Iron-Series Electrocatalysts for Water Splitting

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The development of non-noble metal-based electrocatalysts with high performance for hydrogen evolution reaction and oxygen evolution reaction is highly desirable in advancing electrocatalytic water-splitting technology but proves to be challenging. One promising way to improve the catalytic activity is to tailor the d-band center. This approach can facilitate the adsorption of intermediates and promote the formation of active species on surfaces.

electrocatalysis iron-series metal-based materials d-band center

1. Introduction

Hydrogen production through water electrolysis has become a key link that cannot be omitted from the whole production process and has thus become one of the pillars of the future large-scale new energy industry. Electrochemical water splitting for oxygen and hydrogen production and applications is the main pollution-free way to obtain clean hydrogen energy, drive fuel cells, and realize carbon-free emission [1][2][3]. In recent years, the energy conversion efficiency of electric energy has been greatly improved with the rapid development of electrolytic water technology. Moreover, the cost of electrolytic water splitting has also been drastically reduced due to the exploration of catalysts for water electrolysis that are cheap, efficient, stable, easy to prepare, and result in low environmental pollution [4][5][6][7].

Electrochemical water splitting, a powerful technique, involves applying voltage to a system to promote the decomposition of the water molecules adsorbed on the electrode surface to produce hydrogen and oxygen [8][9][10][11][12]. Given that the use of catalysts with high electrocatalytic activity could reduce the applied voltage, selecting the appropriate catalysts can minimize energy consumption to the greatest extent. In other words, the properties of the catalysts directly affect the efficiency of water splitting [13][14].

Until now, the catalysts with outstanding activities for the oxygen evolution reaction (OER) are still mainly based on Ir- and Ru-based materials, and those for the hydrogen evolution reaction (HER) are still mainly based on Pt-based materials [15][16][17][18][19]. The commercial applications of precious metals are severely limited by their expensive cost and scare supply. Therefore, the preparation of non-precious metal-based catalysts that can replace those based on precious metals is one of the most important topics in the field of electrocatalytic water splitting [20][21]. Cheap substitutes for electrolytic water electrode materials have been developed. They mainly include oxides [22][23], hydroxides [24][25], hydroxyl oxides [26][27], phosphates [28][29], and sulfides [30][31]. Their catalytic active centers are generally transition metal atoms and a few alkali metal atoms because the *d* orbitals of transition-state elements with underfilling electrons can accept electrons or electron pairs [32]. Subsequently, the receptor and donor can form intermediates through coordination, so as to reduce the activation energy of the reaction and promote the reaction at lower energy, that is, they act as catalysts for water splitting [33][34][35].

Among various catalysts, iron-series elements, namely iron-, cobalt-, and nickel-based materials, have attracted considerable attention [36][37][38][39][40][41]. On the one hand, these elements are abundant on earth and therefore the corresponding materials are cost-effective and easy-to-manufacture. On the other hand, many kinds of Fe-, Co-, and Ni-based materials exhibit outstanding performance for OER and/or HER. Interestingly, by studying various reports, it is found that these kinds of materials have some characteristics and advantages, including unfilled *d*-orbitals that can provide coordination spaces. In other words, tuning the d-band center of iron transition series metal-based materials is a rough strategy for developing electrocatalysts for water splitting. However, there has not been a review about this important topic in electrocatalysis. Therefore, summarizing the results of the research on catalysts based on iron-series metals is necessary and provides clear ideas for research in the future. Herein, it is attempted to offer the readers a comprehensive review of the recent progress in the development of descriptors that correlate electrocatalytic activity of the iron-series electrocatalysts with the d-band center.

2. Iron-Series Electrocatalysts for Water Splitting

On the basis of the catalytic reaction that mainly occurs on the active surfaces of catalysts, various compounds of iron transition series elements and their corresponding catalytic reactions can be classified as follows:

Nickel oxide: Nickel oxide (NiO) can effectively open the O–H bond of the water that had adsorbed on surfaces to produce adsorbed hydrogen atoms [42]. Therefore, it is conducive to the HER. For example, Qiao’s group prepared NiO nanorods with surfaces that were rich in O-vacancies and showed a low overpotential of ~110 mV to produce the current density of 10 mA cm^{-2} for the HER in alkaline solutions [43]. In addition, many studies have used NiO as catalyst for the OER and also achieved good results [44]. With the deepening of research, NiOOH instead of NiO has been found to be the real catalyst for the OER [45]. In fact, this phenomenon is considered as a method for energy storage in supercapacitors [46]. Therefore, NiO can be used as both the anode and the cathode for overall water splitting.

Cobalt oxide: There are many kinds of cobalt oxides with different atomic ratios such as Co_3O_4, CoO, and Co_2O_3 [47][48][49]. Although different cobalt oxides have different atomic ratios, similar to those of NiO, the catalytic active sites of cobalt oxides are also mainly cobalt atoms and oxygen vacancies. For example, when CoO is used as the catalyst for HER, O–H is adsorbed to the Co(111) surface, which is rich in oxygen vacancies, and the remaining hydrogen atom is connected to the adjacent oxygen atom, thus forming an intermediate with increased stability. Cai et al. studied the OER properties of Co_3O_4 with rich oxygen vacancies and found that when oxygen defects were introduced into single crystalline ultrathin Co_3O_4 nanosheets with O-terminated (111) facets under alkaline conditions, the as-prepared defect-rich Co_3O_4 nanosheets showed improved OER activity [50]. When oxygen vacancies were introduced, the increase in the electron concentration of the cobalt atoms and the decrease in valence state resulted in interaction with the surrounding oxygen atoms, thus reducing adsorption energy and changing the OER mode of Co_3O_4. Meanwhile, oxygen vacancies can also reduce the band gap of Co_3O_4, thus increasing the conductivity of Co_3O and accelerating the kinetics of OER. The application of Co_2O_3 in electrolytic water splitting has been less studied than that of the first two compounds, which is likely related to its difficulty in preparation.

Ferric oxide: Iron oxides also have several compounds with different Fe/O ratios, such as Fe_2O_3 and Fe_3O_4. As for Fe_3O_4, it can be regarded as a mixture of Fe_2O_3 and FeO, among which, Fe atoms mainly exist in the valence states of Fe^{2+} and Fe^{3+}. When Fe_2O_3 is used as the electrode material for the OER, iron atoms on the surface of the material would first adsorb water molecules and then form Fe–O–H. This phenomenon shows that the iron oxide still needs to undergo a phase transition to form FeOOH during the OER [51]. Among iron oxides, Fe_3O_4 is the most commonly used electrode material for OER. However, due to its low conductivity, it is often combined with other substances or loaded on collectors with high conductivity. For example, Ni-doped Fe_3O_4 particles supported on iron foil show good OER properties because the coexistence of Fe^{2+} and Fe^{3+} creates a large number of active sites that are similar to oxygen vacancies [52].

Hydroxide (M hydroxide; M = Fe, Ni, Co): Given that reducibility follows the order of $Fe(OH)_3 > Co(OH)_2 > Ni(OH)_2$, $Ni(OH)_2$ is more suitable and stable for HER than $Fe(OH)_3$, which is easily reduced into Fe_2O_3, while $Fe(OH)_3$ is more stable and suitable for the OER. On the other hand, $Co(OH)_2$ can be used as an electrode material for OER, HER, and overall water splitting [53]. During the OER, $Co(OH)_2$ is transformed into high-valence cobalt-based compounds, such as Co_3O_4 and CoOOH, which acted as the real active materials for the OER [54].

Hydroxyl oxide (M oxyhydroxide; M = Fe, Ni, Co): For many oxides or sulfides in alkaline solution, hydroxyl oxide acts as the real active materials for the OER. For example, during the OER in alkaline solution, Co_9S_8 transforms into CoOOH and $Ni(OH)_2$ transforms into NiOOH [55][56]. The OER catalytic activities of these three metal hydroxyl oxides follow the order of FeOOH > CoOOH > NiOOH [57]. Importantly, recent studies have found that bimetallic hydroxyl oxides are also important electrocatalytic materials. For example, binary Fe–Co oxyhydroxide, binary Fe–Ni oxyhydroxide, and binary Ni–Co oxyhydroxide have been proven to have excellent electrocatalytic properties [58][59][60]. Bimetallic hydroxyl oxides have good OER performance because the combination of these two substances promotes the gathering of active atoms on the surfaces of the catalyst, thus resulting in a sharp increase in the number of efficient catalytic active sites.

The above analysis indicates that hydroxyl oxides based on iron-series metals show outstanding OER performance and structural stability. At the same time, hydroxides and metal oxides based on iron-series metals often have superior HER performance and structural stability. Moreover, the combination of different hydroxyl oxides based on iron-series metals is helpful for further improving the OER performance of catalysts. The combination of oxides, hydroxides, or hydroxyl oxides based on iron-series metals is helpful for improving the catalytic performance mainly because of their surface oxygen vacancy concentration, exposed catalytic active area, and the conductivity. These factors are also related to the surface structures of the catalysts. The reported catalyst-related factors mainly include enriched oxygen vacancy surfaces [61][62][63][64][65], ion adsorption [66][67], edge effects [68][69][70][71], single-atom catalysts [72][73][74][75][76][77], and high specific surface areas [67][78][79][80][81][82]. These listed factors are common characteristics of high-performance electrocatalysts. However, the relationships between the electronic structure and performance of the catalysts have not yet been explored. The interface properties of materials are mainly determined by their own electronic structures, such as the outer orbital arrangement and the density of states of the atoms.

The d-band center theory for iron transition series metal-based catalysts with the unfilled 3*d* orbitals of iron-series metal atoms has attracted wide attention in recent years because the energy difference between the d-band center and Fermi level (i.e., $E_f - E_c$) can feasibly predict and explain the adsorption of small molecules, including OH* and H*, on the metal surface, and can thus explain the relationships between electronic structures and catalytic performances [83][84].

The d-band center theory is a theoretical model proposed by Nørskov and Hammer in 1995 to explain the adsorption of substances on catalysts [85]. When the adsorbed material forms a bond with the catalyst, the adsorption capacity is mainly affected by the position of the d orbital center of the metal atom of the catalyst. Therefore, the d-band center theory can be reasonably used to explain the relationships between the electronic structure and the adsorption capacity of the catalyst, as well as to reveal the good coordination ability and electrocatalytic performance of the catalyst from the perspective of electronic structures and energy level changes [86]. The d-band centers of the catalyst atoms can be regulated through the incorporation of dopants, vacancies, strains, and heterostructures. Considering the relatively low electrocatalytic water-splitting activity of single iron-series compounds, various efforts have been made to improve electrocatalytic performances through two effective ways: one is to increase the unit activity on each active site (intrinsic), and the other is to increase the number of active sites (extrinsic) [87][88].

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