Progress in Preparation and Research of Water Electrolysis Catalyst for Transition Metal Phosphide

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Abstract. Confronted with growing energy crisis and environmental challenges, water electrolysis for hydrogen production can provide high-density, clean and renewable energy, but limited by sluggish kinetics of two half reaction, anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER). Noble-metal-based electrocatalysts can decrease overpotential and accelerate kinetics dramatically, but limited by its scarcity and high cost. Transitional metal catalysts are abundant, low cost and have potential to become excellent catalyst due to unique electronic structure. Beginning from basic principle of electrocatalysis, this paper focuses on the synthesis method of transitional metal phosphide (TMP), and further discusses modification methods of TMP, including phase tuning, element doping/alloying, interfacial/structural engineering and three-dimensional architecture. Finally, the challenges of TMP are analyzed and future research focuses are prospected.

Keywords: Transition Metal Phosphide, Electrocatalysis, Hydrogen Evolution, Oxygen Evolution.

1. Introduction

As the global energy and environmental crisis intensifies, fossil energy is not only limited in reserves, but also influenced by the international political and economic environment. Conventional hydrogen production methods include coal gasification, photocatalytic water splitting, electrolysis and methane gas reforming with annual output of 70 million tons worldwide (data in 2019). However, methods such as gas reforming, coal gasification and photolysis are limited by pollution and low efficiency and are not suitable for large-scale industrial production. The water electrolysis for hydrogen production can produce extremely pure hydrogen (volume fraction >99.9%) without large-scale instruments, and the supply rate of hydrogen can be adjusted to coordinate with the supply network by changing electrochemical parameters, which is a key link in the framework of national sustainable energy strategy and technology network.

Technology in water electrolysis for hydrogen production can provide high energy density, clean and sustainable hydrogen energy, but it is subject to the slow kinetics of hydrogen evolution reaction and oxygen evolution reaction, which can be done under the prerequisite that the energy barrier far beyond the theoretical water decomposition reaction should be resolved. Noble-metal-based
electrocatalysts can effectively reduce the overpotential and accelerate the reaction process, but they are limited by scarcity and high cost. There are abundant reserves in transition metal catalyst with low price and unique electronic structure, which turns out to be the potential catalyst, but it is still limited by the poor performance or the backward preparation technology. Catalyst modification methods such as phase regulation, element doping/alloying, interface/structural engineering and 3D framing can optimize the catalyst from two aspects: One is the "quantity" to increase the number of active sites and the other refers to "quality" to increase the intrinsic activity. This paper will focus on the transition metal phosphide with dual catalytic properties, high conductivity and stability, and the three-dimensional framing method widely used in the fields of lithium ion batteries, supercapacitors, electrocatalysis, etc., to develop non-noble metal catalysts to solve the energy problem. Currently 96% of hydrogen is produced by conventional processes, and only 4% of the total quantity is produced by electrolysis of water with low energy conversion efficiency.

The complexity of the experimental process (56%~73%) is still a key reason for the realization of commercialization. At present, Pt in HER with acidity and Ir in OER and Ru compounds are still considered to be the most effective catalysts for HER and OER. However, their scarcity and high prices limit their further development, as a result, the development of resource-rich and highly catalytic non-noble metal catalysts is of great importance. So far, there have been a variety of non-noble metal catalysts with considerable catalytic activity for HER and OER, including transition metal hydroxides, oxides, sulfides, carbides, nitrides, etc., among which transition metal phosphates (TMPs) have attracted the attention of scholars due to their dual catalytic and excellent electrical conductivity of HER and OER.

There are six categories as TMPs, FePx, NixPy, CoxPy, MoPx, WPx and Cu3P, all of which present great potential as alternatives to catalysts of noble metals HER and OER. Several groups of researchers have reviewed basic principles, evaluation methods, preparation methods, and new trends and challenges. In the introduction, this paper starts from the electrocatalysis and the electrodecomposition mechanism of water, and gradually analyzes the reaction mechanism of HER and OER. Then the preparation methods of TMPs and material modification methods are summarized and expounded: The preparation methods include liquid phase preparation method, solid state reduction method, gas-solid reaction method and electrodeposition method. The control methods include the stoichiometric ratio of M/P, element doping and alloying, surface and structural engineering (including three-dimensional framing and heterogeneous structure formation) and the formation of TMP/C composite materials. Finally, the surface oxidation and the difficulty of OER in acidic media, the preparation of TMPs with specific crystal orientation, and the coupling of electrocatalysts and photocatalysts are analyzed.

2. Electro catalytic Reaction of Water
Electrochemical hydrogen electrolysis is an important method to prepare hydrogen on a large scale, including two semi-electrode reactions, hydrogen evolution reaction at the cathode and oxygen evolution reaction at the anode. The theoretical potential required to calculate the total reaction according to theoretical thermodynamics is 1.23V(ΔG = 237.2 kJ/mol), but due to the sluggish kinetic effect, an additional potential (overpotential) is required to start the reaction. The reason why the catalyst can change the rate of electrode reaction is that there is some interaction which changes the reaction path and reduces the over-potential and activation energy of the reaction. Therefore, a great deal of research is devoted to reducing the over-potential of water decomposition to reduce the kinetic barrier during water decomposition.

2.1. Electro catalytic Hydrogen Evolution Reaction
Hydrogen evolution reaction is a two-step reaction. The first step is to combine hydronium ions with electrons to form hydrogen intermediates which are adsorbed on the catalyst. This step is called Volmer step. The second step involves the chemical Tafel step or the electrochemical Heyrovsky step. There are, therefore, two sets of HER mechanisms: the Volmer-Tafel mechanism and the
Volmer-Heyrovsky mechanism. Different mechanisms can be inferred by drawing a Tarfel diagram and calculating the Tarfel slope. The mechanism of HER in alkaline solution is roughly the same as that of acid, except that hydrogen intermediate (H*) is generated by the decomposition of water molecules (H2O+e−→H*+OH−). (As shown in Figure 1 below).

Figure 1. Schematic diagram of Volmer-Heyrovsky and Volmer-Tafel mechanism of HER reaction

2.2. Electrocatalytic Oxygen Evolution Reaction
Oxygen evolution reaction is a four-electron process that occurs at the anode. Compared with the two-electron hydrogen evolution reaction, the four-electron evolution reaction is limited by high overpotential and slow kinetics. There are three adsorption intermediates, OOH*, O* and OH*. The reaction mechanism of OER is generally considered as follows. The first step is the decomposition of water in acidic electrolyte or alkaline solution containing OH-ligands, and the last three steps are the oxidation of OH* to O*, O* to HOO*, and finally the oxidation of HOO* to O2, as shown in Figure 2 below.

Figure 2. Schematic diagram of OER reaction in acidic and alkaline environments

3. Transition Metal Phosphates
In transition metal phosphates (TMPs), electrons tend to transfer from metal atoms to phosphorus atoms with more electronegativity, and negatively charged phosphorus atoms can effectively capture protons during HER reaction to increase the reaction rate. Therefore, the presence of phosphorus atoms leads to better binding of the catalyst surface to the reaction intermediate/product, resulting in
higher electrocatalytic activity of TMP. The following contents will give top priority to the preparation and modification of TMP.

3.1. Preparation Method of Transition Metal Phosphates
Xiao and Bussell et al. discussed a series of synthetic routes for TMPs, which can be roughly divided into four types based on the phosphorus sources used [1]. (1) The liquid phase preparation method. Trietylphosphine (TOP) is generally used as a phosphorus source for reactions in organic solvents. The phase of TMPs can be controlled by adjusting the temperature. The TMPs nanoparticles prepared by this method have a uniform size with polyhedral structure. However, it has a high requirement for the inertia of organic solvents, and the low yield also makes it difficult to apply them on a larger scale [2]. (2) The second is the solid state reduction method. Based on this method, diammonium phosphate ((NH4)2HPO4) is mixed with metal salts for reduction at an atmosphere of 400-1000°C, and the phase can be adjusted with the temperature [3]. This method usually requires a large amount of energy and is often used to prepare bulk phase materials, which have fewer active sites than nanomaterials, so this method has no advantages in electrocatalysis. (3) The third is the gas-solid reaction method. Placing hypophosphate or red phosphorus in the upper stream of a tubular furnace and the metal precursor involved in the reaction should be placed in the lower stream. The high temperature of the tubular furnace sublimates NaH2PO2 or red phosphorus, which reacts with the metal precursor to produce TMPs with high contents of phosphorus, such as MoP2 and CoP3. This method requires a low temperature, which, however, may produce toxic gases such as PH3 and phosphorus vapor during the reaction [4]. (4) The fourth is electrodeposition. By this method, TMPs can be directly grown on a conductive substrate by reducing H2PO2- and metal ions. This method can avoid the high temperature required for phosphating and thus reducing the use of catalyst for fuel preparation, but it is usually accompanied by the formation of corresponding metal phosphate, which makes the catalyst impure. However, there is no one-size-fits-all synthetic preparation strategy, and different TMP preparation methods are applicable for different scenarios (As shown in Table 1 below).

| Table 1. The preparation method for TMPs and summary on applicable scenarios |
|-------------------|---|---|---|---|
| M/P ratio | Doping elements | Nanocarbon | Functional modification |
| Liquid phase preparation | √ | × | √ | √ |
| Solid state reduction | √ | √ | × | × |
| Gas-solid reaction method | √ | √ | √ | √ |
| Electrodeposition method | × | × | × | × |

3.2. Modification and Optimization of Transition Metal Phosphating Catalyst
The unique electronic structure and conductivity of phosphorus in TMPs enable TMPs to have extremely high catalytic activity and stability under acid and base conditions. In addition, TMPs has a variety of phases, and different reactions of phases result in different stoichiometric ratios. Therefore, adjusting the stoichiometric ratio of M/P to regulate the phase is a favorable means to regulate the electronic structure of TMPs. In addition, doping and alloying methods of heterogeneous atoms are also beneficial means to regulate electronic structures to enhance the catalytic performance of TMPs, so that the dual-function catalysis (HER and OER) of the original TMPs can be better demonstrated. In addition, 3d framing based on structural engineering and the formation of transition metal phosphate-nanocarbon composite materials are also important methods for modification and optimization, as detailed below.

3.2.1. Phase regulation. Liu et al. proposed the cluster effect of phosphorus and metals in TMPs in HER with phosphorus atoms as proton receptors and metal atoms as hydride receptors [5]. Taking NiP2 as an example, the presence of phosphorus atoms diluted the original Ni active site and provided a new active site. The Ni-P bond energy and the reaction intermediate or reaction product bond to a weaker degree than the pure metal Ni, so that the hydrogen in the reaction can be better formed and
desorption. However, different M/P stoichiometric ratios can affect the degree of cluster effect and determine the intrinsic catalytic activity of catalysts. Dismukes group prepared Ni2P and Ni5P4 nanoparticles by the same method and found that Ni3P4 had better catalytic activity than Ni2P [6]. The difference of intrinsic HER kinetic catalytic activity was explained by DFT calculation. Pan et al. prepared a variety of single-phase nickel phosphates (Ni12P5, Ni13P and Ni14P) by pyrolysis [7], and their electro-catalytic performance was ranked as Ni12P5<Ni13P<Ni14P, which was consistent with the conclusion that the higher the phosphorus content, the higher the activity of HER. In some cases, the choice of a base can also have a significant impact on experimental performance. For example, the electro-catalytic performance of MoP2 nanometers grown on carbon cloth is 63.4mV/dec, 𝜂<sub>5</sub> = 58mV, while the taffel slope of MoP2 nanoparticles grown on molybdenum foil is 57mv/dec, 𝜂<sub>10</sub> = 143mV.

Although the taffel slope is similar, MoP2 has a lower overpotential. Compared with Mo foil, this carbon cloth substrate has a higher specific surface area, thus having a higher actual catalyst load [8]. Therefore, it can be concluded as follows: in most cases, a higher P/M ratio means a better catalytic performance of HER. However, the use of metal substrate may affect the conductance and thus the electrocatalytic process can be influenced and the morphology and structure of the substrate are also potential influencing factors. Therefore, an appropriate P/M ratio should be selected when designing HER and OER catalysts.

3.2.2. Element doping and alloying. The Jaramillo group demonstrated the influence of alloy effects on the performance of TMPs OER by drawing volcanic maps [11]. After studying a series of FeCoP based alloy compounds, they found that all FeCoP based alloy compounds exhibited better catalytic performance than pure CoP and FeP (as shown in Figure 3 below). The high performance of the alloy TMPs can be attributed to its hydrogen adsorption free energy Δ𝐺<sub>H</sub>, which varies with H* coverage, while the H* coverage can be changed by different doping.

![Figure 3](image-url)

**Figure 3.** LSV diagram of FeCoP alloy compound, the function of crystal structure of volcanic diagram, Δ𝐺<sub>H</sub> and H*

Liu et al. the FeCoNi unit [9], binary and ternary phosphide were prepared by gas-solid reaction, and the conclusion was made by comparison of binary and ternary TMPs that the unit catalyst can be adulterated or alloyed by means of taking advantage of the synergy between the elements, and thus effectively regulating the electronic structure of catalyst and by optimizing the reaction intermediate adsorption, the intrinsic electric catalytic performance can be improved. When the ratio of metal
elements is 1:1, better performance can be achieved, and the ternary TMPs can be characterized with better performance.

3.2.3. Three dimensional architecture. Structured nanomaterials can change or introduce new photoelectricity and other physical properties of materials, and have the effects of avoiding agglomeration of nanoparticles, repeatedly exposing active sites of materials, promoting material transfer in the reaction process, and even introducing new structure-activity relationships. Wang et al. constructed a self-supported three dimensional Ni$_3$P$_5$-Ni$_3$P nanosheet by direct phosphorylation of commercial nickel foam using phosphorus and steam [10]. The nickel foam substrate was used as a three-dimensional porous skeleton, and the Ni$_3$P$_5$-Ni$_3$P nanosheet was grown on it, which not only increased the number of active sites, but also promoted the process of material transfer in the catalytic process. Due to Ni's strong positivity and its cluster effect with phosphorus atoms, Ni$_3$P$_5$ has stronger electrocatalytic activity. The synergistic effect between Ni$_3$P$_5$ and Ni$_3$P enhanced the activity. Tang et al. proposed a set of general fixed processes for the preparation of phosphates [11], sulfides and selenides heterostructures. Taking sulfide as an example, heterostructure of Ni$_3$P/CoP/CC is a three-dimensional structure with CoP nanowires grown on a carbon cloth that acts as a fluid collector and Ni2P nanowires attached to the nanowires. This three-dimensional structure greatly promotes the release of hydrogen during hydrogen production and ensures sufficient active sites. In most cases, the three-dimensional framing reaction is more about the influence of substrate morphology on the catalyst, such as the effect of porous structure to increase the area of active site, promote mass transfer rate, and avoid catalyst agglomeration, etc. However, the the actual ECSA involved in the three-dimensional framing reaction is difficult for estimation, and it is difficult to quantify the specific influence and mechanism. This approach can be considered when preparing catalysts that focus more on engineering implementation than mechanism HER and OER.

3.2.4. Transition metal phosphates - nanocarbon complexes. The preparation of TMPs-nano carbon composite is also an effective method to exceed the catalytic performance of pure TMPs. The introduction of nanocarbon not only improves the conductivity of the composite but also enhances its specific surface area to expose more active sites. Currently, there are two main methods to introduce carbon nanoparticles into THE TMPs system, including (1) in situ generation of carbon nanoparticles through high-temperature pyrolysis of polymer, MOFs or other organic precursors, and (2) directly mixing graphene, carbon nanotubes and other precursors into the solution of the precursors and growing them in situ on the substrate. When introducing nano-carbon, it is very important to select the appropriate precursor containing the target element. If the precursor has good dispersion, the TMPs nanoparticles obtained after pyrolysis in the precursor will also be evenly distributed in the structure of nano-carbon. Such a micro-nano structure can expose more active sites and thus increasing the reaction rate. Li et al. took MOF in UIO - 66 as the host through chemical vapor deposition method to make the uniform deposition in the hole with MnO$_3$ [12], and ZrO$_2$ can be removed through pyrolysis and (NH$_4$)$_2$HPO$_4$ was used as a source of phosphorus to have gas-solid reaction, the MoP retained UIO - 66 nanostructures, the ZrO$_2$ space generated by pyrolytic elimination produced more active site, which is more advantageous to material transfer in the process of HER reaction. For phosphates, the higher the phosphorus content, the lower the conductivity. Therefore, compared with FeP, FeP$_2$ has lower conductivity, so it is more necessary to introduce some carbon materials with high conductivity to improve the reaction rate. Han et al. grew graphene in situ on nickel foam by pyrolyzing methane [13], and formed the Ni2P-graphene composite structure after phosphating. The graphene generated in situ not only promoted the charge transfer process, but also protected nickel foam from corrosion under acidic conditions and increased its stability.

4. Conclusion and Prospect
Electrocatalysis will become one of the important ways to obtain sustainable energy in the future. Because of their high chemical stability, good electrical conductivity and low electrical resistivity,
transition metal nanomaterials and nanocomposites are regarded as effective substitutes for noble metal catalysts. Transition metal phosphates have attracted more attention due to their double catalysis, high conductivity and stability. Only six types of TMPs are currently suitable for water decomposition, but their abundant phase and adjustable M/P ratio greatly enrich their availability. Currently, there are many methods to improve the catalytic performance of TMPs, including adjusting the stoichiometric ratio of M/P, heteroatom doping or alloying, metal substrate, introduction of nano carbon, etc. In addition, there are challenges and opportunities for TMPs to be used in water decomposition electrocatalysis. For example, the problems in surface oxidation of TMPs, preparation of TMPs with specific crystal plane orientation, the coupling of TMPs as a photocatalyst for water with electrocatalytic reaction and so on needs to be further explored. The development of OER catalyst under acidic medium to play the dual catalytic TMPs is also a research hotspot. More precise and universal theoretical models are also key to better prediction of catalytic performance. In the future; transition metal phosphates will have more substantial development and opportunities.

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