

Hydrogen Evolution Reaction

Subjects: [Others](#)

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In recent years, heteroatom doping has been found to be an effective strategy to improve the electrocatalytic hydrogen evolution reaction (HER) performances of nickel-based catalysts in acidic, neutral, and alkaline media.

nickel-based catalysts

heteroatom doping

electrochemical hydrogen evolution reaction

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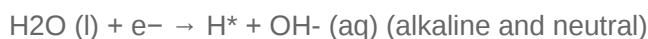
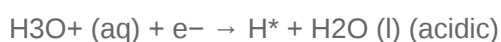
1. Introduction

As the pace of industrialization accelerates, non-renewable energy resources like fossil fuels are continuously consumed and their reserves are gradually reduced. Excessive consumption of fossil fuels is also causing the problem of continuous deterioration of the natural environment. The search for new sustainable energy sources has become a major concern in many countries^[1]. In the past few decades, energy resources such as wind, solar, hydroelectric power, and hydrogen, have been regarded as sustainable and environmentally friendly alternatives to fossil fuels^[2]. Hydrogen is among the most attractive energy sources for sustainable development owing to its high energy density. In addition, the combustion product of hydrogen, which is water only, is pollution-free.

Nowadays, H₂ mainly comes from the steam methane reforming of natural gas, which converts methane and water steam into carbon monoxide and hydrogen. However, this process has low energy efficiency, high cost, and produces carbon-containing residues that affect the purity of hydrogen and pollute the environment^[3]. Another hydrogen production technology is the use of electricity to electrolyze water so as to produce hydrogen. Hydrogen production through water splitting using solar-generated electricity has been considered as an efficient and clean way and has attracted much attention^[4]. Water electrolysis consists two half reactions: the hydrogen evolution reaction (HER) at the cathode, and the oxygen evolution reaction (OER) at the anode^[5]. The cathodic hydrogen evolution process involves two electronic transfers, and the pathways have been proposed as follows: ^[6].

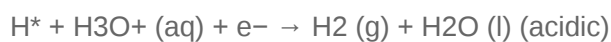
(1)

Volmer step:



(2)

Heyrovsky step:



or Tafel step:



(H*: adsorbed hydrogen at the active site of the catalyst)

At present, the most effective electrocatalysts for HER are platinum-based materials. However, the low abundance and high cost of platinum has limited its application in industry^[7]. Therefore, the development of catalysts with low cost, large reserves, good stability, and high catalytic activity has become a key step in the industrial production of H₂ from water electrolysis. As a result, those inexpensive and readily available transition metal (Mo, Fe, Co, and Ni)-based electrocatalysts have been massively developed^{[8][9][10][11]}.

Nickel-based catalysts with high stability and activity have been widely concerned for H₂-evolving reaction^[12]. Various types of nickel-based catalysts have been continuously developed, such as nickel oxides, hydroxides, phosphides, sulfides, nitrides, alloys, and so on^{[13][14][15][16][17][18]}. The catalytic performances of these nickel-based catalysts can be further improved through fine surface design, elemental doping, and addition of carbon materials^[19]. Studies have shown that doping or alloying of those catalysts that have been developed is an effective strategy to improve their performances^[20]. Doping with other elements, can induce the formation of more active sites and new active centers^{[21][22]}. In addition, appropriate elemental doping can also improve the intrinsic activity of the catalyst by increasing its conductivity and changing its electronic structure^{[23][24]}.

Although elemental doping has been widely explored and considered as an effective strategy to enhance the HER performance of the nickel-based catalysts, there still exist difficulties in controlling the type, amount, and dispersion of the dopants^[25]. Therefore, authors summarize and discuss recent progresses made in the design and manufacture of doped Ni-catalysts, hoping to deepen the understanding of the doping mechanism and provide reference for the design and manufacture of other doped transition metal-based catalysts.

2. Applications

During the past years, continuous efforts have been made in improving the HER performances of nickel-based electrocatalysts so as to achieve promising substitutes for Pt-based materials. Among various developed methods, elemental doping can be used to improve HER performance of Ni-based materials because appropriate doping can increase the charge transfer rate, adjust the free energy of hydrogen adsorption, and introduce new active centers to the catalysts. For example, incorporation of Ru dopants into Ni(OH)₂ accelerated the charge transfer rate, and Ru dopants also functioned as the new active centers for H adsorption and the following H₂ formation. As for NiP₂, Se dopants could optimize the adsorption energy of hydrogen intermediates, and therefore improved the HER performance^[20].

Considering the recent remarkable progress made by researchers in doped Ni-based HER catalysts, it's only suitable for Ni-based materials, but also applicable to other transition metal-based catalysts.

1. Single- vs. double-doping mode. Heteroatom doping can affect its free energies of H^{*} adsorption and H₂ release on Ni metal. However, most heteroatom doping is in single-doping mode, and its ability to adjust the electronic structure might still be limited. Instead, the double-doping mode can trigger synergistic effect and can fine-tune the electronic structure of the catalyst rather than too strongly or too weakly; thereby, improving the HER performance. Hence it is desirable that more efforts could be made in the judicious selection of different doping modes so as to achieve an optimization of the HER catalysts.

2. Single atom doping. As mentioned above, the introduction of single-atom Ru into Ni₅P₄ would cause localized structure polarization and then create electron-rich Ru sites, reducing the energy barriers of hydrolytic ionization [26]. In addition, the localized interstitial structures would optimize the hydrogen adsorption energy; thereby, enhancing the HER performance of the Ni₅P₄-Ru catalyst. Hence, we highlight single-atom doping as a strategy worthy of reference for promoting catalyst performances. Notably, single-atom doping is still of great difficulty because with smaller particle size, the free energy of metals increases significantly and therefore aggregation will occur. However, the judicious selection of an appropriate substrate that provides strong interactions with the metal species can stabilize the metal centers and significantly prevent this aggregation (e.g., Ni vacancies in nickel hydroxides can stabilize the Ru sites); hence, single-atom doping can be achieved [27][28].

3. Making full use of DFT calculations. DFT calculations play an increasingly important role in catalysis research. Apart from using DFT as a standard tool for answering such questions like why doping heteroatoms can increase the activity of a certain catalyst, we highlight that researchers could also employ DFT calculations as a powerful technique to predict the performances of nonexistent catalysts and therefore select out those catalysts with appropriate electronic structures for further experimental investigation. For example, Wang et al. theoretically designed and introduced a series of nonmetals (B, C, N, and O) into NiPS₃ catalyst, and predicted that B and C dopants could transform the semiconducting basal plane to a metal-like property [29]. Their further experimental results corroborated the DFT predictions, showing that introduction of B or C dopants did successfully activate the inert basal plane and promote the conductivity of the NiPS₃ catalyst, hence enhancing the HER performance.

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