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Review

In-situ electrochemical activation designed hybrid electrocatalysts for water electrolysis

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ABSTRACT

Developing transition metal-based electrocatalysts with rich active sites for water electrolysis plays important roles in renewable energy fields. So far, some strategies including designing nanostructures, incorporating conductive support or foreign elements have been adopted to develop efficient electrocatalysts. Herein, we summarize recent progresses and propose in-situ electrochemical activation as a new pretreating technique for enhanced catalytic performances. The activation techniques mainly comprise facile electrochemical processes such as anodic oxidation, cathodic reduction, etching, lithium-assisted tuning and counter electrode electro-dissolution. During these electrochemical treatments, the catalyst surfaces are modified from bulk phase, which can tune local electronic structures, create more active species, enlarge surface area and thus improve the catalytic performances. Meanwhile, this technique can couple the atomic, electronic structures with electrocatalysis mechanisms for water splitting. Compared to traditional chemical treatment, the in-situ electrochemical activation techniques have superior advantages such as facile operation, mild environment, variable control, high efficiency and flexibility. This review may provide guidance for improving water electrolysis efficiencies and hold promising for application in many other energy-conversion fields such as supercapacitors, fuel cells and batteries.

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1. Introduction

1.1. Background

The past few decades have witnessed the increased energy consumption along with world population growing and industrialization expanding. Fossil fuels as the dominant energy basis are now facing rapid depleting accompanied with severe environmental problems such as pollution and carbon emission [1–4]. Therefore, it is vital but still challengeable to construct sustainable energy systems while protecting environment concurrently.

Nowadays, many clean and alternative natural resources (such as solar and wind) are under extensive exploitation to be transformed and stored as electricity power [5–10]. However, the conversion efficiencies are limited by variability and intermittency of these natural resources. To solve the unstable energy supply, one promising approach is to convert electrical energy into stable chemical products. For example, the electricity-driven water

splitting technology can achieve the conversion from solar/electric energy to chemical energy in clean and efficient way [11–13]. Moreover, the hydrogen product is an ideal energy carrier to fulfill demands of fuels, fundamental supplying in refining petroleum, ammonia synthesis or “methanol economy” [14–16]. Therefore, enhancing efficiency of water electrolysis undoubtedly plays significant roles in renewable sources conversion and energy system adjustment in the future.

1.2. Fundamental principles of water electrolysis

Driven by electricity, water can be completely spitted into hydrogen (H₂) and oxygen (O₂) as the following equation:



In detail, water electrolysis consists of two half-cell reactions: hydrogen evolution reaction (HER) at the cathode ($2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g})$) and oxygen evolution reaction (OER) ($2\text{H}_2\text{O} (\text{l}) \rightarrow \text{O}_2 (\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$) at the anode. Theoretically, the applied potential of electrolysis cell voltage is 1.23 V under the standard condition (25 °C, 1 atm = 1.013 × 10⁵ Pa). In practice, the real water electrolysis needs a much larger voltage to overcome unfavorable

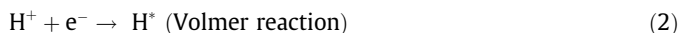
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drawbacks such as high overpotentials and sluggish kinetics, especially for OER. Thus it is essential to gain insight into electrochemical reaction process for providing guidelines of designing efficient catalysts.

Generally, the HER process is a two-electron transfer process in individual Volmer-Heyrovsky or Volmer-Tafel mechanism, where the adsorbed hydrogen (H^*) as intermediate on the electrode surface participates in the reaction pathways. The HER process highly depends on pH value of electrolytes. In acid solution, the HER proceeds according to the following steps:

- (i) Proton discharging to form an adsorbed hydrogen atom:

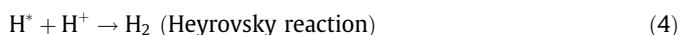


Subsequently, molecular H_2 can be formed via the following two alternative steps depending on the surface of electrodes.

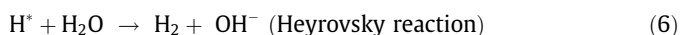
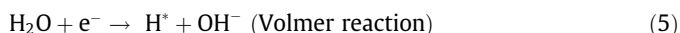
- (ii) The quick coupling of two adsorbed hydrogen atoms to generate a hydrogen molecule:



- (iii) Combination of one adsorbed hydrogen atom with a proton to generate a hydrogen molecule:



In alkaline condition, molecular H_2O participates in Volmer and Heyrovsky reactions due to the low concentration of H^+ :



The free energy of hydrogen adsorption (ΔG_{H^*}) is a crucial descriptor for the HER catalyst [17–19]. The negative ΔG_{H^*} represents favorable combination of H^* with the surface of electrode and Volmer step, whereas too negative value may cause slow proceeding of subsequent Tafel or Heyrovsky steps. In contrast, the positive value of ΔG_{H^*} leads to weaker interactions between protons and electrode surface and thus an inefficiency of the entire process.

On the anode of OER process, it is a more complicated reaction containing four-electron transfer and more surface-adsorbed intermediates. It is also a pH-dependent process (in alkaline or acid) [20–22], where the alkaline OER is mostly researched as shown in the following pathway:

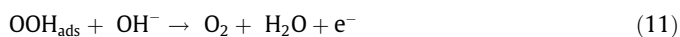


The “*” means active site of the catalyst and “ads” means the adsorption on the catalyst. The generation of molecular O_2 can be proceeded by two possible pathways as follows:

- (i) The combination of two O_{ads} intermediates to form O_2 :



- (ii) O_{ads} coupling with OH^- to form OOH_{ads} and subsequent combination with OH^- to form O_2 :



In theory, the thermodynamic potential value of OER is 1.23 V at 25 °C (vs. reversible hydrogen electrode (RHE)). Actually, a much higher potential is required for OER because of activation barriers and solution resistances, which will cause excessive energy con-

sumption and decrease conversion efficiency. In screening proper electrocatalysts for OER with low cost and high efficiency, first low transition metals such as Ni, Co and Fe and their derivatives [23–27] are demonstrated to be comparable to state-of-the-art noble electrocatalysts of Ir/Ru species.

1.3. General designing of nanostructured electrocatalysts

According to theory predictions, the HER activity as a function of ΔG_{H^*} can be described by a volcano plot (Fig. 1) [28]. In the plot, the value of ΔG_{H^*} for noble metal Pt is close to zero meaning the best activity. Besides, non-noble metals such as first row transition metals (Ni, Co, Fe, Mn and Cu), Mo and W exhibit competent activities and stabilities [21,29–31]. When coordinated with electronegative nonmetal atoms (e.g., C, N, P, and S), the electronic environments of transition metals can be modified to afford comparable activity to Pt [17,32–34]. The recent progresses of transition metals-based materials (mainly Ni, Co, Fe, Mo and W) and non-metal materials in comparison with noble metals have been listed in Table 1 for HER and Table 2 for OER. Therefore, transition metals and their derivatives hold promising in application for industrial water electrolysis in the future, which are also the main focus in this review.

It is acknowledged that electrochemical water splitting utilizing solid electrocatalysts is a typical heterogeneous catalysis process. The surface sites of materials as well as electron/mass transfer can be the two principal factors taken into consideration. Accordingly, the designing principles of efficient electrocatalysts are mainly based on the following aspects [91–95]: (i) increasing surface areas; (ii) increasing number of active sites; (iii) improving the electrical conductivities and (iv) tailoring electronic/chemical properties through incorporation/integrating of foreign species. In detail, the (i) and (ii) aim to increase the density of available active sites on the surface of materials; the (iii) approach is to enhance utilization efficiencies of active sites and the entire mass/electron transfer rate. The (iv) may integrate the above three factors to improve the electrocatalytic performances in a complex way. Overall, the HER activity enhancement can be achieved by creating sufficient surface sites and increasing their utilization efficiencies.

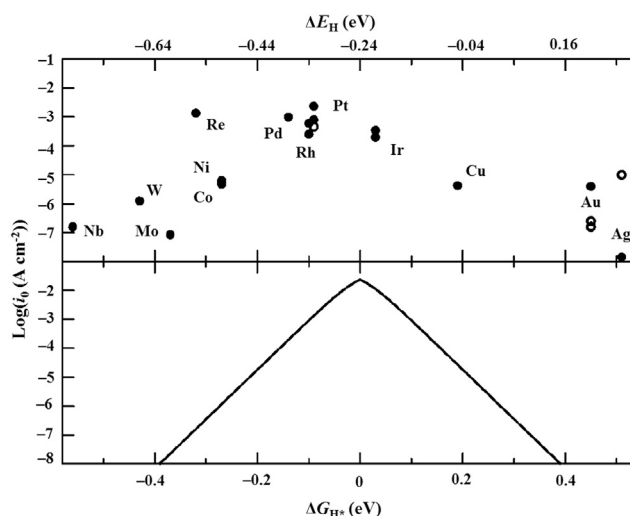


Fig. 1. Experimental exchange current data [$\log(i_0)$] (top) for hydrogen evolution (HER) in different metal plotted as a function of calculated hydrogen chemisorption energy per atom, ΔE_H (top axis). Reprinted with permission from Ref. [28], Copyright © 2005 The Electrochemical Society.

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