Research Progress of High Entropy Materials as Water Electrolysis Catalysts in Recent Years

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Abstract: Hydrogen energy has drawn considerable attention in recent years, among which the efficient production of hydrogen energy from water electrolysis has become a hot research topic in this field. The oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) in water electrolysis are the core of the catalytic efficiency. High entropy materials have excellent combinatorial properties due to their "cocktail effect", high entropy effect, slow diffusion effect, and lattice distortion effect. They have outstanding catalytic effect in the process of water electrolysis, and thus become a hot research topic in recent years. This review combines the two hot topics by introducing the up-to-date research progress of high entropy materials in catalyzing water electrolysis. First, evaluation indexes of electrocatalytic performance are explained. Second, this review demonstrates specific materials from the classification of high entropy alloys, high entropy oxides and nitrided high entropy materials, which includes the structure of the materials and their specific catalytic performance. Finally, it summarizes the research progress of high entropy materials in water electrolysis catalysis as well as gives an outlook on the future design direction of the materials.

Key words: high entropy materials; water electrolysis; electrochemical catalysts; hydrogen energy.

1. Introduction

The concept of high entropy materials was introduced in 1995[1], but it was not until after 2010 that high entropy materials entered a high-speed development phase when the exploration and applications about it became more and more intensive. High entropy materials are solid solutions composed of five or more principal elements, in which the elemental molar ratios are equal or approximately equal. They can be categorized as high entropy alloys[2], high entropy oxides[3], nitrided high entropy materials[4], etc. Due to the tunability of their principal elements, high entropy materials can use the properties of different main elements to adjust their properties, thus possessing high toughness[5], corrosion resistance[6], fatigue resistance[7], etc. This phenomenon is often referred to as the "cocktail effect"[8]. In addition, high entropy materials also have high entropy effect in thermodynamics[9], slow diffusion effect in kinetics[10], and lattice distortion effect in structure[11].

The efficient production of hydrogen energy[12] can mitigate the problems of depletion of traditional energy sources and environmental pollution, among which the method of water electrolysis has been attracting much attention. The half reaction of hydrogen evolution is the main source of hydrogen. How to improve the efficiency of hydrogen production, while focusing on the half reaction of hydrogen evolution, should also focus on the other side of the oxygen evolution half reaction[13]. In the past few years, research on high entropy materials in the direction of OER as well as HER catalysis[14] has been a hot topic, and these studies are very important for the goal of efficient preparation of hydrogen energy. Conventional non-noble metal electrode materials, such as Fe-Ni nanoparticles[15], Co-Cu alloys[16], and TiO2[17] have high overpotentials[18] required for electrolysis and other indicators such as Tafel slope[19] and catalytic stability[20] are not satisfactory as well. In contrast, noble metal materials, such as Ru and Ir[21,22], possess better catalytic properties but do not bring excessive economic effects due to their high cost. To solve the above problems, elements in high-entropy materials can be properly adjusted to achieve good catalytic performance using combinations of non-noble or noble metals, which possess lower overpotential, smaller Tafel slope, and more durable catalytic activity, resulting in more efficient and economical catalysis. It is worth noting that different surface morphologies of high entropy materials also affect their applications. For example, there is a significant difference in catalytic effect between the powder form[23] and the nanofiber form[24]. This paper compiles the research results of high entropy materials as catalysts for water electrolysis in recent years, analyzes and prospects how to achieve better electrocatalytic performance of high entropy materials, with the hope of bringing more inspiration for the research in this direction.
2. Evaluation indexes

2.1 Overpotential

Overpotential is the potential difference of electrodes, also called superpotential. It is the difference between the non-equilibrium potential and the equilibrium potential of the electrode reaction. The electrochemical measurements mentioned in this review are performed on an electrochemical workstation using a typical three-electrode system with the sample electrode, Hg/HgO electrode or Ag/AgCl electrode and graphite rod as the working electrode, reference electrode and counter electrode, respectively. The reaction environment is a 1.0 M KOH solution at room temperature. During the test, linear scanning voltammetry (LSV) is used to apply a linear potential between the counter electrode and the working electrode. The commonly used potential scan rate is between 0.001 V s\(^{-1}\) and 0.1 V s\(^{-1}\).

In order to disregard the potential difference between electrolytes and make the experimental processing easier, the result needs calibrating. The calibrated potential is labeled as "vs. RHE" in the abscissa. In this review, the potential at a current density of 10 mA cm\(^{-2}\) is taken as the overpotential of a material. The smaller the value of the overpotential, the better the catalytic performance of the material.

2.2 Tafel slope

The Tafel slope is obtained from the LSV curve. The ordinate of Tafel plot (Potential (V vs. RHE)) is the abscissa of LSV plot (Potential (V vs. RHE)), and the abscissa of Tafel plot (log(j/mA cm\(^{-2}\))) is the absolute value of the ordinate of LSV plot (Current density (mA cm\(^{-2}\))) transformed by taking the logarithm of the base of ten. A straight line is obtained after the transformation. The Tafel fitting equation can be obtained as follows:

\[ \eta = a + b \log(j) \]  

(2.1)

where \( \eta \) is the overpotential, \( j \) is the corresponding current density, \( a \) is constant, and \( b \) is the Tafel slope in mV dec\(^{-1}\).

The Tafel slope indicates the change in overpotential requires for a 10-fold change in current. It is easy to see that the smaller the Tafel slope, the smaller the voltage rise for the same current change, and thus the better the catalytic performance of the material.

2.3 Stability

Catalytic stability is also an important indicator of the electrocatalytic performance of a material. There are generally chronopotential, chronocurrent, and cyclic voltammetry (CV) methods. In the chronopotential method, the U-t curve under long time catalytic operation is measured by keeping the current constant and observing the change of potential during the operation. If the change is small, the catalytic activity of the material is well maintained. The same is true for the chronocurrent method. Cyclic voltammetry method is to treat the material with successive CV scanning and measure the change of linear polarization curve before and after the treatment. If the discrepancy of the two curves is minor or no discrepancy, the catalytic activity of the material is considered to be well maintained and thus has high stability.

3. Research progress in high entropy materials

High entropy materials have excellent OER and HER catalytic properties. In this part, we will first introduce the preparation methods of different materials in recent years. Next, evaluation indexes such as the overpotential, Tafel slope, catalytic stability, and charge transfer resistance (Rct) are selected to evaluate the catalytic properties of the materials. Finally, summary about their excellent structural characteristics is given.

3.1 High entropy alloys

In 2020, Tang et al.[25] prepared a porous CoCrFeNiMo high-entropy alloy by microwave sintering method. The research team used metal powder as the raw material and Mg powder as the space holder. The powder was pressed into discs and then went through microwave sintering to obtain CoCrFeNiMo. By analyzing the diffraction peaks of XRD patterns (as in Fig. 1a), it was found that the CoCrFeNiMo alloy has a face-centered cubic structure and most of the Mg has evaporated. Under transmission electron microscope (as in Fig. 1b), it was observed that a large number of stacking faults and twin crystal structures exist, which provide enormous active sites for electrocatalytic OER. Experimental groups were set up with Mg content as the variable, and x in CoCrFeNiMo-xMg were 0, 10, and 20, respectively. After LSV scanning (as in Figure 1c, d), the overpotentials of CoCrFeNiMo-20Mg and CoCrFeNiMo-0Mg at a current density of 10 mA cm\(^{-2}\) were 220 mV and 270 mV, and the Tafel slopes were 65.7 and 59.0 mV dec\(^{-1}\), respectively. By comparing the polarization curves before and after CV (as in Fig. 1e), it was found that the discrepancy was minor, confirming the high stability of the electrocatalysts.
Unlike Tang who directly used metal powder as raw materials, Jian et al.[26] used metal oxide powder to make precursors and made them into discs by spark plasma sintering (SPS). They obtained the high entropy alloy Fe0.5CoNiCuZnx powder by electrolysis using the precursors as cathodes and Na2CO3 and K2CO3 as electrolytes. After thermodynamic analysis, the theoretical decomposition voltages of Na2CO3 and K2CO3 are higher than all oxides, allowing electrolysis of oxide mixtures with the electrolytes keeping stable. By adjusting the composition of the oxide precursors, they could change the Zn content in the HEA. After XRD analysis (as in Fig. 2a), it was found that with the increase of Zn content, the HEA grain size decreased, the crystal planar spacing increased, and thus improved OER catalytic performance. At a current density of 10 mA cm-2, the overpotential of HEA(Zn0.8) was 340 mV, which was lower than that of HEA(Zn0) (380 mV) and commercial IrO2-Ta2O5-Ti (360 mV) (as in Fig. 2b). The Tafel slope decreased with increasing Zn to 84 mV dec-1 (HEA(Zn0)), 58 mV dec-1 (HEA(Zn0.2)), 51 mV dec-1 (HEA(Zn0.5)) and 48 mV dec-1 (HEA(Zn0.8)), respectively (as in Fig. 2c).

In 2022, Yang et al.[27] synthesized FeCoNiCrMn films by magnetron sputtering deposition after ultrasonic treatment of Ni base. They named the samples as NF5, NF15, and NF30 according to the deposition time of 5 min,
15 min, and 30 min. Each sample was then self-reconstructed by CV scanning, and the treated samples were named as NF5CV, NF15CV and NF30CV. After electrocatalytic test (as in Fig. 3a), the overpotentials of NF5CV, NF15CV and NF30CV were 291 mV, 282 mV and 293 mV respectively. The overpotential decreased with the increase of deposition time, probably because the film peeled off under the internal stress with the increase of deposition time. The Tafel slope of NF15CV was 64.3 mV dec\(^{-1}\) (as in Fig. 3b), which indicated a good electron transfer rate. After the stability test by chronopotential method for 16 h (as in Fig. 3c), the electronic structure of the NF15CV surface was changed and the overpotential increased only 0.15% at a current density of 10 mA cm\(^{-2}\), showing an excellent electrochemical stability.

### 3.2 High entropy oxides

In 2021, Sun et al.[28] used the citric acid-nitrate method. They first compressed the nitrates of Cr, Mn, Fe, Co, Ni into discs and then made spinel structured high entropy oxide (S-HEO) \((\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4\) by heating at 1100°C. The atoms in S-HEO are able to flexibly occupy the point positions in the tetrahedral and octahedral structure (as in Fig. 4a), so it can be used as a conversion anode material for lithium-sodium ion batteries, where the reduction peak of the anode is elevated during the CV process. To measure its accurate electrocatalytic performance, the team performed self-reconstruction for S-HEO by CV scanning and found that element Fe showed the major catalytic performance during OER. S-HEO contains abundant cations, which can modulate the electronic structure and provide a large number of intermediates for OER. Thus its OER performance is much better than that of unitary or binary materials. After LSV scanning (as in Fig. 4b, c, d), S-HEO has a low overpotential of 322 mV at a current density of 10 mA cm\(^{-2}\) and its Tafel slope is 54.5 mV dec\(^{-1}\). It still retains 89.6% of current density after 20 h operation at 1.5 V, showing excellent OER catalytic performance.

![Fig. 3](https://example.com/fig3.png)

**Fig. 3** (a) LSV curves for FeCoNiCrMn; (b) Tafel plots; (c) Chronopotentiometric stability study for OER of NF15CV at a current density of 10 mA cm\(^{-2}\).
Compared with studying the OER catalytic performance of a specific material, Kim et al.[29] explored the influence of specific elements on the electrocatalytic performance of high-entropy oxide (Mg0.2Fe0.2Co0.2Ni0.2Cu0.2)O. The research team powdered the metal nitrate precursor and calcined it at 1000 °C. They also prepared medium entropy oxides (MEOs) by removing one of the elements for comparison. Through XRD analysis (as in Fig. 5a), it was found that both HEO and MEOs have a rock-salt structure. As the concentration of Cu2+ increased, the local environment of Cu2+ would evolve from octahedral to rhombohedral, resulting in local structural distortion. According to the XPS spectrum of O 1s (as in Fig. 5b), the proportion of trivalent cations (Me(III)) in MEO (w/o Cu) was larger than that of divalent cations (Me(II)). This phenomenon meant there were more defect sites with low oxygen coordination numbers and oxygen vacancies in MEO (w/o Cu), making it more conducive to OER. According to the LSV scanning and the Tafel plots (as in Fig. 5c, d), the overpotentials of MEO (w/o Cu) and HEO at a current density of 10mA cm−2 were 454mV and 1000mV, respectively, and the Tafel slopes were 60mV dec−1 and 182mV dec−1. It might be that the Cu2+ hindered the transformation of Fe2+ and Co2+ from divalent to trivalent, thus causing its OER performance to decline.

Similarly, Thi et al.[30] also explored the influence of different elements on the electrocatalytic performance of high-entropy oxides. The team dissolved lanthanum nitrate and transition metal sulfides in distilled water and prepared La(CrMnFe2Ni)O3 (labeled as L5M). They...
doubled the metal sulfide concentration to obtain the experimental groups L5M2Ni, L5M2Co, L5M2Fe, L5M2Mn and L5M2Cr. According to XRD analysis (as in Fig. 6a), all the samples showed an orthorhombic perovskite structure, that is, ABO₃ structure, in which A is a rare earth element or alkaline earth element, and B is composed of transition metal elements. After the electrocatalytic performance test (as in Fig. 6b, c), L5M2Co showed the best OER catalytic performance, with the overpotential of only 325 mV at a current density of 10 mA cm⁻², and the Tafel slope of only 51.2 mV dec⁻¹. According to Fig. 6d, as the ratio of Co³⁺/Co²⁺ increased, the overall OER performance of all samples became better. The octahedral structure of Co in perovskite can absorb electrons from water molecules. Fe is adjacent to Co in the periodic table, thus Co³⁺ can be well activated due to charge effects and spin effects. It can be seen from the Fig. 6d that L5M2Ni also showed good OER performance, but its Co³⁺/Co²⁺ ratio is not high. This may be explained by the high amount of Mn³⁺ and Mn⁴⁺ in L5M2Ni. According to related research[31], samples consisting of Mn¹.₅⁺ to Mn²⁺ own excellent OER performance.

3.3 Nitrided high entropy materials

In 2021, Liu et al.[32] prepared FeCoNiCuMnN/CC, FeCoNiN/CC, FeCoNiCuN/CC and FeCoNiMnN/CC by using metal nitrates as raw materials and calcining them on carbon cloth in NH₃ atmosphere. Through scanning electron microscope observation (as in Fig. 7a, b), the morphology of nanowires and nanosheets in the sample was clearly visible. These nanostructures had rough surfaces and abundant curving sites, which could well improve the electrocatalytic performance. Through LSV scanning (as in Fig. 7c, d), the team found FeCoNiN/CC had the best electrocatalytic performance, with an overpotential of only 220 mV at a current density of 10 mA cm⁻², while FeCoNiMnN/CC had the smallest Tafel slope of 113 mV dec⁻¹. The experiment also explored the effect of different annealing temperatures on the catalysis, and found that the HER catalytic performance was the best when the annealing temperature was 400 °C. The overpotential was only 182 mV, the Tafel slope was 113 mV dec⁻¹, and it had excellent durability.
Compared with directly manufacturing high-entropy nitrides, Gao et al. [33] found another way to nitride high-entropy alloys to improve their performance. The team first prepared CoCrFeNiMn coating (HEA) on the surface of stainless steel by high-velocity oxygen fuel (HVOF) spraying method, and then performed plasma nitriding treatment on the sample to obtain N-HEA. After XRD analysis (as in Fig. 8a), it was found that there was no significant difference between the diffraction peaks of HEA and N-HEA, which confirmed that no other nitrides were formed during the experiment but only the alloy surface was remodeled. After nitriding treatment, more nitrogen atoms entered the interstices of the metal oxide, thereby improving the electrical conductivity and electron transfer rate. This treatment not only increased the surface active area, but also enhanced its intrinsic catalytic performance, which was beneficial to the OH- absorption. After the OER catalytic performance test (as in Fig. 8b, c), the overpotential of N-HEA was 307 mV at a current density of 10 mA cm$^{-2}$, which was lower than that of HEA at 363 mV. Its Tafel slope was 32 mV dec$^{-1}$, which appeared significantly lower than that of HEA (61.4 mV dec$^{-1}$). Through the Nyquist plots obtained by EIS analysis (as in Fig. 8d), the charge transfer resistance ($R_{ct}$) of N-HEA was only 3.98 $\Omega$, which was much lower than that of HEA at 36.27 $\Omega$, confirming the improvement of electron transfer rate after nitriding treatment.
4. Conclusion

The efficient preparation of hydrogen energy can well alleviate the problems of traditional fossil energy depletion and environmental pollution. The development of high entropy materials provides more solutions for hydrogen production through water electrolysis. In this review, the preparation methods of high entropy alloys, high entropy oxides, nitrided high entropy materials and the catalytic performance of water electrolysis in recent years are summarized. Overpotential, Tafel slope, the catalytic performance of water electrolysis in recent years, only a small part of this field has been excavated. Great challenges and opportunities still lie ahead. The future research of high entropy materials in this field can be considered from the following 3 aspects:

(a) Regulating element composition. Due to the "cocktail effect" of high entropy materials, different element combinations can well adjust the electronic structure, making the material exhibit strong "hydrophilicity". They can absorb more water molecules or hydroxide ions, thereby achieving better OER/HER catalytic performance.

(b) Surface treatment. For a high entropy material with given elements, its electrocatalytic performance can still be improved through physical or chemical treatment, such as increasing defect sites in the material and nitriding the material.

(c) In-depth study of high entropy oxides. Judging from this review, the catalytic performance of high entropy oxides is generally better than that of high entropy alloys. This indicates that the future research on catalytic materials for water electrolysis should be advanced towards high entropy oxides in order to reduce their production costs and realize their large-scale applications.

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