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Low-dimensional materials for alkaline oxygen evolution electrocatalysis

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ABSTRACT

The urge for renewable and clean energy technologies has cultivated the concept of hydrogen economy, in which water electrolysis for hydrogen production is one indispensable component. As the water electrolysis efficiency is primarily restricted by the anodic oxygen evolution reaction (OER), intensive research efforts have been put into this field to acquire good knowledge of the reaction mechanism and obtain active, durable, and cost-effective electrocatalyst materials. Many invaluable findings have been achieved in the past years, with some problems being found in the meantime. It is good timing to summarize what have been achieved and identify what to overcome, which would be helpful to unscramble current OER research status and stimulate insightful thoughts in future studies. In this review article, we briefly introduce current understanding of OER electrocatalysis mechanism and the use of catalyst descriptor parameters for correlation with the activity property. We then summarize recent achievements on development of OER catalyst materials, which are categorized and discussed based on their morphological dimension. Perspectives on the existing challenges and future directions in the OER research are also provided.

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1. Introduction

The concerns of fossil fuel depletion and environmental issues have driven considerable research activities into developing renewable and clean energy technologies that can sustain the societal needs in the long run. Hydrogen economy is widely considered as one feasible solution to solve all these concerns (Fig. 1) [1]. H₂ stores a high density of chemical energy in the molecules, with water being the only combustion product. The development of fuel cell technology in recent years has also paved the road for converting the chemical energy stored in H₂ into electric energy for utilization at high efficiency. All its good features make H₂ an ideal and clean energy carrier. However, energy-efficient and costeffective H₂ production is demanded to complete the chemical loop to realize the conceived H₂ economy. This is because hydrogen does not naturally exist in the form of H₂ but as a component of

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compounds, mostly water and hydrocarbons. Considering completion of the chemical loop with zero emission, splitting water for H₂ generation becomes the only option and emerged as one important research topic. Researchers have actively explored different approaches, for instance, electrochemically [2], thermochemically [3], photocatalytically [4], and photoelectrochemically [5], to split water. Water electrolysis is deemed as one most feasible solution in the near future. This electrochemical process consists of two half-cell reactions, i.e., hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode. Because OER involves four electron transfers and more complex steps than HER that causes significantly more sluggish kinetics, efficiency of water electrolysis technology is primarily restricted by OER properties. In this review article, our focus is on OER electrocatalysis and catalyst development in aqueous solution.

The overall OER half-cell reaction reverse to oxygen reduction reaction can be depicted differently in acidic and alkaline electrolytes:

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$







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Fig. 1. Conceived hydrogen economy and mass hydrogen production using water electrolysis. Adapted from Ref. [6] from NREL.

 $40H^- \leftrightarrow 0_2 + 2H_20 + 4e^- \tag{2}$

The reaction has a standard Nernstian potential (*E*) of 1.23 V vs. reversible hydrogen electrode (RHE). Thermodynamically, OER can occur once a positive overpotential is applied to the electrode (i.e., $\eta = E_{-}1.23 > 0$). Kinetically, occurrence of this reaction largely relies on used catalyst materials. The OER rate, typically represented by current density (*i*), is describable using the Tafel equation [7]:

$$i = i_0 e^{\alpha_C F \eta/RT} \tag{3}$$

$$\alpha_G = n_f / \nu + n_r (1 - \alpha_{rds}) \tag{4}$$

where i_0 is the exchange current density, α_G is the global charge transfer coefficient, η is the overpotential, n_f and v are the number of electrons transferred to the active sites and the number of elementary steps preceding the rate-determining step (*rds*), respectively, n_r and α_{rds} are the number of electrons transferred to the active sites and the symmetry factor during the *rds*, respectively, R is the gas constant, T is the temperature, and F is the Faraday's constant.

Under acidic condition, iridium and ruthenium oxides were among the most active OER catalysts but still require ~0.4 V overpotential to reach a practical current density of $1.5 \text{ A/cm}^2_{\text{geo}}$ [2c]. A more severe issue is the scarcity and thus high cost of these noble metals as well as their relatively poor stability, which largely hinders their use for large-scale water electrolysis applications. Under basic condition, many earth-abundant element-based materials, most notably in the form of their oxides, were found active in OER [2a]. Considering cost-effectiveness of catalyst materials that are of particular significance for mass H₂ production, alkaline OER electrocatalysis likely represents the future research direction. Till date, however, most reported catalyst materials did not suffice the requirements yet, in terms of both activity and durability properties, for real applications. More research studies, both mechanistically to better understand OER mechanisms and practically to develop new catalyst materials, are demanded. In this review article, we try to glimpse recent research progresses on OER electrocatalysis understanding and catalyst material development under alkaline condition, for summarizing previous achievements and providing personal perspective of future research directions in this field.

2. Current understanding of OER electrocatalysis

As being revealed from the Tafel equation, the OER kinetics is primarily dominated by i_0 , which represents the intrinsic activity property at 1.23 V. The i_0 can be correlated to the rate law as follows:

$$i_0 = 4Fk_A f(C_{OH^-}) = 4FAe^{-E_A/RT} f(C_{OH^-})$$
(5)

where k_A is the rate constant, $f(C_{OH^-})$ is the concentration term in the OER rate law, and A and E_A are the pre-exponential factor and activation energy in the Arrhenius law, respectively. Similar to most other catalytic reactions, the OER kinetics is eventually dominated by E_A associated with this electrochemical reaction. To decrease E_A to promote the reaction kinetics, a good understanding of the OER electrocatalysis mechanism as well as the determining factors are crucial.

The occurrence of OER on reducible metal oxides was discovered to be accompanied with redox of the active sites (Fig. 2) [8]. Typically the active sites undergo electrochemical oxidation to a higher oxidation state that initiates interaction and reaction with hydroxyl ions, followed by generation of intermediates such as oxyhydroxyl and peroxide species and release of water, electrons, and eventually oxygen as products. The active sites being oxidized to a higher state would then go back to the initial state that completes one catalysis cycle. The interactions between the active sites and reacting species would alter energy levels of transition states and active



Fig. 2. Schematics of (a) pathway (Reproduced from ref. 8 with permission from Wiley, copyright 2018) and (b) energy diagram of OER electrocatalysis on reducible metal oxide. OER, oxygen evolution reaction; RHE, reversible hydrogen electrode.

intermediates and consequently the affiliated energy barriers and even the reaction pathway. In other words, the overall energy barrier, i.e., the OER kinetics, is primarily determined by active site–reacting species interactions.

There have been many research efforts to identify catalyst descriptor parameters that control active site-reacting species interactions and establish the relationships with the activity property, the knowledge of which would guide rational catalyst search to promote the OER kinetics by balancing the interactions. Such research efforts in general catalysis research can be traced back to the early 20th century, with the Bronsted-Evans-Polanyi principle (also referred to as the Bell-Evans-Polanvi or Evans-Polanvi-Semenov principle) finding that the difference in activation energy between two reactions of the same family has a proportional relationship with the difference in their enthalpy of reaction (ΔH_{RX}) [9]. In the following years, researchers continued to study on this topic and published a series of work on proposing semiquantitative property-activity relationships to describe reducible oxide catalysis. Specifically to the OER research, the catalyst activity property was discovered to follow a decent volcano relationship with the enthalpy of transition from a lower to a higher oxidation state for oxides (ΔH_F) [2c,10]. The E_A was found to show a good linear correlation with the oxygen vacancy formation energy of oxides (ΔE_{vac}) (also referred to as the surface reducibility). These findings strongly suggested that the OER activity is controlled and describable by certain governing parameters of reducible oxides.

3. Past achievements in low-dimensional material development as OER catalyst

3.1. Zero-dimensional OER catalyst

Structurally, zero-dimensional (0D) catalysts refer to functional materials between 1 and 100 nm in size with a surrounding interfacial layer, including guantum dots, nanoparticles, and clusters. Currently, 0D materials have attracted great attention due to their unique advantages of small size, large surface area, and short effective charge transfer length, which make them promising in electrocatalysis, especially toward OER. Generally, bulk materials are less active for the OER owing to their low surface area. Thus, design of nanostructures to create a larger surface area is regarded as an effective approach to optimize the performance of OER catalysts. Recently, Yang and Pan have fabricated Co₃O₄ quantum dots with a crystallite size of approximately 2 nm through multiple lithiation-delithiation cycles of mesoporous Co₃O₄ nanosheets [11]. In their study, X-ray photoelectron spectroscopy (XPS) characterizations suggested that oxygen vacancies could be gradually generated during multicycle of lithiation and delithiation, and thus, the ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ in the sample would increase correspondingly. When being used as OER electrocatalysts, the obtained sample required 270 mV overpotential to reach 10 mA cm⁻², and no obvious current decay was observed within 30 h, which was superior to that of previously reported Co-based catalysts and also better than the benchmark IrO₂.

Because of the large surface energy of nanoparticles and other 0D structures, these catalysts tend to aggregate and restack when in applications, which will significantly decrease the exposed active sites on surface and have a negative impact on their catalytic efficiency. To resolve this issue. Shi and his co-workers have developed a facile oil-bath strategy with one-step reaction using benzyl alcohol route as a surfactant-free approach to synthesize waterdispersible Co₃O₄ quantum dots [12]. The transmission electron microscopy (TEM) image shown in Fig. 3 demonstrated good dispersion of the obtained quantum dots, without any obvious aggregation. Most of the prepared quantum dots exhibited a cubelike shape with a size of around 4.5 nm, showing a well-defined crystalline structure with a lattice spacing of 0.2 nm, which could be indexed to (400) planes of spinel Co₃O₄. They were used in a Clark electrode system using a well-established $Ru^{2+}(bpy)_{3}S_{2}O_{8}^{2-}$ method with $[Ru(bpy)_3]Cl_2$ as a sensitizer and sodium persulfate as a sacrificial electron acceptor to estimate their performance in the visible light-driven OER. It could be seen that the benzyl alcohol-Co₃O₄ quantum dots could accelerate the OER reaction with a greater initial oxygen evolution rate as compared with commercial Co₃O₄ nanoparticles. The estimated turnover frequency was high up to $2.7 * 10^{-4} \text{ s}^{-1}$ per Co atom, and the enhanced activity could be explained by their monodispersity and small size, decreased hole--electron recombination probability, as well as the longer lifetime of photoexcited charge carriers which was caused by the quantum confinement effects of the 0D structure.

Carbon materials, such as graphene and carbon nanotube (CNT). have been widely used and well regarded as good substrates to anchor inorganic oxide quantum dots, which can prevent the aggregation of these 0D catalysts and simultaneously enhance the electronic conductivity. For example, 0D ZnCo₂O₄ coupled with Ndoped carbon nanotubes (NCNTs) have been designed and prepared by Su et al., by a facile one-pot hydrothermal process to obtain high oxygen evolution performance [13]. The electronic states study disclosed that the electron cloud would migrate between the ZnCo₂O₄ and NCNTs, revealing the synergistic effect at interface in boosting the oxygen electrochemistry. The transferred electrons provided a high valence state for Co and also reduced the needed energy for Co³⁺ to CoO₂ conversion. Meanwhile, the CNT substrate could serve as the conductivity substrate for achieving high electron transport efficiency. In the OER measurement, the new hybrid catalyst could generate the current density of



Fig. 3. (a) TEM image, (b) magnified TEM image, and (c) HRTEM image of benzyl alcohol-Co₃O₄ quantum dots. The inset in (b) showed the corresponding SAED pattern. Reproduced from ref. 12 with permission from Royal Society of Chemistry, copyright 2014. HRTEM, high-resolution transmission electron microscopy; SAED, selected-area electron diffraction; TEM, transmission electron microscopy.

10 mA cm⁻² at a small overpotential of 420 mV in 0.1 M KOH, which was comparable to IrO_2/N -CNT (410 mV) and superior than Co_3O_4/N -CNT (440 mV) and $ZnCo_2O_4$ (460 mV). In addition, $CoMn_2O_4$ quantum dots with different sizes (between 2.0 and 5.4 nm) have been selectively prepared at various temperatures in air atmosphere by Shi et al. [14]. The TEM images in Fig. 4 demonstrated that they were monodisperse with narrow size distributions, and their

corresponding HRTEM images displayed the characteristic fringes with a d-space of 0.24 nm, assigned to the (211) plane of $CoMn_2O_4$ crystal. After that, the obtained 0D catalysts were loaded on the CNT, with N,N-Dimethylformamide (DMF) and hexane used for respectively dispersing CNTs and $CoMn_2O_4$ quantum dots, to get higher electric conductivity and lower aggregation (seen in Fig. 4g). The authors have systematically investigated the relationship



Fig. 4. (a-c) TEM and (d-f) HRTEM images of CoMn₂O₄ quantum dots with an average particle size of (a) and (d) 2.0 nm, (b) and (e) 3.9 nm, and (c) and (f) 5.4 nm. The insets of (a-c) showed the particle size distribution determined from at least 100 particles for each sample. (g) Schematic preparation of CoMn₂O₄/CNT hybrids for oxygen-involving reactions. Reproduced from ref. 14 with permission from Springer, copyright 2017. CNT, carbon nanotube; HRTEM, high-resolution transmission electron microscopy; TEM, transmission electron microscopy.

between their size and their performance in oxygen evolution process. Among them, the 3.9-nm quantum dots exhibited the highest activity, which was explained by its moderate amount of surface-adsorbed oxygen species, lower band gap energy, and the larger charge carrier concentration. In another study, Govindhan et al. have reported on a facile and effective in-situ strategy for the synthesis of an advanced nanocomposite material composed of Co quantum dots [15]. The obtained OD Co has an average size of 3.2 nm, and then they were uniformly dispersed on the reduced graphene oxide as an effective OER catalyst. During the synthesis, the formation of Co quantum dots could be observed via changes in color, from light yellow to dark black, suggesting the reduction of Co ions and graphene oxide. In the electrochemical measurement in 0.1 M KOH, the economical hybrid could deliver a high mass activity and also show a low overpotential of 370 mV to reach 10 mA cm⁻², as well as a small Tafel slope of 37 mV dec⁻¹. Moreover, encapsulating transition metal dots into layered graphene can confer high electrical conductivity and good stability to the transition metal nanoparticles. Hu et al. have recently demonstrated a facile and cost-effective strategy to craft MoC₂-doped Ni-Fe alloy nanoparticles encapsulated within N-doped graphene, which is denoted as NG-NiFe@MoC₂ [16]. This new catalyst is obtained by one-step annealing of NiFe Prussian blue analogs and Mo-grafted polyvinylpyrrolidone hybrid precursors. After careful composition optimization, the developed 0D NG-NiFe@MoC2 exhibits remarkable performance for OER, with a small overpotential of 320 mV to achieve the current density of 10 mA cm^{-2} .

Apart from metal-based OD OER catalysts, metal-free carbon nanodots have also been used as efficient catalysts for OER. Liu et al. have synthesized and developed amidogen-modified carbon dots through hydrothermal treatment as an efficient OER application [17]. The TEM image was shown in Fig. 5a, which indicated that the average particle size was about 5 nm. XPS spectrum in Fig. 5b revealed that N 1s of the N-modified carbon dots was in the form of amidogen-N (-NH₂) and protonated amine (-NH₃⁺). After that, linear sweep voltammetry (LSV) investigations were carried out, which showed that pristine carbon dots were almost inactive toward electrochemical oxygen evolution (Fig. 5c). In contrast, N modification could confer it much higher OER activity, generating a current density of 16.5 mA cm⁻² at a potential of 1.6 V versus RHE, which was even little higher than that of IrO_2/C (13.2 mA cm⁻²). Meanwhile, the forward and backward cyclic voltammetry scans for the carbon dots almost overlapped, suggesting that the capacitance current was very low. Fig. 5d disclosed the positive correlation between N content and OER activities, which suggested that amidogen N species were the active centers for oxygen production. As the amidogen group contained one pair of free electrons, hydrogen bonds could be formed for adsorbing water molecules, thus leading to further improved OER activity.

3.2. One-dimensional OER catalyst

One-dimensional materials possess tube-like or wire-like structures with the diameter of the order of a nanometer and with the ratio of the length to width being greater than 1000. They have attracted intense attention for their excellent physical and chemical properties and are promising as high-performance catalysts used in energy conversion and storage fields. Wang et al. have presented a self-template strategy to prepare hierarchical porous Co₃O₄ nanotubes [18]. Cobalt-aspartic acid super-long nanowires were first prepared by a simple hydrothermal method, and then they were transformed into porous nanotube structures via oxidation in air at elevated temperatures, with their representative SEM and TEM images shown in Fig. 6a–c. During the oxidation process for structure conversion, the authors claimed that the outward diffusion of interior metal–coordinating components, the



Fig. 5. (a) TEM image of NH2-carbon nanodots. Inset, HRTEM image with the characteristic 0.21-nm spacing corresponding to graphite (100). (b) XPS spectrum of N 1s. (c) LSV curves of <u>N</u>-modified carbon nanodots, IrO₂/C, and pristine carbon nanodots. (d) Relationship between the N contents and OER activities of <u>N</u>-modified carbon nanodots. Reproduced from ref. 17 with permission from Wiley, copyright 2016. HRTEM, high-resolution transmission electron microscopy; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy.



Fig. 6. (a) SEM image of the solid Co-aspartic acid super-long nanowires. (b) SEM and (c) TEM images of the as-converted Co_3O_4 mesoporous nanotubes. (d) Polarization curves and (e) Tafel plots of porous Co_3O_4 nanotubes (Co_3O_4 -MNTs), porous Co_3O_4 nanowires (Co_3O_4 -MNWs), and commercial RuO₂ for water oxidation. Reproduced from ref. 18 with permission from Wiley, copyright 2016. SEM, scanning electron microscopy; TEM, transmission electron microscopy.

gas release from the oxidation/dissociation of the internal organic components, and the fracture of the ultralong precursors were pivotal factors to obtain the final mesoporous nanotubes. After that, their corresponding OER polarization curves were investigated in 0.1 M KOH aqueous solution (Fig. 6d), which showed that the asprepared porous Co₃O₄ nanotubes exhibited a low onset overpotential of 310 mV and required an overpotential of 390 mV to reach the current density of 10 mA cm^{-2} . These performances were significantly superior to those of corresponding Co₃O₄ nanowires. Furthermore, it was noted that its OER current began to exceed that of commercial RuO₂ particles when the applied potential surpasses 425 mV overpotential. Meanwhile, the Tafel slope of porous Co₃O₄ nanotubes was 76 mV dec⁻¹, much lower than those of Co₃O₄ nanowires (93 mV dec⁻¹) and commercial RuO₂ (90 mV dec⁻¹), as seen in Fig. 6e. This implied that the unique hierarchical mesoporous tubular architectures could supply a more convenient charge transfer at the interface between Co₃O₄ nanotubes and electrolyte.

However, Co₃O₄ still showed some disadvantages as an electrocatalyst owing to their strong causticity in alkaline solution, intrinsic poor electrical conductivity, and undesirable morphology or crystalline structure [19]. Therefore, a substrate with preferable conductivity, high specific surface area, and mechanical stability is favorable to uniformly disperse one-dimensional (1D) nanomaterials on the surface and maximize the electrocatalytic activity. Yan and Sun recently have reported the synthesis of nanorod-shaped Co₃O₄ anchored on multiwalled CNTs (MWCNTs) with the assistance of diethylenetriamine, by a simple mild solution-phase process [20]. The as-prepared hybrid exhibited a large brunauer–Emmett–Teller–specific surface area of around 252 m² g⁻¹ and showed excellent electrocatalytic activity toward oxygen evolution in alkaline media and also displayed prominent stability during the long-time durability measurement.

In the drive toward green and sustainable chemistry, carbon nanomaterials without metal elements have also been explored and studied extensively as water oxidation catalysts, which were labeled as metal-free catalysts [21]. Lu et al. recently have shown that upon mild surface oxidation, hydrothermal annealing, and electrochemical activation treatments, MWCNTs were effective for OER [22]. Different oxidation degrees on MWCNTs were prepared as follows: 1) weak oxidation: MWCNTs stirred in HCl solution under mild condition; 2) mild oxidation: MWCNTs treated with piranha solution (7 ml of 98% H₂SO₄ and 3 ml of 30% H₂O₂); 3) strong oxidation: MWCNTs oxidized by the mixture of HNO3 and H₂SO₄ solution. After that, the as-prepared oxidized MWCNTs (o-MWCNTs) underwent a hydrothermal reaction process at 180 °C overnight, and the obtained samples were denoted as ho-MWCNTs. Subsequently, ho-MWCNTs were loaded onto the glassy carbon electrode and activated by cycling in the potential range of 0-0.8 V vs. Ag/AgCl in 0.1 M KOH, which were regarded as echo-MWCNTs. It was found that the OER catalytic activity increased with each step of the treatment, with progressively lowered onset potentials and greatly enhanced current densities. Combined with density function theory calculations, it was concluded that the oxygencontaining functional groups such as ketonic C=O generated on the surface played a crucial role in accelerating the oxygen evolution process, by alternating the electronic structures of the adjacent carbon atoms, benefiting for the OER intermediates adsorption.

Apart from this, Gale's group have demonstrated that pristine CNTs constructed by 2-7 concentric tubes and an outer diameter of 2–5 nm could exhibit good activity for OER in alkaline media [23]. CNTs with different number of walls and diameters were obtained from commercial sources, and all of them have been purified to reduce the possible effect of metal catalysts before use. Fig. 7 was the TEM micrographs of CNTs samples used in this investigation, with the number of walls taken as the average of the measurement from the TEM images. The authors claimed that the inner walls contributed greatly to the electronic transport properties, whereas the outer walls served as a protective barrier to prevent endohedral reactions. Therefore, the presence of inner tubes could increase the number of conducting channels and create the possibility of interactions between the walls. Meanwhile, the outer wall would provide active sites for the adsorption and dissociation of the generated intermediate species. When used as OER catalysts, the measured current density at 1.8 V (vs. RHE) for triple-walled CNTs was 56 mA cm⁻², nearly 10 times higher than 5.9 mA cm⁻² tested on single-walled CNTs and 35 times higher than 1.6 mA cm^{-2} obtained on MWCNTs, as seen in Fig. 7h.



Fig. 7. TEM micrographs of CNTs for (a) CNT-1, single-walled CNTs with an outer diameter of 1.97 nm, (b) CNT-2, double-walled CNTs with an outer diameter of 3.3 nm, (c) CNT-3, mainly triple-walled CNTs with an outer diameter of 3.8 nm, (d) CNT-4, mainly triple-walled CNTs with an outer diameter of 4 nm, (e) CNT-5, mainly CNTs with 3–10 walls and an outer diameter of 5.1 nm, (f) CNT-6, mainly CNTs with more than 12 walls and an outer diameter of 13.9 nm, and (g) CNT-7, mainly CNTs with more than 30 walls and an outer diameter of 20–40 nm. (h) LSV curves of OER for CNTs measured in 1 M KOH at a scan rate of 1 mV s⁻¹. Reproduced from ref. 23 with permission from Elsevier, copyright 2015. CNT, carbon nanotube; OER, oxygen evolution reaction; RHE, reversible hydrogen electrode.

3.3. Two-dimensional OER catalyst

Currently, two-dimensional (2D) nanomaterials have attracted considerable and growing research studies for investigating and further optimizing their electrocatalytic properties, especially for OER. After being exfoliated into ultrathin nanosheets, almost all of the atoms are exposed on the surface, which not only dramatically increases their surface areas but also confers them abnormal physiochemical behaviors when compared with bulk counterparts [24]. It is known that RuO₂ is regarded as the most active and benchmark OER catalyst, and our group has reported the preparation of 2D RuO₂ nanosheets via a solvothermal method for 2D Ru nanosheets synthesis and followed by oxidation treatment in air. The achieved 2D RuO₂ nanostructures exhibited a low-onset overpotential during OER activity measurement and needed 260 mV overpotential to reach 10 mA mg⁻¹, which was much smaller than that of Ru powder (280 mV) and commercial Pt/C (565 mV) [25]. Because of the high cost and limited reserve of noble metals, it is highly desirable yet challenging to develop active and earth-abundant OER catalyst for the water oxidation reaction.

Co- and Ni-based compounds were regarded as potential high OER performance catalysts in recent development. Huang et al. have prepared few-atomic-layered γ -CoOOH nanosheets via a facial atomic-scale phase transformation strategy (Fig. 8) [26]. In their experiment, 2D α -Co(OH)₂ nanosheets were first prepared by a wet chemistry process and then they were sonicated into ultrathin nanosheets by liquid exfoliation in the presence of Cl⁻ anions and water condition. Subsequently, these 2D α -Co(OH)₂ nanocrystals with enlarged interlayer spacing were subjected to dehydrogenation and transformed into γ -CoOOH nanosheets by NaClO oxidation. TEM and atomic force microscopy images confirmed the 2D structures with the thickness of around 1.4 nm, which indicated the half-unit-cell height of γ -CoOOH cell for these achieved 2D nanocrystals along the c-axial direction. X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy characterizations demonstrated the structural distortion of CoO_{6-x} octahedrons and the changes of Co valence state for γ -CoOOH nanosheets compared with their bulk counterpart. The polarization curves recorded in 1 M KOH solutions showed a significant smaller onset potential of 1.47 V for γ -CoOOH, which was markedly lower than 1.53 V for bulk γ -CoOOH. Meanwhile, IrO₂ catalyst has also been used for comparison, which showed evidently 30 mV higher overpotential to get 10 mA cm⁻², as well as a higher Tafel slope value. These results suggested the promise of 2D nanomaterials to be used as efficient, robust, and economic OER electrocatalysts.

Zhang and Xie have realized regulating the delocalized spin states based on Ni-based compounds by introducing structural distortion to their confined 2D atomic layers, and the electrochemical results have disclosed the strong relationship between their catalytic activities and the spin states of metal atoms [27]. The authors have prepared ultrathin NiSe2 nanosheets with clean surfaces using an inorganic-organic hybrid intermediate-assisted liquid exfoliation strategy. Combined with Density Functional Theory (DFT) calculations, it was concluded that introducing structural distortion in 2D atomic layers would make the spin states of Ni more delocalized and induce d-electron across the entire system. This could provide not only high electrical conductivity but also low adsorption energy between the active sites and reaction intermediates, resulting in remarkably improved OER activity. As active sites were pivotal in the catalytic process, enhancing the intrinsic activity and increasing the active sites should be two effective routes to improve the electrocatalytic oxygen evolution performance. The same group has designed and created rich vacancies on 2D NiCo2O4 nanosheets by topochemical transformations from few-layered NiCo hydroxides [28]. The morphology characterizations were shown in Fig. 9a and b, in which the TEM and AFM images demonstrated the 2D structure with thickness of about 1.56 nm. High-resolution XPS spectra of O 1s core have been tested as seen in Fig. 9c. The peak at 531.2 eV was associated with the defect sites with a low oxygen coordination. It was disclosed that the area peak at 531.2 eV for 2D nanocrystals with rich vacancy was extremely larger than that of bulk and ultrathin sheets poor in oxygen vacancies, suggesting that more oxygen vacancies have been produced on the sample surface. DFT investigations showed that the confined oxygen vacancies in the 2D nanosheets could lower the adsorption energy of water molecules,

a Atomic-scale phase transformation for synthesis of γ -CoOOH nanosheets



Fig. 8. (a) Synthetic route for the γ-CoOOH nanosheets. (b) TEM and (c) AFM images for the γ-CoOOH nanosheets, with the inset in (b) showing the corresponding HRTEM image. (d) Polarization curves in 1.0 M KOH medium with the prepared samples. Reproduced from ref. 26 with permission from Wiley, copyright 2015. AFM, atomic force microscopy; HRTEM, high-resolution transmission electron microscopy; TEM, transmission electron microscopy.



Fig. 9. (a) TEM and (b) AFM images for the NiCo₂O₄ ultrathin nanosheets rich in oxygen vacancies, with the inset in (a) displaying the Tyndall effect. (c) XPS of the O 1s spectra for the samples. (d) Polarization curves are measured on the prepared samples, with the inset showing the enlargement of the region near the onset. Reproduced from ref. 28 with permission from Wiley, copyright 2015. AFM, atomic force microscopy; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy.

facilitating the OER processing. Electrochemical measurements confirmed the expectation, with the 2D NiCo₂O₄ rich in oxygen vacancies exhibiting a large current density of 285 mA cm⁻² at 0.8 V and a small overpotential of 0.32 V (Fig. 9d). Both of these were superior to the corresponding values of bulk samples and 2D NiCo₂O₄ with few oxygen deficiencies, providing new guidelines for the design of advanced OER electrocatalysts.

To further improve the OER performance on 2D catalysts, defects engineering was highly desired to make use of the nanosheet structure more efficiently. In recent work, our group has put forward one strategy to introduce in-plane tiny holes on the limited nanosheet surfaces, which might provide them with higher surface area, richer defects, grain boundaries, and edge sites as well as distorted surfaces [29]. DFT calculations indicated that the punching holes in 2D Ni(OH)₂ could increase the adsorption of OH and O species to the catalyst surface and facilitate ions to transport, showing great potential for hole engineering on 2D catalyst toward high OER activity. In experiment, Zn ions were first inserted and then later etched out from the Ni(OH)₂ matrix, resulting in the 2D holey OER catalyst. The whole fabrication progress was illustrated in Fig. 10a, and the gradual tiny holes generation could be confirmed by the TEM observations (Fig. 10c-e). Electrochemical measurement verified the advantage of the created holey structure, where the LSV results had the smallest onset potential and the sharpest current increase for the 2D holey catalyst, superior to those without holey structures.

3.4. Hierarchical nanoarray OER catalyst

In this review, specialized hierarchical nanoarray OER catalysts refer to those integrated electrodes with high active materials supported on the current collect substrate, which usually exhibit excellent performance in electrochemical measurements. The substrate normally possesses good electric conductivity to afford fast electron transfer during the electrocatalysis process, and also this in situ grown strategy can reduce the resistance between the current collector and the supported catalysts. Meanwhile, the arrays catalysts have large open structure, which makes easy access to the electrocatalytically relevant species in the electrolyte to the active sites and facilitates the quick release of formed gas bubbles from the catalyst surface, continuously exposing active sites to the reaction.

Sun's group has constructed and reported a series of hierarchical nanoarray-integrated electrocatalysts toward water splitting, which can provide fast diffusion of relevant species in the electrolyte, avoid the aggregation of catalyst arrays, and ensure good stability during electrocatalysis [30]. Recently, they have reported new cobalt phosphate nanoarray materials as a high-performance electrode for oxygen evolution in neutral media [31]. Ti mesh was taken as the substrate, and the Cophosphate nanoarrays were prepared via hydrothermal synthesis, annealing transformation, and electrochemical oxidative polarization in turn. The corresponding morphologies were shown in Fig. 11 to illustrate their hierarchical nanoarray configurations. SEM image indicated that the Ti mesh surface was fully covered with nanowire arrays, and TEM measurement supported the nanowire structure. In addition, the selected-area electron diffraction (SAED) pattern demonstrated its amorphous nature (Fig. 11c), indicating that the electrochemical treatment in PBS solution would convert the solid crystalline CoP nanowires into porous amorphous Co phosphate phase. When used as OER catalysts in 0.1 M PBS medium (at neutral pH), the recorded LSV curves suggested that bare Ti mesh showed very poor OER activity with the need of large overpotential of 770 mV to drive 5 mA cm^{-2} . Among all these tested catalysts, Co phosphate arrays required much small overpotentials of 400 and 450 mV to afford geometrical catalytic current densities of 5 and 10 mA cm⁻², respectively. This behavior was much higher than that of hierarchical nanoarray CoP catalyst (need of



Fig. 10. (a) Schematic illustration for the formation of clean and freestanding tiny 2D holey $Ni(OH)_2$ nanosheets. (b) LSV curves measured in 1.0 M KOH electrolyte with pH = 14. (c–e) TEM images to depict the gradual holes generation process, for the pristine Zn:Ni(OH)₂, holey Zn:Ni(OH)₂, and holey Ni(OH)₂, respectively. Reproduced from ref. 29 with permission from Wiley, copyright 2017. TEM, transmission electron microscopy.



Fig. 11. (a) SEM morphology, (b) TEM image, and (c) SAED pattern for the prepared Co phosphate catalyst. (d) Recorded LSV curves for the hierarchical nanoarray Co phosphate catalyst and other controlled samples. Reproduced from ref. 31 with permission from Wiley, copyright 2017. RHE, reversible hydrogen electrode; SAED, selected-area electron diffraction; SEM, scanning electron microscopy; TEM, transmission electron microscopy.

overpotential of 620 mV for 5 mA cm⁻²), revealing the great potential for electrochemical topotactic technology in preparing nanoarray catalyst for applications.

Anion engineering can provide effective regulation on the electronic structure of catalytic materials, with little influence on the crystal structure and catalytic active sites. Very recently, we have reported an integrated electrode constructed by *P*-decorated Ni₃S₂ nanosheets arrays by a facile two-step method [32]. The suitable controlled incorporation of P anions into the Ni₃S₂ matrix could have little influence on the crystal structure and meanwhile could effectively modify the electronic structure, increase the concentration of charge carrier, supply more delocalized electrons, facilitate more active sites to be electrically activated, optimize the hydrogen adsorption Gibbs free energy, strengthen the interaction for water molecules, and benefit the oxidation of Ni²⁺ to Ni³⁺ oxo-/ hydroxides. The as-synthesized hierarchical P-decorated Ni₃S₂ nanosheet array catalyst exhibited high response in OER measurement, with a small onset overpotential of 270 mV, and an anode current density of 100 mA cm^{-2} at an overpotential of 420 mV, both of which were lower than those of the contrastive samples.

Feng et al. have designed and developed a novel nanoarray structure composed of $FeOOH/CeO_2$ heterolayered nanotubes supported on nickel foam (NF) as highly efficient electrocatalysts

for OER [33]. Although FeOOH held great promise for OER, its poor kinetics and mass-transfer ability would hinder its efficiency. To resolve this problem, the multivalence of Ce ions, attributed to the flexible transition between the Ce^{3+} and Ce^{4+} oxidation states, would provide strong interactions with FeOOH matrix. Meanwhile, the good electronic conductivity and high oxygen storage capacity of CeO₂ were used to confer FeOOH enhanced catalytic activity. In their preparation, ZnO nanorod arrays were first grown on NF substrate to construct the hierarchical nanoarray structure, and then CeO₂ and FeOOH were electrodeposited on the surfaces of ZnO. After removing the ZnO nanorod arrays using 1.0 M NaOH, the final FeOOH-CeO₂ catalyst was obtained. The molar ratio between FeOOH and CeO₂ could be optimized, and their electrocatalytic activities would reach the highest level when the molar ratio was 1:1. The onset potential of this hierarchical hybrid was only 210 mV, and it was about 50 mV lower than those of pure FeOOH and CeO₂ nanotube arrays, demonstrating the strong interaction at the interface and the beneficial OER activity enhancement resulting from the synergistic effect. Furthermore, when the overpotential was changed from 250 to 300 mV, the current densities of the hybrid electrode would increase from 31.3 to 140.2 mV cm⁻², which was much higher than 9.86-34.79 mV cm⁻² for FeOOH and 6.21 to 20.83 mV cm⁻² for CeO₂, indicating high energy conversion



Fig. 12. (a) Fabrication process of FeOOH-Co-FeOOH hybrid catalyst. (b) and (c) SEM images of the prepared FeOOH-Co-FeOOH hybrid catalyst with different magnifications. (d) SEM image of a typical FeOOH-Co-FeOOH hybrid nanotube. (e) TEM image of FeOOH-Co-FeOOH hybrid nanotube. (f) Recorded polarization curves of the hybrid catalyst and other controlled samples for OER measurements. Reproduced from ref. 34 with permission from Wiley, copyright 2016. OER, oxygen evolution reaction; SEM, scanning electron microscopy; TEM, transmission electron icroscopy.

efficiency of this novel hybrid nanoarray catalyst. In addition, the same group has also developed another hybrid-integrated electrode composed of FeOOH-Co-FeOOH nanotube arrays supported on NF for OER [34]. Fig. 12a depicted the fabrication process, in which ZnO nanorod arrays were first electrodeposited on NF as a template to construct the hierarchical nanoarray OER catalyst. After that, electrodeposition of metal Co was carried out on the ZnO nanorod surfaces, and the template ZnO nanorod arrays were dissolved and removed in 1.0 M NaOH media to obtain Co nanotube arrays. Finally, the FeOOH layers were electrodeposited on the inner and outer surfaces of the supported Co nanotubes. Figs. 12b and 10c were the representative SEM images showing the entire NF surface was completely covered by nanotube arrays, with the diameter and wall thickness of a typical tube being about 300 and 60 nm, respectively. Meanwhile, the side view SEM image in Fig. 12d demonstrated that the length of a single nanotube was 1.3 µm. Furthermore, TEM image in Fig. 12e disclosed the sandwiched-like structure of its wall, confirming the FeOOH-Co-FeOOH hybrid structure. To estimate its OER activity, the polarization curves were measured in 1.0 M KOH as displayed in Fig. 12f. Obviously, the asprepared integrated nanoarray catalyst had the lowest onset potential and highest current density among all these catalysts, verifying the advantage of this unique architecture and also opening up new opportunities for the development of next-generation high-performance OER catalysts.

In addition to pure inorganic OER catalysts, some organic components have also been explored for the oxygen evolution study. Jin and Xiao have cooperated in developing a nanowires-array-support/active cobalt plating to synthesize Co-phytate nanoplates as an advanced hierarchical nanoarray oxygen-evolving electrode [35]. Cu foil was taken as the substrate for growing Cu(OH)₂ nanowire arrays first, and then electroless deposition of Co on Cu foil was conducted in a coating bath. At last, phytic acid was added for oxidation and coordination treating, and the Co-phytate nanoplates were in situ grown on the coating-active Co, forming the as-designed Co-phytate nanoplate arrays (as seen in Fig. 13a). In the electrochemical OER measurement, the obtained new hierarchical nanoarray catalyst exhibited an ultrahigh current



Fig. 13. (a) Fabrication of electrodes and the molecular formula of phytic acid. (b) LSV curves of the various electrodes in 1.0 M KOH with the scan rate of 2 mV s⁻¹. Reproduced from ref. 27 with permission from American Chemical Society, copyright 2016. (c) Synthetic process of hierarchical MOF nanosheet array. (d) LSV plots obtained with different catalysts in 0.1 M KOH at 10 mV S⁻¹. Reproduced from ref. 35 with permission from Nature Publishing Group, copyright 2017. MOF, metal-organic framework.

density of 10 and 52 mA cm^{-2} at the low overpotentials of 265 and 320 mV, respectively (as displayed in Fig. 13b). This performance was much better than other compared catalysts, including the planar substrate-supported counterpart and commercial RuO₂. In another study, Chen and Zhao have presented a generic approach to prepare ultrathin nanosheet array of metal-organic framework (MOF) on various substrates [36]. Fig. 13c illustrated the facile onestep chemical deposition method, in which the organic ligands have been added into an aqueous solution of metal salt (nickel acetate and iron nitrate) in the presence of NF substrate. The obtained MOF arrays consisted of alternating organic hydrocarbon and inorganic metal-oxygen layers. After that, the electrocatalytic performance of this integrated MOF material was estimated in 0.1 M KOH electrolyte. According to the LSV curves shown in Fig. 13d, this hierarchical MOF catalyst demonstrated an overpotential of 240 mV to reach the current density of 10 mA cm⁻², which was much smaller than other controlled catalysts, such as Ni-MOF (296 mV) and Fe-MOF (354 mV). The high performance of this new catalyst would motivate us to study and explore more functional materials to be used as novel catalysts in electrochemical reactions.

4. Concluding remarks and perspectives

In this review, we have overviewed the motivation of OER research and recent achievements in alkaline OER mechanism understanding and catalyst development, as summarized in Table 1. More specifically, mechanistic studies have discovered the redox behavior of the active site on reducible oxides that play an essential role in facilitating interaction with reacting species and controlling OER electrocatalysis. With the aid of computational simulations, OER pathways were proposed which helped better understand the reaction at molecular level. A few catalyst descriptor parameters that exhibit linear correlation with active site-reacting species interactions and thus E_A and volcano correlation with reaction kinetics, such as ΔH_F and ΔE_{vac} , have been proposed for use to provide guidance in OER catalyst research. A large variety of earthabundant element-based materials, in particular reducible metal oxides, of different dimensions and in various forms have been prepared and investigated for the OER properties. Many of the developed materials have been demonstrated with promising OER activity property and thus a potential for use in water electrolysis.

In the meantime, it needs to be realized that there are still open questions and challenges awaiting solutions. At the reaction mechanism level, the OER pathways were proposed based on limited experimental observations in conjunction with computational simulations. This is because of the transient characteristic of transition states and active intermediates that no current techniques are capable of direct characterization. However, computational simulations, especially density functional theory calculations, are still often technologically restricted by the computation power and many made approximations. Whether these theoretical simulations reflect OER electrocatalysis under real reaction condition remains a concern. To examine effectiveness of the computations and achieve more insights into OER mechanism, development of new in situ ultrafast spectroscopy to collect more experimental evidence of intermediate generation becomes necessary.

At the catalyst research level, the proposed use of catalyst descriptor parameters and the observed linear correlation with active site-reacting species interactions have been effectively facilitating OER catalyst development. In principle, by searching new catalyst material to optimize the descriptor parameter that would balance active site-reacting species interactions to minimize E_A and thus promote i_0 , the OER kinetics can be greatly promoted. Despite the intensive research efforts in recent years, however, most of developed catalyst materials still have insufficient activity and thus require significant overpotential in OER. There are two possible reasons accounting for the activity issue. First, recent computational catalysis studies discovered a scaling correlation for catalyst-chemical interactions, which would suggest the presence of a minimum E_A in OER which cannot be overcome in current mechanism. If this is the case, a new catalytic structure that enables new OER mechanism and allows further decease in E_A has to be explored. The second reason is related to the fact that most OER catalysts are oxide-based materials and have relatively low electrical conductivity. A low conductivity would cause inefficient electron transfer and an overpotential drop at the active sites, as $\eta = E - 1.23 - IR$ where *I* and *R* are current and material internal resistance, which would eventually cause a decrease in the OER

Table 1

Summary of literature-reported low-dimensional electrocatalysts for alkaline OER.

Electrocatalysts	Structure	Size	Activity	Electrolyte	Ref.
Co ₃ O ₄	Quantum dots	2 nm	$\eta_{10} = 270 \text{ mV}$	1 M KOH	11
benzyl alcohol-Co ₃ O ₄	Quantum dots	4.5 nm	$TOF = 2.7^* 10^{-4} s^{-1}$ per Co atom	PBS	12
ZnCo ₂ O ₄ -N-doped carbon nanotubes	Quantum dots	3–3.5 nm	$\eta_{10}=420\ mV$	0.1 M KOH	13
CoMn ₂ O ₄ -carbon nanotubes	Quantum dots	3.9 nm	$\eta_{10}=380\ mV$	0.1 M KOH	14
Со	Quantum dots	3.2 nm	$\eta_{10}=370\ mV$	0.1 M KOH	15
N-doped graphene—NiFe@MoC ₂	Quantum dots	20 nm	$\eta_{10}=320\ mV$	1 M KOH	16
Amidogen-modified carbon	Quantum dots	5 nm	$\eta_{10} > 320 \text{ mV}$	0.1 M KOH	17
Co ₃ O ₄	Nanotubes	Diameter = 400 nm	$\eta_{10}=390\ mV$	0.1 M KOH	18
Co ₃ O ₄ -carbon nanotubes	Nanorods	Diameter = 10 nm	$\eta_{10}=310\ mV$	1 M KOH	20
Oxidized multiwalled carbon nanotubes	Nanotubes	Diameter = 20 nm	$\eta_{10}=360\ mV$	1 M KOH	22
Triple-walled carbon nanotubes	Nanotubes	Diameter = 3.8 nm	$\eta_{10}=450\ mV$	1 M KOH	23
RuO ₂	Nanosheets	Thickness $= 1.2 \text{ nm}$	$\eta_{10\text{mAmg}}^{-1} = 260 \text{ mV}$	1 M KOH	25
γ-CoOOH	Nanosheets	Thickness $=$ 1.4 nm	$\eta_{10} = 300 \text{ mV}$	1 M KOH	26
NiSe ₂	Nanosheets	Thickness $= 1.0 \text{ nm}$	$\eta_{10}=330\ mV$	1 M KOH	27
NiCo ₂ O ₄	Nanosheets	Thickness $=$ 1.6 nm	$\eta_{10}=320\ mV$	1 M KOH	28
Ni(OH) ₂	Nanosheets	_	$\eta_{10}=335\ mV$	1 M KOH	29
Co phosphate	Nanowire arrays	_	$\eta_{10}=450\ mV$	0.1 M PBS	31
P-decorated Ni ₃ S ₂	Nanosheet arrays	_	$\eta_{100}=320\ mV$	1 M KOH	32
FeOOH-CeO ₂	Nanotube arrays	_	$\eta_{10} > 200 \text{ mV}$	1 M NaOH	33
FeOOH-Co-FeOOH	Nanotube arrays	_	$\eta_{20}=250\ mV$	1 M KOH	34
Co-phytate	Nanoplate arrays	_	$\eta_{10}=265\ mV$	1 M KOH	35
NiFe-MOF	Nanosheet arrays	-	$\eta_{10}=240~mV$	0.1 M KOH	36

MOF, metal-organic framework; OER, oxygen evolution reaction.

rate. To address this issue, development of catalyst materials with improved conductivity would be necessary.

In addition to the OER activity property, the durability property is another important metric in catalyst material research. Considering a high electrode potential, oxidation atmosphere, and concentrated alkaline electrolyte environment, maintenance of integrity and stability of catalytic structure is challenging. This would also explain why most OER catalyst materials, or at least the surface active sites, are oxide based because materials in the form of other compounds would not likely sustain under this harsh condition. Interestingly, some metal nitrides [37], phosphides [38], and borides [39] were recently reported with good activity and durability for OER electrocatalysis, which were attributed to their excellent electrical conductivity and corrosion resistance. Meanwhile, special configurations, such as nanocages [40], usually possess much enhanced electrocatalytic activity owing to the structural advantages. In this regard, nitrides, phosphides, and borides, as well as some their conductive derivatives in special structures, would possibly hold a good promise as an OER catalyst and represent a future research direction.

Identifying the real OER active sites is very meaningful but extremely challenging, primarily due to reconstruction of catalyst surface sites caused by potential stimulus and interactions with electrolyte species as well as with active intermediates in OER under electrochemical condition. An anodic oxidation peak is usually observed ahead of OER occurrence on transition metal—based electrocatalysts, which is ascribed to valence increase of the transition metal components, for instance Ni²⁺ \rightarrow Ni³⁺. This variation demonstrates the generation of corresponding oxyhydroxide on Nibased catalyst surface. Although some Ni sulfides and phosphides are deemed as active OER catalysts, this pre-exponential oxidation peak is often observed. Careful TEM characterizations of the tested catalysts illustrate formation of thin oxide surface layer. In this regard, the OER active sites of these materials are likely in situ generated oxyhydroxide derivatives on their surface.

Besides, it needs to be noted that most previous studies of OER catalyst materials were conducted under the half-cell condition in the electrolyte, whereas the ultimate objective is to apply the developed catalysts in full-cell water electrolyzer that operates under different condition. Whether the evaluated properties under the half-cell condition are similar to those being expected in the electrolyzer remains largely underinvestigated. To develop active and durable OER catalysts applicable to water electrolysis, the performance of catalyst materials will need to be evaluated not only in the electrolyte but also in the electrolyzer. With continuous research efforts to better understand the reaction at molecular level, explore new catalyst materials, and evaluate the properties under water electrolysis condition, the development of highly efficient, durable, and cost-effective OER catalysts for practical H₂ production is anticipated.

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