results, Fe is quite often used as a dopant to improve the catalytic activity of Ni and Co based catalyst. However, as the elemental abundance of Fe is several order of magnitude higher than any other transition metals, development of the OER catalyst having iron oxide as its key

component is highly desirable. This has inspired several works devoted towards the development of Fe based electrocatalysts for OER. However, despite great success of these works a comprehensive review about this topic is yet not published.

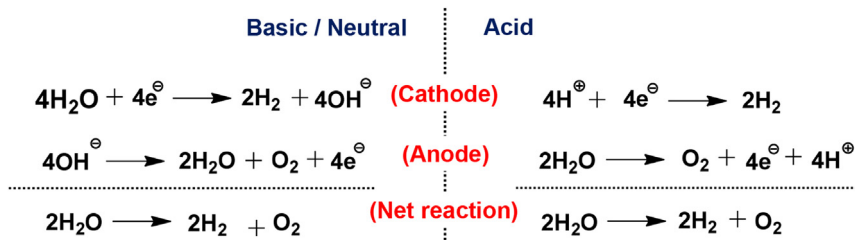
In this regard, the primary objective of this work is to summarize the recent progress in the field of iron based heterogeneous electrocatalysts for OER. We begin by describing the vital role of Fe in bimetallic catalysts such as Fe-Co and Fe-Ni based systems. As several excellent reviews entirely devoted to this topic are already available, instead of restating the obvious facts we focus our attention to only mechanistic aspects of these catalytic systems. Those who are interested in the recent progress in these catalysts are advised to refer excellent reviews on the relevant subjects [18,26–28]. For convenience, we have categorized monometallic iron based catalysts as Fe oxides/hydrated oxide (FeO_x), FeO_x/CNT composites, Fe@CN composites, Fe pnictides, and Fe chalcogenides. In each category a specific attention has been devoted design, synthesis, catalytic performance of these catalysts and strategies employed for improving their performance are described in detail. We have also included an in depth account on some newly emerging iron based electrocatalysts. A brief overview on current challenges and future perspective on this rapidly developing field is also outlined.

2. Oxygen evolution reaction

A typical electrolyzer is composed of three components namely an electrolyte, a cathode and an anode. To speed up the water splitting reaction, hydrogen and oxygen evolving catalysts are coated on the surface of cathode and anode, respectively. Water molecules are decomposed into hydrogen and oxygen under an externally applied potential. Depending upon the solution pH the OER may occur in different pathways. In acidic condition, OER proceeds by transforming two water molecules into protons and oxygen molecule (Scheme 1). Whereas, in alkaline and neutral solution OER involves oxidation of four hydroxide ion to water and dioxygen.

OER mechanism and reaction pathways are relatively complex and irrespective of identity of parent catalyst, OER generally occurs on the hydrous oxide layer formed in situ on the surface of the parent catalyst [29–31]. Hence, a brief overview of OER process on the surface of transition metal oxide can help to understand the activity trends observed. It must be noted that oxides of same metals prepared by different methods may have vastly different surface structures and OER on the resultant catalyst may occur by a distinctly different mechanism. Several mechanisms are proposed to describe the OER on different catalyst surfaces [32]. In most cases, the first step of process involves formation of intermediate such as MOH and MO. However, these mechanisms diverge from each other during subsequent steps which lead to the formation of oxygen. In spite of these differences, a general mechanism for the OER on oxides in acidic as well as alkaline solutions can be summarized as follow (Scheme 2).

There are two distinct pathways to generate dioxygen from MO intermediate. In the first pathway (Scheme 2.3), two MO centers directly combine to produce O₂. In the second route the MO intermediate



Scheme 1. Cell reactions for water electrolysis in different pH conditions.

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